Study of the Spectral Interferences of Zirconium on Other Analytes in the Analysis of Nuclear Materials by CCD-based ICP-AES

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INTRODUCTION

Trace metallic impurity analysis is one of the prime steps of chemical quality control of nuclear fuels and associated materials (1-17). Due to the high neutron absorption cross-section of rare earth elements, they have stringent specification limits because the presence of other elements beyond the specification limits changes the metallurgical properties of fuel materials. To achieve the desired burn-up, optimum life span of the fuel in the reactor, and successful running of the reactor, it is required to have specific physical and chemical quality control and quality assurance measures for nuclear fuels and associated materials.

Zirconium is accepted worldwide as the cladding material used in the nuclear industry due to its low neutron absorption cross-section. In addition, U-Zr, U-Pu-Zr, Zr-Nb, and other binary and ternary alloy materials are also gaining importance in the nuclear industries (18-25). Thus, there is the need to develop 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 an over-estimation of the analytes due to spectral interferences. For the determination of trace metallic constituents, either they have to be separated physically from the trace metals using the d.c. arc carrier distillation technique (1-6) or chemical separation followed by ICP-AES analysis of the raffinate (7-15).

ABSTRACT

The major problem of determining trace analytes in nuclear materials by inductively coupled plasma atomic emission spectrometry (ICP-AES) is the spectral interference of matrix elements such as U, Pu, Zr, Th, etc., originating from their line-rich emission spectra. Chemical or physical 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. However, separation involves handling of the materials which increases the chances of contamination.

In this study, the spectral interferences of zirconium on the different analytical lines of 13 analytes (B, Cd, Sm, Dy, Gd, Na, Mg, Cr, Ca, V, Sn, Pb, and Ag) were evaluated to identify the interference-free lines of those elements in the presence of a Zr matrix. A charged coupled detector (CCD) was used because it offers more flexibility in the choice of additional analytical lines. The sensitivity and the detection limits of the analytical channels of the elements in the presence of a zirconium matrix were calculated. An analytical method was also developed for the determination of zirconium by ICP-AES, including identification of suitable analytical lines (343.823 nm, 257.139 nm, and 272.262 nm) and their analytical performance such as sensitivity and detection limits.

Because sample handling in d.c. arc distillation is minimized, the chances of contamination are also reduced. However, the technique suffers from poor precision. Inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis requires increased sample handling during chemical separation of the major matrix and thus the chances of contamination are increased. But the benefits of ICP-AES are better detection limits, as well as precision, than with d.c. arc carrier distillation. For ICP-AES analysis, a suitable extractant and feed conditioning are required which results in a 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 performances of the method (precision, detection limits, linear dynamic range, sensitivity, etc.) are superior.

In our previous study, an attempt was made to understand the spectral interference of U on other analytes using CCD-based ICP-AES (26-27). In the present study, the spectral interference of Zr was studied on 13 analytes (B, Cd, Sm, Dy, Gd, Na, Mg, Cr, Ca, V, Sn, Pb, and Ag) using a charged coupled device (CCD)-based detector. This technology offers the option of choosing additional, interference-free analytical lines of the analytes. An analytical method was also developed for the determination of Zr which involves identification of the suitable analytical lines of Zr (339.198 nm, 343.823 nm, 257.139 nm, and 272.262 nm) and examination of their analytical performance (detection limits, sensitivity, etc.).

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EXPERIMENTAL

Instrumentation

The analytical experiments were carried out using a computer-controlled, high resolution, simultaneous atomic emission spectrometer (Spectro Arcos, Germany) with ICP and D.C. arc as the excitation sources and a charged coupled device (CCD) as the detector. The instrumental specification and experimental parameters are summarized in Table I. The detector system, consisting of linear arrays of the CCD detectors (3648 pixels/array), is thermally stabilized and together with an optical system provides the ability to choose alternate analytical lines. Figure 1 is a cross-sectional view of the detector.

Reagents and Standard Solutions

The standard solutions for the 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 double-distilled water were used for preparing 0.5 M HNO₃.

