

Determination of Spectral Interference of Zirconium On Some Critical Analytes By CCD Based Inductively Coupled Plasma – Atomic Emission Spectrometric Technique

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Abstract

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is multi elemental, rapid, simple technique for the determination of trace level analytes, but suffers from spectral interference of matrix elements like U, Pu, Zr, Th etc. originating from their line rich emission spectra causing detrimental effect on the determination of analyte elements at trace levels in the nuclear materials. This can be overcome by using carrier distillation technique wherein carrier selectively distills analytes into D.C. arc-AES leaving behind the matrix into the electrode crater, being physical separation of the matrix. This technique is generally used to determine common metallic elements. For the determination of rare earth elements being refractory in nature like U, Th, etc. at sub-ppm levels, carrier distillation technique cannot be used. Hence, chemical separation of the matrix followed by their determination by AES technique is the usual practice, which may involve contamination of the sample during pre-treatment. Charged Coupled Detector (CCD) with flexibility of the choices of additional analytical lines of analytes, e.g., for Ce, 413.38 nm, 413.765 nm, 418.66 nm and 448.691 nm lines were selected and studied which may have lesser interference from Zr, facilitating direct determination of analytes at trace levels without any type of separation. Present paper involves the detailed study of spectral interference of zirconium on different analytical lines of Ba, Bi, Ce, Er, La, Lu, Mo, Nd, Pr, Sb, Sc, Ti, Tl, U, W, Y, Yb to select suitable analytical lines based on contributions of Zr on each analytical line, detection limits and sensitivity. Zirconium being major matrix, its determination by ICP-AES was performed by identifying four suitable analytical lines, namely, 339.198 nm, 343.823 nm, 257.139 nm and 272.262 nm including monitoring of sensitivity, detection limits etc. Based on these interference studies,

it is possible to determine 17 analytes under investigations in Zr matrix on ppm basis by ICP-AES using their appropriate analytical lines without any chemical/physical separation.

Keywords Zirconium, Spectral interference, CCD based ICP-AES, Detection limits, Sensitivity

Introduction

In nuclear industry, the determination of trace metallic impurities is one of the important steps for chemical quality control of nuclear fuels and associated materials. To achieve desired burn-up, successful life span of the fuel in the reactor and also for smooth running of the reactor, it is essential to have stringent physical and chemical quality control and quality assurance measures for the nuclear materials. Some of the trace metal constituents in nuclear materials can affect its performance significantly due to their metallurgical and neutron absorption characteristics. The Inductively Coupled Plasma – Atomic Emission Spectrometric (AES) technique being simultaneous multi-elemental with acceptable analytical performance (detection limit, sensitivity, large linear dynamic range, etc.) is routinely used for the determination of trace metals in nuclear fuels and associated materials which forms an important and integral part of the chemical quality control at different stages of fuel fabrication.

The major matrix constituents in nuclear fuels, viz. U, Pu, Th and associated nuclear materials like graphite, etc. have rich emission spectra and hence it is essential to obtain trace elemental (analyte) spectrum devoid of interferences from that of U, Th and/or Pu, etc. The well-known established technique is D.C.arc -AES using carrier distillation method. In this technique the major matrix gets suppressed whereas the analytes are smoothly swept into the arc. Thus it is a direct technique, with minimum chances of contamination owing to less sample handling. However the technique offers poor precision. This technique is used for the determination of analytes with reasonable specification limits¹⁻⁶. ICP-AES technique is generally used for the determination of rare earth elements after chemical separation of the matrix to achieve sub-ppm levels of specification limits for analytes by preconcentration as they cannot be determined directly by feeding higher amounts of the matrix solution due to the less tolerance of solid material which can be fed into the plasma causing choking of the nebuliser. Hence in this method there are chances of contamination of the sample but has superior detection limits and precision than D.C. arc – AES 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 levels⁷⁻¹². 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.) is superior. In our previous study, an attempt was made to understand the spectral interference of Uranium on other analytes using CCD-based ICP-AES¹³⁻¹⁵.

