Determination of Common Analytes at Trace Levels in Zr Matrix by ICP-AES Without Chemical/Physical Separation

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INTRODUCTION

Trace metallic impurity analysis is one of the prime steps in chemical quality control of nuclear fuels and associated materials. To achieve the desired burn-up, successful life span of the fuel in the reactor, and successful running of the reactor, it is required to have stringent physical and chemical quality control and quality assurance measures of the nuclear fuels and associated materials. The atomic emission spectroscopy (AES) technique, being simultaneously multi-elemental and having acceptable analytical performance (detection limits, sensitivity, linear dynamic range, etc.), is regularly used for the determination of trace metallic analytes in nuclear fuels and associated materials (1-17). Zirconium (Zr) is accepted worldwide as a cladding material in the nuclear industry due to its low neutron absorption cross-section. U-Zr, U-Pu-Zr, Zr-Nb, etc., and binary and ternary alloy materials are also gaining importance as nuclear fuels and associated materials in the nuclear industries (18-27). Thus, there is a need for developing a method for the determination of trace constituents in a Zr matrix. Due to its line-rich emission spectra, the presence of Zr even at trace levels can lead to the over-estimation of analytes due to spectral interferences. For the determination of trace metallic constituents, they either have to be separated physically from the trace metals using the d.c.

ABSTRACT

Chemical (ICP-AES) or physical (d.c. arc carrier distillation technique) separation of the major matrix, followed by the determination of trace metallic impurities in the raffinate, is a well accepted protocol in the nuclear industries to avoid spectral interferences from emission-rich matrices such as U, Pu, Zr, Th, etc. With ICP-AES analysis, the RSD is better (less than 5%), separation is time-consuming, involves handling of the materials which increases the chances of contamination, while the precision of the d.c. arc technique is 15-25%. Thus, there is a need to have an ICP-AES-based methodology where the analytes can be determined in a nuclear matrix at trace levels without requiring chemical separation.

In this paper, an attempt was made to develop a method for the determination of trace constituents in a Zr matrix without separation by using the flexibility of a charge coupled device (CCD) detector for choosing additional interference-free analytical lines for Mn, Fe, Ga, In, Sr, K, Li, Eu, Co, Zn, Ni, Cu, Al, and Si. It was observed that the analytes can be determined up to 0.1 µg/mL in the presence of Zr. The results were also compared with routinely used methods and found to be satisfactory. In addition, an analytical method was developed for the determination of zirconium by ICP-AES, including the identification of suitable analytical lines (343.823 nm, 257.139 nm, and 272.262 nm) and studying the analytical performance such as sensitivity, detection limits, etc.

arc carrier distillation technique (1-6) or by chemical separation, followed by ICP-AES analysis of the raffinate (7-15). Different approaches were found in the literature for the determination of analytes in Zr matrices (28-29).

In d.c. arc, where sample handling is less and thus also the chances of less contamination, the method suffers from poor precision. In ICP-AES, where more sample handling is required during chemical separation of the major matrix, the chances of contamination are greater but the detection limits as well as precision are better than with the d.c. arc carrier distillation technique. In ICP-AES, a suitable extractant and feed conditioning are required resulting in preferential extraction of the major matrix without loss of the analytes even at trace levels. Therefore, a method needs to be developed where sample handling is minimum and the analytical performance of the method (precision, detection limits, linear dynamic range, sensitivity, etc.) superior. In our previous study (30-31), an attempt was made to understand the spectral interference of uranium on other analytes using CCD-based ICP-AES.

In the present study, a method was developed for the determination of Mn, Ga, Sr, Li, Eu, Co, Zn, Ni, Cu, and Si using a charge coupled device (CCD) detector without requiring any physical or chemical separation. The CCD-based detector provides the option of choosing additional analytical lines free from Zr interference as listed in Table I.

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The present method was compared with two existing methods for the determination of trace metallic constituents in a Zr matrix: ICP-AES analysis after quantitative removal of the major matrix without loss of impurities at trace levels and d.c. arc carrier distillation technique where trace constituents are swept out physically into the arc while the matrix remains in the electrode. The analytical performance was found to be comparable and satisfactory. Also, an analytical method was developed for the determination of Zr which involves identification of suitable analytical lines of Zr (339.198 nm, 343.823 nm, 257.139 nm, and 272.262 nm) and the analytical performance (detection limits, sensitivity, etc.) of those lines, etc., was investigated.