ICP-AES has a very high linear dynamic range of 10⁴-10⁶ which may be sufficient for two-point calibration. But in the present case and to obtain more precise and accurate values, we did multi-point calibration curves for each element using their standard solutions. An amount of 0.5 M HNO₃ was used as the standard blank for all elements. The other concentrations which were used to obtain calibration curves were 0.1 µg/mL, 0.5 µg/mL, 1 µg/mL, 2 µg/mL, 5 µg/mL, 10 µg/mL, 20 µg/mL, 50 µg/mL, 100 µg/mL, 200 µg/mL, 500 µg/mL, and 1000 µg/mL for all elements. With regard to detector calibration, it is always advisable to do proper peak search for all analytical lines

TABLE I
Specifications and Operating Conditions of ICP-AES

Instrumental Specifications	
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 130-450nm 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 Condition	
Coolant flow	16 L/min
Auxiliary flow	0.6 L/min
Total time of measurement	28 s
Pump speed	30 rpm
RF power output	0.8 - 1.5 kW
Input power	230 V AC

Fig. 1. Cross-sectional view of the array of pixels in CCD-based detector.

used to get proper peak position, more counts, and appropriate calibration curves for each analytical line. This is generally done using 100 µg/mL of elemental standard. In the present case, this exercise was also carried out for all analytical lines of all the analytes.

To understand the spectral interference of Zr on other analytes, pure Zr solutions of different concentrations were used and the contributions at each analytical line were monitored.

RESULTS AND DISCUSSION

Determination of Zirconium by ICP-AES

Zirconium is a multi-electronic element having line-rich emission spectra. Due to the availability of high numbers of emission lines, the sensitivity of the lines were found to be less and the detection limits poorer with a photomultiplier 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 which included the identification of suitable analytical lines. Four emission lines of Zr were identified (339.198 nm, 343.823 nm, 257.139 nm, and 272.262 nm) and the calibration curves established. It was found that the 343.823 nm, 257.139 nm, and 272.262 nm lines can be used for the determination of Zr up to 1000 µg/mL with less than 5% RSD, while for the 339.198 nm line, 200 µg/mL is the upper limit of detection for Zr (Table II). The sensitivity and detection limits of Zr with the above-mentioned analytical lines were evaluated using the slopes of the calibration curves and the concentration equivalent to the intensity equal to the average of the blank value plus three times the standard deviation of the above measurement (i.e., $\bar{x} + 3\sigma$). According to the analytical

TABLE II
Sensitivity 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
Blank	BDL*	BDL*	BDL*	BDL*
0.05	0.049	0.047	0.055	0.048
0.10	0.102	0.104	0.113	0.104
0.50	0.507	0.546	0.528	0.488
1	1.03	1.05	1.08	1.03
2	2.05	2.15	2.14	2.12
5	5.04	5.47	5.25	5.06
10	10.27	10.51	10.65	10.45
20	20.62	21.52	21.32	21.349
50	49.066	54.097	52.646	50.825
100	97.716	102.065	106.519	102.998
200	185.747	199.549	209.303	201.579
500	337.206	471.176	482.468	474.171
1000	339.024	845.756	952.495	919.305
Det. Limit (µg/mL)	0.02	0.09	0.341	0.1219

*BDL = Below Detection Limit.

performance, the emission line of Zr at 343.823 nm was found to be the best.

Spectral Interference of Zr on the Analytes

Interferences may originate from various transitions of the complex matrix system and spectral interference is the most significant in ICP-AES analysis. Usually, for the determination of a particular analyte at trace levels, the most sensitive line is chosen. However, if the particular line is overlapped by some interfering line, another line needs to be selected which may be less sensitive and with poorer detection limits. Two analytical lines cannot be resolved in mainly two situations: (a) when the resolution of the instrument is poor and (b) when there is overlap between the two analytical channels which can never be separated regardless of the best resolution used in the instrument. In the first case, an instrument with better resolution

can solve the problem while for the 2nd case the spectral interference needs to be studied and the correction factor evaluated, or otherwise one needs to choose alternative analytical lines for their determination. Improvement of the resolution of the instrument may resolve the lines only if the optics are responsible for the spectral overlap. If overlap of the lines is from a broadening process in the plasma, improvement of the instrumental resolution will be inefficient. Therefore, alternative emission lines need to be investigated for their analytical applicability. In some cases it may be that only the analytical line free from spectral interference has to be chosen. If this is the case, appropriate correction factors need to be evaluated.