Zirconium finds its applications in nuclear industry as a cladding material, while U-Zr, U-Pu-Zr, Zr-Nb and binary and ternary alloy materials are useful as nuclear fuels. This is mainly due to its many unique characteristics such as low thermal neutron absorption cross section (0.18barn), have good mechanical properties and corrosion resistance. In order to become suitable as nuclear material, one of the criteria is to conform to trace metal impurities as per the specifications laid down by fuel designer¹⁶⁻²². Using D.C. arc-AES technique based on carrier-distillation method, we have reported determination of trace common metallic elements in Zr matrix without chemical separation²³⁻²⁵. In U-Zr and Zr-Nb alloys, trace metals were reported after chemical separation by ICP-AES²⁶⁻²⁷. Owing to multi-electronic configuration of Zr has rich emission line spectra, which might cause spectral interference on analytes thereby leading to higher limits of detection. In order to achieve lower detection limits especially in case of rare earths, it becomes inevitable to perform chemical separation of Zr prior to determination of trace metallic elements by ICP-AES technique along with common metallic elements. In this process, it was observed that the presence of Zr even at micro-gram levels may cause spectral interference on analytes leading to their in-accurate determinations. Hence it was essential to understand Zr contributions on various emission lines for analytes in detail. Using CCD-based ICP-AES technique, we have reported the spectral interference of Zr on some of the critical common analytes and rare earths²⁸⁻²⁹.

The present study is the continuation of the previous work, wherein some more elements, namely, Ce, Nd, Lu, Pr, Er, Y, U, Ba, Bi, Tl, Yb, La, Mo, Sb, W, Sc and Ti have been studied in detail for their determination using charged coupled device (CCD) based detector without any physical or chemical separation from major matrix zirconium³⁰. This detector offers choice of additional analytical lines, free from the major matrix, which were explored and identified. These analytes with interference free emission lines from Zr can be used for their direct determinations on ppm basis using 1mg/ml of Zr sample solution by ICP-AES depending upon the specification limits requirements for these trace elements. This necessitated determination of Zr by using suitable analytical lines and it's quantification to

understand its tolerance on each analyte under study including analytical performances (detection limits, sensitivity etc.) for the identified lines.

Experimental Details

Instrument

An atomic emission spectrometer instrument Spectro Arcos procured from Germany having dual excitation sources, ICP as well as D.C. arc was used, the details for which are mentioned elsewhere²⁸⁻²⁹. Also, the main features of this unit being that it is provided with charged coupled detectors with which one can choose suitable additional analytical lines during study.

Reagents and standard solutions

CertiPUR[®] ICP multi standard solutions (E-Merck, Darmstadt, Germany) at 1 mg/ml were used for the preparation of solutions of rare earth, common metallic elements in the range of 0.05 µg/ml-20 µg/ml and for Zr in the range of 0.05 µg/ml -1000 µg/ml were prepared by suitable dilutions with supra-pure 0.5M HNO₃. Appropriate amount of nuclear grade U₃O₈ received from NFC was dissolved in minimum amount of concentrated HNO₃ and was made up in 4M HNO₃ to get 10 mg/ml U stock solution. From this, U standards were prepared in the range of 0.05 - 20 µg/ml in 0.5M HNO₃. Multi-point standardization was carried out using 0.5M HNO₃ as lower standard and 0.05 µg/mL - 5 µg/mL of the corresponding higher elemental standard for various analytes and for Zr in the concentration range of 0.05 µg/mL - 1000 µg/mL after proper peak search using 20 µg/mL of each analyte separately. For all the analytes including Zr, calibration plots were obtained. Blank correction was carried out using 0.5M HNO₃.

Results and Discussion

The entire study has been classified into four categories, which is discussed below:

(a) Determination of Zirconium by ICP-AES

In order to understand the extent of interference from Zr on each analyte, quantification of the same was essential. Hence the calibration curves for Zr using four analytical lines, namely, 339.198 nm, 343.823 nm, 257.139 nm, and 272.262 nm were obtained which are shown in Fig.1 . It was found that except for Zr-339.198 nm, the upper limit of detection for Zr is 200 µg/mL, while Zr- 343.823 nm, Zr-257.139 nm, and Zr-272.262 nm lines can be used for their determinations up to 1000 µg/mL with less than 5% RSD (Relative Standard Deviation). The

detection limits for these analytical lines of Zr were found to be 0.02 µg/mL, 0.09 µg/mL, 0.34 µg/mL and 0.12 µg/mL respectively. Based on the analytical performances, namely, detection limits, sensitivity, the emission line of Zr at 343.823 nm was found to be the best for its determination.