EXPERIMENTAL

Instrumentation

The analytical experiments were carried out using a computer-controlled, high resolution, simultaneous inductively coupled plasma atomic emission spectrometer (ICP-AES) (Spectro Arcos, Germany),

TABLE I
Interference-free Lines
for Analytes in Zr Matrix

Mn	257.611 nm
Fe	259.941 nm, 261.187 nm
Co	230.786 nm
Ni	231.604 nm, 221.648 nm
Cu	324.754 nm
Ga	417.206 nm
In	230.606 nm
Si	212.412 nm, 251.612 nm
Sr	421.552 nm
K	766.491 nm
Li	670.780 nm
Eu	420.505 nm, 381.967 nm, 393.048 nm, 390.710 nm
Zn	213.856 nm, 206.200 nm
Al	394.401 nm

with ICP and d.c. arc as the excitation sources and a charge coupled device (CCD) as the detector. The instrumental specifications and experimental parameters are summarized in Table II. The detector system, consisting of linear arrays of the CCD detector (3648 pixels/array), thermally stabilized together with an optical system, provides the ability to choose alternate analytical lines.

Standard Solutions and Reagents

The standard solutions for rare earth and other common impurity elements were prepared from CertiPUR® ICP multi-standard solutions (E-Merck, Darmstadt, Germany) by proper dilution with 0.5 M HNO₃. Suprapur® HNO₃ (E-Merck, Darmstadt, Germany) and

quartz doubly distilled water were used for making 0.5 M HNO₃. Multi-point standardization was carried out using 0.5M HNO₃ as the lower standard and 0.05–1000 µg/mL of the corresponding elemental standard as the higher standard for each line after proper peak search. To understand the spectral interference of Zr on other analytes, pure Zr solutions of different concentrations were used and the contributions at each analytical channel monitored.

For the analytical lines, having contribution from 1000 µg/mL Zr, ≤ 0.05 µg/mL was considered as free from spectral interference from Zr (the correction factor being negligibly small). For the determination of trace analytes, these interference-free lines were taken. The synthetic samples were

TABLE II
ICP-AES Specifications and Operating Conditions

Instrumental Specifications	
Model	Arcos FHS12 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)
Wave length range	130-800 nm
Entrance slit width	15 microns
Resolution (FWHM)	0.01 nm from 130-450nm 0.02 nm from 450-800nm
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	6 L/min
Auxiliary flow	0.6 L/min
Total time of measurement	28 s
Pump speed	30 rpm
RF power out put	0.8 – 1.5 kW
Input power	230 V AC

prepared by dissolving high purity ZrO_2 (locally prepared and checked by inter-laboratory comparison experiments involving different laboratories of the Department of Atomic Energy, India) with 0.005% HF-HNO_3 by heating under an IR lamp (temperature $\sim 80^\circ\text{C}$). The fluoride ion was removed completely by repeated heating with concentrated HNO_3 . Finally, the acidity of the sample solution was brought to $\sim 1\text{M HNO}_3$. Then it was spiked with appropriate aliquots of the analytes for the preparation of synthetic samples and used for the ICP-AES experiments.

The routinely adopted method for trace metal assay in a Zr matrix is chemical separation of Zr (quantitatively) from the analytes using 30% TBP-dodecane (five contacts) from an aqueous solution of $\sim 4\text{M HNO}_3$, followed by feeding of the aqueous phase into the plasma for analysis. The above-mentioned routine procedure was adopted and the data were compared with the newly developed methods.

The analytical results were also compared with the method of determination of those trace analytes in the same solid ZrO_2 matrix using the d.c. arc carrier distillation technique [5% carrier consisting of

a mixture of AgCl and SrF_2 (4:1)] using the same instrument (also attached with d.c. arc excitation source). The comparison was found to be satisfactory.