Due to the advancement of the CCD detector (i.e., array of pixels) and the ability to choose an alternate analytical line, this lessens spectral interference. A detailed study was carried out to choose the

appropriate emission line for the trace determination of 13 impurities in the presence of a Zr matrix.

Since B, Cd, the rare earth elements, and Ag have stringent specification limits, careful control of these constituents at each step of the fuel fabrication process is essential. Therefore, it is necessary to study the spectral interference of Zr on the analytical lines of these elements to avoid their overestimation which would be detrimental in qualifying the nuclear materials for the reactor.

Four analytical lines of B (249.773 nm, 249.677 nm, 182.641 nm, and 208.959 nm) were studied.

It was found that the spectral interference of Zr on these lines is negligibly small and all of the lines are suitable for the determination of B. Though the Cd line at 361.051 nm showed strong spectral interference from Zr, the three other analytical lines (214.438 nm, 226.502 nm, and 228.802 nm) are relatively interference-free and also have lower detection limits. For the rare earth element samarium (Sm), the three lines at 359.260 nm, 428.079 nm, and 360.428 nm showed similar analytical performance, yet the first two lines had negligible interference from Zr. Dysprosium (Dy) at 340.780 nm and gadolinium (Gd)

at 335.047 nm showed significant contribution from 1000 µg/mL of Zr. Therefore, these lines are not suitable for the determination of Gd and Dy in a Zr matrix. Dy at 353.602 nm, and Gd at 342.247 nm, 336.223 nm, and 335.862 nm showed moderate contribution from Zr, while Dy at the 353.17nm, 394.468 nm, and 364.54 nm lines showed negligible interference. The analytical performance of the above-mentioned lines of Dy (353.17nm, 394.468 nm, and 364.54 nm) was found to be comparable. For Ag, the 338.202 nm line is the best with respect to analytical performance and shows minimum spectral interference from Zr. The Na analytical line at 588.99 nm and the Mg lines at 279.55 nm and 280.270 nm show no spectral interference from Zr. Similarly, the V lines at 292.402 nm and 309.311 nm were practically interference-free from Zr. For Ca at 393.366 nm and 393.847 nm, there was moderate interference from Zr, while the first line achieves a lower detection limit. For Sn, the line at 242.949 nm was found to be the best for spectral interference as well as for analytical performance. The Cr lines at 267.716 nm and 205.618 nm showed moderate spectral interference from Zr. Table III summarizes the contribution of 1000 µg/mL of Zr on the analytical lines of the different elements, while Table IV tabulates the sensitivity and detection limits of these analytical lines in the presence of a Zr matrix. The spectral interference of Zr was found to increase linearly with Zr concentrations for all of the analytical lines listed in this paper.

The study on spectral interference of Zr on different analytes mainly leads to three situations: (a) spectral interference is significant – the line cannot be used for analytical purpose; (b) spectral interference is negligibly small – the line is suitable for its analytical application without any correction

TABLE III
Contribution of 1000 µg/mL of Zr on Other Analytes

Element	Line (nm)	Contribution (µg/mL)	Element	Line (nm)	Contribution (µg/mL)
B	249.773	0.032	Na	589.59	0.05
	249.677	0.09		588.99	BDL
	182.641	0.04	Mg	279.55	BDL
	208.959	0.03		280.27	BDL
Cd	214.438	0.018		285.21	0.28
	226.502	0.017		279.07	0.6
	228.802	0.021		202.647	0.23
	361.051	5.44	Ca	396.847	0.147
Sm	359.26	0.083		393.366	0.146
	428.079	0.064		317.933	0.2
	360.428	0.2		315.887	0.353
Dy	353.17	0.026	V	183.801	0.361
	394.468	0.04		422.673	0.22
	340.78	1.376		292.464	7.5
	353.602	0.354		311.071	0.73
Gd	364.54	0.034		292.402	BDL
	342.247	0.12		309.311	BDL
	335.047	1.07	Cr	267.716	0.13
	336.223	0.13		205.618	0.15
Ag	335.862	0.19		283.563	0.47
	328.068	20.98		284.325	0.21
	338.289	0.21		284.984	0.29
	338.202	0.06	Sn	188.991	0.62
Pb	220.353	0.19		140.045	3
	405.778	0.47		242.949	0.31

BDL = Below Detection Limit.