(b) Identification of analytical lines for elements under study free from spectral interference of zirconium

From the directory of the wavelength tables provided within the instrument, the best analytical lines which can be considered for the determination of analytes were identified and are shown in Table 1.

(c) Contributions of Zr on various analytical lines for the analytes and the performance of the analytes

Spectral interference of Zr on various analytes

In ICP-AES, the spectral interference is quite significant which is mainly due to various transitions of the complex matrix system. Generally, to determine an analyte at trace levels, the most sensitive line is chosen for analysis. But, if this line is overlapped by some other interfering line leading to erroneous estimates for analyte, one needs to select another line which may be less sensitive and with poorer detection limits but will give accurate determination for the analyte. 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 were needed to be investigated for analytical applicability. In some cases, it may happen that only the analytical line free from spectral interference needs 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.

In Table 2A and Table 2B, the contributions of 1000 µg/mL of Zr on the analytical lines of all the elements under study including sensitivity and detection limits in presence of Zr matrix have been presented. These contributions of Zr using 1000 µg/mL of Zr were recorded at the blank levels for each analyte having many analytical lines (0.5M HNO₃). It was observed that the spectral interference of Zr on various analytical lines was found to increase linearly with Zr concentrations. Also, the choice of the best analytical line for analytes was based mainly on the extent of contribution from Zr at 1000 microgram /mL level followed by its detection limit.

Accordingly, a detailed study was carried out to choose the appropriate emission line/s for the trace determinations of 17 analytes in the presence of Zr matrix which is discussed in detail below:

Ba (Barium)

Three lines of Ba namely, 230.424 nm, 233.527 nm, 455.404 nm were studied. Amongst these three lines, Ba 233.527 nm analytical line was found to be the best with respect to detection limit and practically no spectral interference, while Ba 455.404 nm analytical line showed detection limit comparable with the best line and having moderate spectral interference from Zr which can be overcome using correction factor mentioned. Ba 230.424 nm was found to have severe spectral interference with 100 times poor detection limit than the best line and hence should not be used.

Bi (Bismuth)

For Bi, six analytical lines namely, Bi 143.683 nm, 153.317 nm, 190.241 nm, 222.825 nm, 223.061 nm and Bi 306.772 nm were studied. Amongst these six lines, Bi 223.061 nm analytical line was the best requiring moderate correction factor, while Bi 306.772 nm was also found to be useful with detection limit 100 times higher than the best line, to be used after incorporating moderate correction factor. The remaining four lines of Bi 143.683 nm, Bi 153.317 nm, Bi 190.241 nm and Bi 222.825 nm cannot be used due to severe spectral interferences from Zr.

Ce (Cerium)

For Ce, four analytical lines, namely, Ce 413.38 nm, Ce 413.765 nm, Ce 418.66 nm and Ce 448.691 nm were investigated. Ce 413.765 nm was found to be the best analytical line with negligible correction factor, while Ce 413.38 nm line was found to be the next most suitable

line with detection limit comparable with the best line but requires moderate correction factor. Ce 448.691 nm and Ce 418.66 nm lines showed severe spectral interferences from Zr; hence both the lines cannot be used for analysis.

Er (Erbium)

Amongst the four lines of Er, namely, Er 323.058 nm, Er 326.478 nm, Er 337.271 nm and Er 349.91 nm, the best analytical line was found to be Er 337.271 nm with negligible correction factor while two analytical lines, Er 323.058 nm and Er 349.91 nm were also found to be useful with moderate correction factors and detection limits ten times higher than the best line. Er 326.478 nm showed significant spectral interference from Zr and hence cannot be used.

La (Lanthanum)

For La, three analytical lines namely, La 333.749 nm, La 379.478 nm and La 408.672 nm were studied. La 379.478 nm line was found to be the best analytical line with negligible correction factor, while La 333.749 nm showed detection limit comparable with the best line and moderate correction factor. La 408.672 nm with detection limit ten times higher than the best line, required negligible correction factor. Thus, all three analytical lines of La are useful for analysis.