RESULTS AND DISCUSSION

The overall work of this study can broadly be divided into three sections for discussion: (a) Determination of zirconium by ICP-AES involving the development of the ICP-AES-based methodology for the determination of Zr and includes identification of the different emission lines of Zr, establishing calibration curves, and studying their analytical performance such as detection limits, sensitivity, etc. (b) Detailed study of the spectral interferences of zirconium on the analytes on different analytical channels along with their analytical performance. (c) Development of a method for the determination of the analytes without chemical separation. In this segment, based on the spectral interference study (previous section), an attempt was made to develop a method for the determination of the analytes in a Zr matrix without separation and the analytical results were compared with routinely used methods.

ICP-AES Determination of Zr

Zirconium is a multi-electronic system with line-rich emission spectra. Due to the availability of different emission lines, the sensitivity of the lines were found to be less and the detection limits poorer with a photo multiplier tube (PMT)-based detection system. Exploring the superior analytical performance of the CCD-based detector system, an analytical method was developed for the determination of Zr by ICP-AES. This study includes identification of suitable analytical lines. Four emission lines of Zr were identified (257.139 nm, 272.262 nm, 339.198 nm, and 343.823 nm), and the calibration curves established (see Figure 1). The emission profiles of the different analytical lines of Zr mentioned in the present case are shown in Figure 2 (A, B, C, and D). It was found that the 257.139 nm, 272.262 nm, and 343.823 nm lines can be used for the determination of Zr up to $1000\text{ }\mu\text{g/mL}$ with an RSD of less than 5%, while for the 339.198 nm line, $200\text{ }\mu\text{g/mL}$ is the upper limit of detection for Zr (Table III). The sensitivity and detection limits of Zr using the above-mentioned analytical lines were evaluated using the slopes of the calibration curves and the concentration equivalent to the inten-

Fig. 1(A). Calibration curves for Zr: 257.139 nm and 272.262 nm.

Fig. 1(B). Calibration curves for Zr: 339.198 nm and 343.828 nm.

Fig. 2 (A, B, C, and D). Emission profiles of the different analytical lines of Zr.
(A) - 257.139 nm, (B) - 272.262 nm, (C) - 343.823 nm, (D) - 339.198 nm.

TABLE III
Determination of Zr by ICP-AES

Zr conc. (mg/L)	Zr 339.198 nm	Zr 343.823 nm	Zr 257.139 nm	Zr 272.262 nm	Zr conc. (mg/L)	Zr 339.198 nm	Zr 343.823 nm	Zr 257.139 nm	Zr 272.262 nm
Blank	BDL	BDL	BDL	BDL	20	20.6	21.5	21.3	21.3
0.05	0.049	0.047	0.055	0.048	50	49.1	54.1	52.6	50.8
0.10	0.10	0.10	0.113	0.104	100	97.7	102.1	106.5	102.9
0.50	0.51	0.55	0.53	0.48	200	185.7	199.54	209.3	201.6
1	1.03	1.05	1.08	1.03	500	337.2	471.2	482.5	474.2
2	2.05	2.15	2.14	2.125	1000	339.0	845.7	952.5	919.3
5	5.04	5.47	5.25	5.06	Detection	0.02	0.09	0.34	0.12
10	10.3	10.5	10.6	10.4	Limit (µg/mL)				

sity equal to the average of the blank value + three times the standard deviation of the above measurements, i.e., $\bar{x} + 3\sigma$. According to the analytical performance, the 343.823 nm line was found to be the best of the four analytical lines mentioned.

Spectral Interference of Zr on the Analytes

Interference may originate from various transitions of the complex system, which transforms the sample concentration into equivalent radiation. Among various kinds of interferences, spectral interference is significant as far as ICP-AES is concerned. Usually, for the determination of a particular analyte at the trace level, the most sensitive line is chosen, while if the particular line is overlapped by some interfering line, some other line needs to be selected which may be less sensitive and with poor detection limits. Improvement of the resolving power of the instrument may resolve the lines only if the optics are responsible for spectral overlap. If overlap of the lines is from the broadening process occurring in the plasma, improvement of the instrumental resolution will be inefficient. Therefore, alternative emission lines need to be investigated for their analytical applications. In some cases, it may happen that only the analytical line, which is not strongly interfered, has to be chosen for the analytical purpose. For these lines, appropriate correction factors need to be evaluated.

In the present case and due to the advancement of detector systems, i.e., array of pixels of a CCD detector, there is the option to choose an analytical line in order to avoid spectral interferences. A detailed examination was made to study the spectral interference of Zr on 14 analytes (see Table IV) and to choose the appropriate emission lines for trace determina-

tion of these elements in the presence of a Zr matrix.