TABLE IV
Determination of Sensitivity and Detection Limits of Different Analyte Emission Lines

Element	Wavelength (nm)	D.L. (µg/mL)	Sensitivity (Counts/µg/mL)	Element	Wavelength (nm)	D.L. (µg/mL)	Sensitivity (Counts/µg/mL)
Ag	328.068	0.002	1.9x10 ⁻⁵	Na	588.995	0.008	1.2x10 ⁻⁵
	338.289	0.003	4.1x10 ⁻⁵		589.592	0.002	2.2x10 ⁻⁵
	338.2	0.0004	1.2x10 ⁻⁵	Pb	220.353	0.009	0.00015
B	182.641	0.002	4.2x10 ⁻⁵		405.778	0.075	0.00046
	208.959	0.0005	2.2x10 ⁻⁵	V	292.402	0.0005	8.3x10 ⁻⁶
	249.677	0.002	3.3x10 ⁻⁵		292.464	0.001	1.2x10 ⁻⁵
	249.773	0.001	2.1x10 ⁻⁵		309.311	0.001	3.6x10 ⁻⁶
Dy	340.78	0.006	2.6x10 ⁻⁵		311.071	0.001	4.9x10 ⁻⁶
	353.17	0.001	4.5x10 ⁻⁶	Sm	359.26	0.003	2.4x10 ⁻⁵
	353.602	0.002	1.7x10 ⁻⁵		360.428	0.005	6.4x10 ⁻⁵
	364.54	0.002	1.4x10 ⁻⁵		428.079	0.007	3.9x10 ⁻⁵
	394.468	0.0009	1.7x10 ⁻⁵	Sn	140.045	0.028	0.007
Ca	183.801	0.005	0.00024		189.991	0.004	0.00033
	315.887	0.004	2.0x10 ⁻⁵		242.949	0.020	0.00018
	317.933	0.003	9.9x10 ⁻⁶	Gd	335.047	0.001	1.0x10 ⁻⁵
	393.366	0.0009	1.3x10 ⁻⁷		335.862	0.013	1.3x10 ⁻⁵
	396.847	0.0004	2.1x10 ⁻⁷		336.223	0.009	1.0x10 ⁻⁵
	422.673	0.002	1.7x10 ⁻⁵		342.247	0.001	1.5x10 ⁻⁵
Cd	214.438	0.0003	7.7x10 ⁻⁶	Mg	202.647	0.006	0.00013
	226.502	0.0008	8.1x10 ⁻⁶		279.079	0.011	0.00029
	228.802	0.0006	8.1x10 ⁻⁶		279.553	0.001	5.3x10 ⁻⁷
	361.051	0.017	0.00042		280.27	0.0005	9.1x10 ⁻⁷
					285.213	0.0002	4.6x10 ⁻⁶
				Cr	205.618	0.016	0.0001
					267.716	0.0005	2.7x10 ⁻⁵
					283.563	0.0013	1.1x10 ⁻⁵
					284.325	0.0027	1.5x10 ⁻⁵
					284.984	0.0013	2.3x10 ⁻⁵

D.L. = Detection Limit.

factor; (c) when spectral interference is moderate – the line can be used for analytical purposes but an appropriate correction factor should be incorporated. Table V summarizes the comparison of the spectral interference of Zr on different analytical lines of the elements mentioned earlier and their analytical performance.