Lu (Lutetium)

For Lu, four analytical lines namely, Lu 219.554 nm, Lu 261.542 nm, Lu 291.139 nm and Lu 307.76 nm were studied. All these lines can be used for the analysis with negligible correction factor, the best being Lu 261.542 nm line. Lu 291.139 nm, Lu 307.76 nm have detection limits ten times higher than the best line while Lu 219.554 nm has detection limit hundred times higher than the best line.

Mo (Molybdenum)

For Mo, four analytical lines, namely, Mo 202.095 nm, Mo 203.909 nm, Mo 204.664 nm and Mo 281.615 nm were studied. Amongst these lines, Mo 202.095 nm and Mo 281.615 nm were found to be the best analytical lines with lowest detection limits and negligible spectral interferences from Zr and hence does not require any correction factors for analysis. Remaining two lines, Mo 203.909 nm and Mo 204.664 nm were also found to be equally suitable lines with detection limits comparable to the best lines and showed negligible spectral interferences from Zr and hence does not require any correction factor for analysis.

Nd (Neodymium)

For Nd, four analytical lines, namely, Nd 401.225 nm, Nd 406.109 nm, Nd 417.73 nm and Nd 430.358 nm were investigated. Nd 406.109 nm and Nd 430.358 nm were found to be the best and equally good analytical lines with incorporation of moderate correction factors for

analysis. Nd 417.73 nm line was also found to be good with detection limits ten times higher than the best line required to use moderate correction factor. Nd 401.225 nm line cannot be used due to significant spectral interferences from Zr.

Pr (Praseodymium)

For Pr, two analytical lines, Pr 411.846 nm and Pr 414.311 nm were found to be useful. The best line was Pr 411.846 nm with negligible correction factor, while Pr 414.311 nm had detection limit comparable with the best line but requires moderate correction factor for analysis.

Sb (Antimony)

For Sb, three analytical lines, Sb 181.115 nm, Sb 206.833 nm and Sb 217.581 nm were investigated. Amongst these, Sb 206.833 nm analytical line was found to be the best with moderate correction factor, whereas Sb 217.581 nm was found to have detection limit comparable with the best line requiring moderate correction factor for analysis. Sb 181.115 nm showed detection limit ten times higher than the best line and can be determined after incorporating moderate correction factor.

Sc (Scandium)

For Sc, four analytical lines, namely, Sc 335.373 nm, Sc 356.770 nm, Sc 361.384 nm and Sc 424.683 nm were studied. Amongst these four lines, Sc 424.683 nm was found to be the best analytical line having very much insignificant spectral interference from Zr, hence can be used directly without the need for any correction factor. The next two useful lines were Sc 335.373 nm and Sc 361.384 nm with detection limits comparable with the best line but as there was no spectral interferences from Zr was observed, can be used directly for determination without incorporating correction factors. Sc 356.770 nm line showed the detection limit 100 times higher than the best line and requires moderate correction factor for the analysis of Sc.

Ti (Titanium)

For Ti, two useful analytical lines, Ti 334.187 nm and Ti 336.121 nm were studied and were found to be equally useful for analysis due to good detection limits and requiring negligible correction factor to take care of interference from Zr for analysis.

Tl (Thalium)

For Tl, two analytical lines, namely, Tl 190.864 nm and Tl 276.787 nm were studied. Tl 190.864 nm was found to be the best analytical line with moderate correction factor required to be used for analysis. Tl 276.787 nm with detection limit 30 times higher than the best line with significant spectral interference from Zr, cannot be used for analysis.

U (Uranium)

For U, four analytical lines, namely, U 279.394 nm, U 367.007 nm, U 385.958 nm and U 409.014 nm were studied. U 385.958 nm was observed to be the best line which can be used after incorporating moderate correction factor. U 279.394 nm and U 367.007 nm were found to have detection limits comparable with the best line but have significant spectral interferences from Zr hence, can be used after incorporating the correction factors for the analysis of U. U 409.014 nm showed severe spectral interferences due to Zr, hence cannot be used.