Mn

Five lines of Mn (257.611 nm, 259.373 nm, 260.569 nm, 294.921 nm, and 403.076 nm) were investigated. It was observed that there was practically no spectral interference from Zr on the former three lines, while the remaining two interfered significantly. The lowest detection limit was at the 257.611 nm line and, therefore, found to be the best for Mn determination in a Zr matrix.

Fe

Iron (Fe) is one of the elements having line-rich emission spectra. Therefore, ten different analytical lines of Fe (259.941 nm, 238.204 nm, 239.562 nm, 244.451 nm, 261.187 nm, 262.567 nm, 262.829 nm, 275.573 nm, 241.331 nm, and 373.486 nm) were studied. It was found that all of these lines showed moderate spectral interference either due to the presence of wings of the nearby Zr line or an overall increase in background. Figure 3 represents the typical contribution of 1000 $\mu\text{g/mL}$ of Zr on the 238.204 nm and 239.562 nm analytical lines of Fe. Of all the mentioned lines, the 259.941 nm and 261.187 nm lines showed less spectral interference because there was no nearby Zr line or no appreciable increase in background intensity at these wavelengths due to Zr. Luckily, the interference-free lines were found to have better analytical performance.

Co

The 237.862 nm line of Co showed considerable spectral interference from Zr, while the other three lines (228.616 nm, 238.892 nm, and 230.862 nm) were relatively interference-free. The 230.786 nm line of Co is considered to be the best choice for its determination in a Zr matrix.

Ni

For Ni, the 231.604 nm and 221.648 nm lines were found to be practically interference-free from Zr, while the 232.003 nm, 227.021 nm, and 300.249 nm lines showed considerable spectral interference. The 174.828 nm and 341.476 nm lines for Ni were strongly interfered by Zr and thus are not at all recommended for the present case. The situation is simple for Ni, because the least interfered lines were found to have the best analytical performance.

Cu

The Cu 324.754 nm and 224.700 nm lines were found to have least spectral interference from Zr, where the former line also has the lowest detection limits out of all the other lines studied (324.754 nm, 327.396 nm, 224.700 nm, 219.226 nm, and 219.958 nm). Therefore, it is recommended to use the 324.754 nm line for the determination of Cu in a Zr matrix.

Ga

Even though the 287.424 nm and 294.364 nm lines of Ga showed better analytical performance, there was considerable spectral interference from Zr, while the 417.206 nm line of Ga was found to have one order of magnitude higher detection limit than that of the former two lines and had practically no spectral interference. The 141.444 nm line of Ga was found to have poor analytical performance as well as strong interference from Zr.

In

For In at the 230.606 nm line, it was observed that there was some interference and the detection limit of this line was also acceptable. The other analytical lines of In (325.609 nm and 303.936 nm) had strong interference from Zr. Therefore, the 230.606 nm line can be