TABLE V (A)
Comparison of Types of Spectral Interference and Analytical Performance
of Various Analytical Lines of the Analytes

Ele- ments	Analytical Line (nm)	Type of Spectral Interference	Analytical Performance (D.L. and Sensitivity)
B	249.773	Negligible (correction factor not required)	Good and comparable with each other
	249.677	Negligible (correction factor not required)	Good and comparable with each other
	182.641	Negligible (correction factor not required)	Good and comparable with each other
	208.959	Negligible (correction factor not required)	Best
Cd	214.438	Negligible (correction factor not required)	Good and comparable with each other
	226.502	Negligible (correction factor not required)	Good and comparable with each other
	228.802	Negligible (correction factor not required)	Good and comparable with each other
	361.051	Significant (shlould not use)	High D.L.
Sm	359.26	Negligible (correction factor not required)	Good and comparable with each other
	428.079	Negligible (correction factor not required)	Good and comparable with each other
	360.428	Moderate (correction factor required)	Good and comparable with each other
Dy	353.17	Negligible (correction factor not required)	Good and comparable with each other
	394.468	Negligible (correction factor not required)	Good and comparable with each other
	364.54	Negligible (correction factor not required)	Good and comparable with each other
	340.78	Significant (should not use)	Good and comparable with each other
	353.602	Moderate (correction factor required)	Good and comparable with each other
Gd	342.247	Moderate (correction factor required)	Best comparable with 335.047
	336.223	Moderate (correction factor required)	Good and comparable with each other
	335.862	Moderate (correction factor required)	Good and comparable with each other
	335.047	Significant (should not use)	Best comparable with 342.247
Ag	328.068	Significant (should not use)	Good and comparable with each other
	338.289	Moderate (correction factor required)	Good and comparable with each other
	338.202	Negligible (correction factor not required)	Best
Pb	220.353	Moderate (correction factor required)	Best
	405.778	Moderate (correction factor required)	D.L. 10 times higher than the best line

D.L. = detection limit

TABLE V (B)
Comparison of Types of Spectral Interference and Analytical Performance
of Various Analytical Lines of the Analytes

Ele- ments	Analytical Line (nm)	Type of Spectral Interference	Analytical Performance (D.L. and Sensitivity)
Na	589.59	Negligible (correction factor not required)	Best
	588.99	Negligible (correction factor not required)	D.L. 4 times higher
Mg	279.55	Negligible (correction factor not required)	Good
	280.27	Negligible (correction factor not required)	Best
	285.21	Moderate (correction factor required)	Best
	279.07	Moderate (correction factor required)	Good
	202.647	Moderate (correction factor required)	Good
Ca	396.847	Moderate (correction factor required)	Best
	393.366	Moderate (correction factor required)	Good comparable with each other
	317.933	Moderate (correction factor required)	Good comparable with each other
	315.887	Moderate (correction factor required)	Good comparable with each other
	183.801	Moderate (correction factor required)	Good comparable with each other
	422.673	Moderate (correction factor required)	Good comparable with each other
V	292.464	Significant (should not use)	Good comparable with each other
	311.071	Moderate (correction factor required)	Good comparable with each other
	292.402	Negligible (correction factor not required)	Best
	309.311	Negligible (correction factor not required)	Good comparable with each other
Cr	267.716	Moderate (correction factor required)	Best
	205.618	Moderate (correction factor required)	D.L. 20 times higher than the best line
	283.563	Moderate (correction factor required)	Good comparable with each other
	284.325	Moderate (correction factor required)	Good comparable with each other
	284.984	Moderate (correction factor required)	Good comparable with each other
Sn	188.991	Moderate (correction factor required)	Best
	140.045	Moderate (correction factor required)	Good comparable with each other
	242.949	Moderate (correction factor required)	Good comparable with each other

D.L. = detection limit.

CONCLUSION

A systematic study was carried out to understand the spectral interference of zirconium on 13 analytes (B, Cd, Sm, Dy, Gd, Na, Mg, Cr, Ca, V, Sn, Pb, and Ag) by CCD-based ICP-AES. The main advantage of using this technique is the arrays of the 3764 detector pixels which cover the entire wavelength range. This offers the choice of additional analytical lines of the elements free from spectral interference of an emission-rich matrix such as Zr, U, Pu, etc. With CCD-based ICP-AES, all analytes can be monitored simultaneously, and hence the sample requirement is less compared to the monochromator-based sequential ICP-AES spectrometer.

Interference-free analytical lines of these elements were identified, and the analytical performance (detection limits, sensitivity, etc.) of these lines were studied. An analytical method was 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 µg/mL), the other three analytical lines studied (343.823nm, 257.139 nm, and 272.262 nm) can be used for Zr determination resulting in ~ 5% RSD.

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