W (Tungsten)

For W, four analytical lines, namely, W 207.911 nm, W 220.448 nm, W 224.875 nm and W 239.709 nm were studied. Both the analytical lines for W, namely, W 207.911 nm and W 224.875 nm were found to be useful with good, comparable detection limits with negligible spectral interference from Zr and hence does not require any correction factor for analysis. W 220.448 nm and W 239.709 nm were found to have detection limits comparable with the best line but due to contributions from spectral interferences of Zr, requires moderate correction factor for the analysis.

Y (Yttrium)

For Y, eight analytical lines, namely, Y 224.306 nm, Y 320.332 nm, Y 324.228 nm, Y 360.073 nm, Y 362.871 nm, Y 371.030 nm, Y 377.433 nm and Y 442.259 nm were studied. Amongst these, Y 377.433 nm line was found to be the best analytical line with negligible spectral interference from Zr and hence does not require to incorporate any correction factor for analysis. The next suitable analytical lines being Y 320.332 nm, Y 360.073 nm and Y 371.030 nm with negligible spectral interferences from Zr and hence does not require any correction factors. In the context of detection limits, Y 360.073 nm showed detection limit being comparable with the best line while for Y 320.332 nm and Y 371.030 nm, the detection limits were ten times higher than the best line; all the three lines have negligible spectral interferences for Zr which can be used directly for analysis. For Y 224.306 nm, Y 324.228 nm, Y 362.871 nm and Y 442.259 nm, the detection limits were ten times higher than the best line and showed moderate spectral interferences due to Zr which can be rectified using appropriate correction factors.

Yb (Ytterbium)

For Yb, four analytical lines, namely, Yb 222.446 nm, Yb 289.138 nm, Yb 328.937 nm and Yb 369.419 nm were studied. Yb 328.937 nm line was found to be the best analytical line with negligible spectral interference and hence does not require any correction factor for analysis. Yb 222.446 nm, Yb 289.138 nm and Yb 369.419 nm were also found to have

negligible spectral interferences from Zr with detection limits comparable with the best line except for Yb 222.446 nm which has detection limits ten times higher than the best line.

The above discussions on the effect of Zr on various analytical lines of elements under study leads to three main scenarios: (1) significant contribution from Zr matrix– the line cannot be used for analytical purpose; (2) insignificant contribution from Zr matrix – the line is suitable for its analytical application without any correction factor; (3) moderate contribution from Zr matrix – the line can be used for analytical purposes but needs to incorporate appropriate correction factor. In Table 3, the comparison of the spectral interference of Zr on different analytical lines of the elements mentioned earlier and their analytical performance including the most suitable analytical lines which can be selected for analytical purposes for the determination of analytes in presence of Zr matrix without physical or chemical separation have been presented.

(d) Finalizing best analytical lines for analytes for their direct determinations in presence of zirconium without chemical and/or physical separation on ppm basis.

In Table 4, the analytical results for the direct determination of the analytes under study on ppm ($\mu\text{g/g}$) basis have been shown based on better detection limits and negligible interference from Zr requiring negligible correction factor for their determinations. Depending upon the specification limits being led down by the sample providing agency, it is possible to get the results just by aspirating 1 mg/ml of the Zr sample solution into ICP using appropriate wavelengths for the analytes mentioned therein on ppm basis, thus providing simple method for the direct determination of analytes in actual zirconium samples using CCD based ICP-AES technique.

Conclusions

A systematic study was carried out to understand the spectral interference of zirconium on 17 trace metals (Ba, Bi, Ce, Er, La, Lu, Mo, Nd, Pr, Sb, Sc, Ti, Tl, U, W, Y, Yb) in Zr matrix, crucial from the viewpoint of requirements in nuclear industry using CCD based ICP-AES technique. The most suitable analytical lines for various elements after detailed studies have been mentioned in Table 4. Also, for all the analytes, sensitivity, detection limits and the tolerance limits of Zr on these analytes were recorded. This data was used to identify additional analytical lines for the determinations of trace metals. The present method also

included the determination of Zr by ICP-AES technique in the range of 0.05 $\mu\text{g/mL}$ to 1000 $\mu\text{g/mL}$ using 257.139 nm, 272.262 nm, 339.198 nm and 343.828 nm, analytical lines of Zr which were suitable, except for 339.198 nm which gets saturated at 200 $\mu\text{g/mL}$. Based on the calibration curves, detection limits for Zr were found to be 0.34 $\mu\text{g/ml}$, 0.12 $\mu\text{g/ml}$, 0.02 $\mu\text{g/mL}$ and 0.09 $\mu\text{g/ml}$ respectively. These studies are helpful in arriving at accurate determinations of trace metals studied in presence of zirconium up to 1000 μg of zirconium on ppm ($\mu\text{g/g}$) basis for actual samples directly without any separation steps.