TABLE IV
Spectral Interference of Zr on Different Analytes

Element	Line (nm)	Contribution (µg/mL)	Correction Factor	D.L. (µg/mL)	Sensitivity (counts/µg/mL)	Element	Line (nm)	Contribution (µg/mL)	Correction Factor	D.L. (µg/mL)	Sensitivity (counts/µg/mL)
Mn	257.611	0.016	1.60E-05	8.6X10 ⁻⁵	2.1X10 ⁻⁶	Ga	141.444	3.254	3.25E-03	0.085	0.006
	259.373	0.014	1.40E-05	0.0002	2.8X10 ⁻⁶		417.206	0.066	6.60E-05	0.012	5.0x10 ⁻⁵
	260.569	0.01	1.00E-05	0.0002	3.4X10 ⁻⁶		294.364	0.237	2.37E-04	0.004	7.0x10 ⁻⁵
	294.921	0.326	3.26E-04	0.0007	9.6X10 ⁻⁶		287.424	0.729	7.29E-04	0.009	0.0002
	403.076	1.212	1.21E-03	0.0011	5.8X10 ⁻⁵	In	230.606	0.23	2.30E-04	0.01	0.00015
Fe	259.941	0.135	1.35E-04	0.0072	1.0x10 ⁻⁵		325.609	2.06	2.06E-03	0.007	8.7x10 ⁻⁵
	238.204	0.142	1.42E-04	0.007	1.0x10 ⁻⁵	Si	303.936	3.265	3.27E-03	0.007	0.0001
	239.562	0.151	1.51E-04	0.0076	1.5x10 ⁻⁵		251.612	0.061	6.10E-05	0.004	4.1x10 ⁻⁵
	244.451	2.133	2.13E-03	0.0212	0.00086		288.158	0.132	1.32E-04	0.0007	5.3x10 ⁻⁵
	261.187	0.154	1.54E-04	0.0076	2.2x10 ⁻⁵		212.412	0.04	4.00E-05	0.003	5.6x10 ⁻⁵
	262.567	0.216	2.16E-04	0.0081	8.6x10 ⁻⁵	Sr	407.771	0.011	1.10E-05	4.1x10 ⁻⁵	2.7x10 ⁻⁷
	262.829	0.398	3.98E-04	0.0054	8.5x10 ⁻⁵		421.552	0.015	1.50E-05	1.5x10 ⁻⁶	4.0x10 ⁻⁷
	275.573	0.235	2.35E-04	0.0081	7.4x10 ⁻⁵		460.733	0.062	6.20E-05	0.020	0.0001
	241.331	0.238	2.38E-04	0.0054	8.3x10 ⁻⁵	K	766.491	0.109	1.09E-04	0.02	0.0003
	373.486	0.449	4.49E-04	0.0081	0.0001		670.78	0.005	5.00E-06	0.0001	4.2x10 ⁻⁶
Co	228.616	0.027	2.70E-05	0.0011	1.5x10 ⁻⁵	Eu	420.505	0.01	1.00E-05	0.0006	2.9x10 ⁻⁶
	238.892	0.036	3.60E-05	0.0008	1.5x10 ⁻⁵		381.967	0.026	2.60E-05	0.0001	2.1x10 ⁻⁶
	230.786	0.044	4.40E-05	0.0002	2.5x10 ⁻⁵		393.048	0.003	3.00E-06	0.0008	4.2x10 ⁻⁶
	237.862	0.294	2.94E-04	0.0011	2.6x10 ⁻⁵		390.71	0.003	3.00E-06	0.0009	5.8x10 ⁻⁶
Ni	231.604	0.064	6.40E-05	0.001	2.8x10 ⁻⁵	Zn	213.856	0.028	2.80E-05	0.001	6.0x10 ⁻⁶
	221.648	0.042	4.20E-05	0.002	2.5x10 ⁻⁵		206.2	0.113	1.13E-04	0.004	9.0x10 ⁻⁵
	232.003	0.103	1.03E-04	0.001	6.5x10 ⁻⁵		202.613	0.035	3.50E-05	0.001	1.0x10 ⁻⁵
	227.021	0.265	2.65E-04	0.011	0.0005	Al	396.152	5.824	5.82E-03	0.0025	2.5x10 ⁻⁵
	300.249	0.2	2.00E-04	0.004	7.2x10 ⁻⁵		394.401	0.231	2.31E-04	0.0037	6.1x10 ⁻⁵
Cu	324.754	0.04	4.00E-05	0.0001	4.5x10 ⁻⁶		308.215	0.113	1.13E-04	0.008	4.1x10 ⁻⁵
	327.396	0.68	6.80E-04	0.0009	8.0x10 ⁻⁶		309.271	0.134	1.34E-04	0.097	2.1x10 ⁻⁵
	224.7	0.075	7.50E-05	0.0015	2.7x10 ⁻⁵						
	219.226	0.123	1.23E-04	0.0118	7.6x10 ⁻⁵						
	219.958	0.226	2.26E-04	0.0069	6.4x10 ⁻⁵						

used for its determination in a Zr matrix with a suitable correction factor as indicated in Table IV.

Si

The analytical lines of Si at 212.412 nm and 251.612 nm were least interfered by Zr and also had low, comparable detection limits. Use of the 152.672 nm and 288.158 nm lines are not recommended since their spectral interference is not moderate.

Sr

The Sr lines at 407.771 nm and 421.552 nm showed a negligibly small spectral interference from Zr, but the 421.552 nm line showed a detection limit of one order of magnitude lower.

K and Li

Even though the analytical line of 766.491 nm for K was interfered moderately, the Li 670.780 nm line

showed practically no interference from Zr.

Eu

The four studied analytical lines of Eu (420.505 nm, 381.967 nm, 393.048 nm, and 390.710 nm) were practically interference-free and also had attractive detection limits (420.505 nm - 0.0006 µg/mL, 381.967 nm - 0.0001 µg/mL, 393.048 nm - 0.0008 µg/mL, and 390.710 nm - 0.0009 µg/mL).

Fig. 3 (A and B). Contributions of 1000 µg/mL of Zr on the 238.204 nm (A) and 239.562 nm (B) analytical lines of Fe.

Zn

The analytical lines of Zn at 213.856 nm and 206.200 nm were found to be relatively interference-free and had better detection limits (0.001 µg/mL and 0.004 µg/mL, respectively), whereas 202.613 nm and 334.502 showed moderate and strong interference from Zr.

Al

Even though the Al analytical line at 396.152 nm was found to be the best analytical line, it showed strong spectral interference from Zr, while the Al lines at 394.401 nm, 308.215 nm, and 309.271 nm showed moderate spectral interference, and the 394.401 nm line showed the lowest detection limit. The two Al lines at 167.078 nm and 176.641 nm were strongly interfered by Zr and found to have comparably poor detection limits.

From these studies it can be concluded that the analytical line with moderate spectral interference can be used for the determination of analytes with suitable correction factors, while lines with strong interference should be disregarded for the determination of trace metallic impurities in a Zr matrix.

Development of Method for the Determination of Analytes Without Chemical Separation

Based on the above spectral interference study, it was found that the 257.611 nm line for Mn; 230.786 nm line for Co; 231.604 nm and 221.648 nm lines for Ni; 324.754 nm line for Cu; 417.206 nm line for Ga; 212.412 nm and 251.612 nm lines for Si; 421.552 nm line for Sr; 670.780 nm line for Li; 420.505 nm, 381.967 nm, 393.048 nm, and 390.710 nm lines for Eu; and the 213.856 nm and 206.200 nm lines for Zr can be used for the determination of these analytes without requiring any kind of separation.

Synthetic samples were prepared and the method was validated. It was observed that Mn, Co, Ni, Cu, Ga, Si, Sr, Li, Eu, and Zn can be determined in a Zr matrix without chemical separation up to 0.1 µg/mL. The analytical results as listed in Table V were found to be satisfactory. These results were further compared with two routinely employed methods: (a) Chemical separation of the Zr matrix with 30% TBP-dodecane, followed by feeding the aqueous phase into the

plasma for the determination of the analytes at trace levels and (b) determination of the analytes in a solid ZrO₂ matrix using the d.c. arc carrier distillation technique. The results were found to be satisfactory.

The overall recovery of a method should be within 90–110%. In the present method, it was found that the mean values for Ni and Li suggested a % recovery for these elements in synthetic samples at 120%. The true value, i.e., amount added, was found to follow within the concentration range specified in Table V with a confidence level of 99.99% (3σ). In the d.c. arc carrier distillation technique, it was also observed that the confidence intervals were mostly more than those of ICP-AES, reflecting lesser precision of the former technique due to arc wandering. Additionally, for synthetic sample 1, the % recovery for all the elements was in the expected range of 90–110%, while for synthetic sample 2, Ni and Li were found to be exceptions. This may be due to analytical errors, which generally increase in the lower level of detection compared to the higher concentration values.

TABLE V
Validation of Methodology With Synthetic Samples and Comparison with Routinely Used Methods