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Figure:

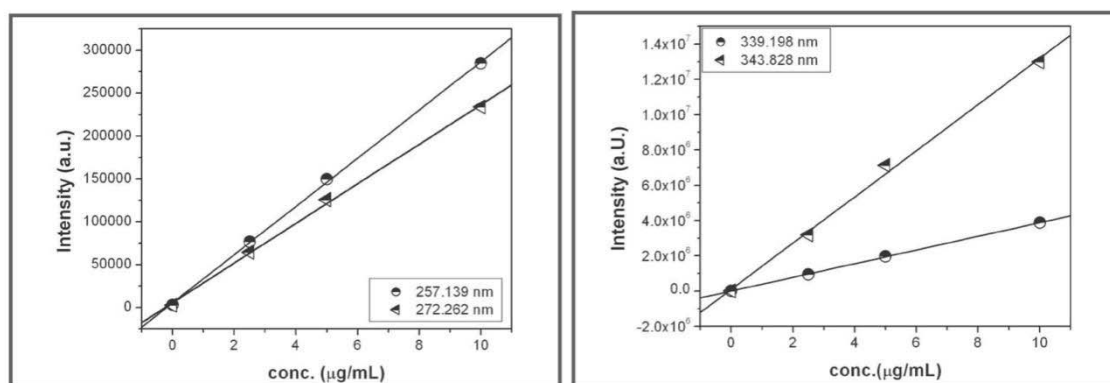


Fig. 1(A). Calibration curves for Zr : 257.139 nm and 272.262 nm.

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

Tables:

TABLE 1: Interference free lines for analytes in Zr matrix

Element	Analytical Line (nm)
Ba	233.527
Bi	223.061
Ce	413.765
Er	337.271
La	379.478
Lu	261.542
Mo	202.095, 281.615
Nd	406.109
Pr	411.846
Sb	206.833

Sc	424.683
Ti	336.121
Tl	190.864
U	385.958
W	207.911
Y	377.433
Yb	328.937

TABLE 2A: Spectral interference of Zirconium on various analytes

Element	Anal. Line(nm)	Contribution (µg/mL)	Correction factor	Detection Limit (µg/mL)	Sensitivity (Counts/ µg/mL)
	230.424	>17.8	NA	6.031x10 ⁻¹	0.014587
Ba	233.527	0.019	1.9x10 ⁻⁵	1.472x10 ⁻³	1.775x10 ⁻⁵
	455.404	0.238	2.38x10 ⁻⁴	1.015x10 ⁻³	2.4172x10 ⁻⁵
Bi	143.683	> 10.527	NA	4.76x10 ⁻¹	0.01917
	153.317	> 41.262	NA	1.808	0.075808
	190.241	5.194	5.194x10 ⁻³	1.781 x10 ⁻¹	0.0018522
	222.825	1.826	1.826x10 ⁻³	7.159 x10 ⁻²	0.001356
	223.061	0.194	1.94x10 ⁻⁴	5.227 x10 ⁻³	0.00015129
	306.772	0.343	3.43x10 ⁻⁴	1.306 x10 ⁻¹	9.7139x10 ⁻⁵
Ce	413.380	0.747	7.47x10 ⁻⁴	6.523 x10 ⁻³	3.8528x10 ⁻⁵
	413.765	0.085	8.5x10 ⁻⁵	3.573 x10 ⁻³	3.9952x10 ⁻⁵
	418.66	> 22.712	NA	4.895 x10 ⁻³	4.0382x10 ⁻⁵
	448.691	2.466	2.466x10 ⁻³	7.605 x10 ⁻²	0.00077383
Er	323.058	0.197	1.97x10 ⁻⁴	1.333 x10 ⁻³	4.5941x10 ⁻⁵
	326.478	8.946	8.946x10 ⁻³	5.669 x10 ⁻⁴	9.9324x10 ⁻⁶
	337.271	0.042	4.2x10 ⁻⁵	1.592 x10 ⁻³	3.7098x10 ⁻⁶
	349.910	0.642	6.45x10 ⁻⁴	1.45 x10 ⁻³	1.3441x10 ⁻⁵
La	333.749	0.116	1.16x10 ⁻⁴	1.408 x10 ⁻³	6.9697x10 ⁻⁶
	379.478	0.045	4.5x10 ⁻⁵	1.608 x10 ⁻³	8.2075x10 ⁻⁶
	408.672	0.049	4.9x10 ⁻⁵	2.664 x10 ⁻⁴	9.8999x10 ⁻⁶
Lu	219.554	0.034	3.4x10 ⁻⁵	1.507 x10 ⁻³	3.0806x10 ⁻⁵
	261.542	0.004	4x10 ⁻⁶	4.779x10 ⁻⁵	1.4908x10 ⁻⁶
	291.139	0.028	2.8x10 ⁻⁵	9.035 x10 ⁻⁴	1.3165x10 ⁻⁵
	307.760	0.016	1.6x10 ⁻⁵	2.952 x10 ⁻⁴	7.906x10 ⁻⁶
Mo	202.095	0.024	2.4x10 ⁻⁵	3.079 x10 ⁻³	1.9838E-005
	203.909	0.044	4.4x10 ⁻⁵	4.141 x10 ⁻³	3.8155E-005
	204.664	0.069	6.9x10 ⁻⁵	2 x10 ⁻³	5.4118E-005
	281.615	0.046	4.6x10 ⁻⁵	6.747 x10 ⁻⁴	2.9765E-005