Synthetic Sample-1					Synthetic Sample-2			
Metal Ion	Amount Added ($\mu\text{g/mL}$)	Present Method Separation ($\mu\text{g/mL}$)	ICP-AES After Distillation ($\mu\text{g/mL}$)	D.C. Arc Carrier ($\mu\text{g/mL}$)	Amount Added ($\mu\text{g/mL}$)	Present Method ($\mu\text{g/mL}$)	ICP-AES After Separation ($\mu\text{g/mL}$)	D.C. Arc Carrier Distillation ($\mu\text{g/mL}$)
Mn	0.5	0.51 $\pm$ 0.04	0.47 $\pm$ 0.04	0.53 $\pm$ 0.06	0.1	0.11 $\pm$ 0.03	0.13 $\pm$ 0.05	0.11 $\pm$ 0.06
Co	0.5	0.49 $\pm$ 0.02	0.51 $\pm$ 0.03	0.47 $\pm$ 0.07	0.1	0.09 $\pm$ 0.03	0.09 $\pm$ 0.03	0.09 $\pm$ 0.06
Ni	0.5	0.51 $\pm$ 0.03	0.52 $\pm$ 0.02	0.49 $\pm$ 0.06	0.1	0.12 $\pm$ 0.02	0.10 $\pm$ 0.01	0.10 $\pm$ 0.05
Cu	0.5	0.50 $\pm$ 0.01	0.48 $\pm$ 0.03	0.52 $\pm$ 0.06	0.1	0.10 $\pm$ 0.01	0.12 $\pm$ 0.05	0.13 $\pm$ 0.06
Ga	0.5	0.49 $\pm$ 0.03	0.51 $\pm$ 0.02	0.47 $\pm$ 0.05	0.1	0.09 $\pm$ 0.02	0.08 $\pm$ 0.03	0.08 $\pm$ 0.07
Si	0.5	0.53 $\pm$ 0.03	0.48 $\pm$ 0.04	0.53 $\pm$ 0.06	0.1	0.11 $\pm$ 0.03	0.12 $\pm$ 0.05	0.12 $\pm$ 0.05
Sr	0.5	0.51 $\pm$ 0.02	0.49 $\pm$ 0.03	0.52 $\pm$ 0.07	0.1	0.11 $\pm$ 0.01	0.08 $\pm$ 0.03	0.12 $\pm$ 0.04
Li	0.5	0.52 $\pm$ 0.03	0.51 $\pm$ 0.03	0.48 $\pm$ 0.06	0.1	0.12 $\pm$ 0.02	0.12 $\pm$ 0.05	0.11 $\pm$ 0.06
Eu	0.5	0.51 $\pm$ 0.01	0.52 $\pm$ 0.03	0.47 $\pm$ 0.05	0.1	0.09 $\pm$ 0.01	0.12 $\pm$ 0.04	0.08 $\pm$ 0.05
Zn	0.5	0.50 $\pm$ 0.03	0.49 $\pm$ 0.02	0.48 $\pm$ 0.07	0.1	0.11 $\pm$ 0.03	0.12 $\pm$ 0.03	0.10 $\pm$ 0.05

CONCLUSION

A systematic study was carried out to understand the spectral interference of zirconium on 14 analytes (Mn, Fe, Ga, In, Sr, K, Li, Eu, Co, Zn, Ni, Cu, Al, and Si). The interference-free analytical lines of these elements were identified and the analytical performance (detection limits, sensitivity, etc.) studied. An analytical method was also developed for the determination of zirconium by ICP-AES, which includes identification of the suitable analytical lines, establishing the calibration curves, and evaluating the sensitivity and detection limits of Zr. It was observed that except for the 339.198 nm line (saturates beyond 200 $\mu\text{g/mL}$), the other three studied analytical lines (343.823nm, 257.139 nm, and 272.262 nm) can be used for Zr determination with $\sim$ 5% RSD.

In the present study, the following analytical lines were found to be appropriate for the determination of trace constituents in a nuclear grade Zr matrix: the 257.611 nm line for Mn; 259.941 nm and 261.187 nm lines for Fe; 230.786 nm line for Co; 231.604 nm

and 221.648 nm lines for Ni; 324.754 nm line for Cu; 417.206 nm line for Ga; 230.606 nm line for In; 212.412 nm and 251.612 nm lines for Si; 421.552 nm line for Sr; 766.491 nm line for K; 670.780 nm line for Li; 420.505 nm, 381.967 nm, 393.048 nm and 390.710 nm lines for Eu; 213.856 nm and 206.200 nm lines for Zn, and the 394.401 nm line for Al.

Based on the interference study, a suitable methodology was developed for the determination of Mn, Co, Ni, Cu, Ga, Si, Sr, Li, Eu, and Zn at trace levels without using any chemical or physical separation, while for Fe, Al, K, and In, appropriate correction factors should be employed.

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