Nd	401.225	2.075	2.075×10^{-3}	4.601×10^{-3}	2.7236E-005
	406.109	0.2	2×10^{-4}	3.702×10^{-3}	3.984E-005
	417.731	0.254	2.54×10^{-4}	1.561×10^{-2}	4.6427E-005
	430.358	0.24	2.4×10^{-4}	7.256×10^{-3}	3.2077E-005
Pr	411.846	0.064	6.4×10^{-5}	5.511×10^{-3}	3.3374E-005
	414.311	0.184	1.84×10^{-4}	2.978×10^{-3}	2.3725E-005

NA – Not applicable

TABLE 2B: Detection limits and sensitivity for various emission lines of analytes

Element	Wavelength (nm)	Contribution (µg/mL)	Correction factor	Detection Limit (µg/mL)	Sensitivity (Counts/µg/mL)
Sb	187.115	0.349	3.49×10^{-4}	1.803×10^{-2}	0.00036385
	206.833	0.143	1.43×10^{-4}	5.697×10^{-3}	0.00014288
	217.581	0.39	3.9×10^{-4}	0.007853	0.00011591
Sc	335.373	0.047	4.7×10^{-5}	0.0002637	9.2255E-007
	356.770	0.12	1.2×10^{-4}	0.01793	6.0168E-006
	361.384	0.091	9.1×10^{-5}	0.0001354	8.5068E-007
	424.683	0.004	4×10^{-6}	0.0002889	9.585E-007
Ti	334.187	0.046	4.6×10^{-5}	0.004604	5.6556E-006
	336.121	0.043	4.3×10^{-5}	0.001748	1.6637E-006
Tl	190.864	0.443	4.43×10^{-4}	0.027	848
	276.787	3.588	3.588×10^{-3}	0.83	27
U	279.394	1.218	1.218×10^{-3}	0.02528	0.00085538
	367.007	2.684	2.684×10^{-3}	0.00514	0.00025145
	385.958	0.278	2.78×10^{-4}	0.01497	0.00016145
	409.014	10.645	10.645×10^{-2}	0.02018	0.00020043
W	207.911	0.061	6.1×10^{-5}	0.003288	7.805E-005
	220.448	0.107	1.07×10^{-4}	0.007447	0.00012411
	224.875	0.085	8.5×10^{-5}	0.006307	6.6452E-005
	239.709	0.108	1.08×10^{-4}	0.003162	7.2284E-005
Y	224.306	0.146	1.46×10^{-4}	0.007314	5.4535E-005
	320.332	0.05	5×10^{-5}	0.001759	5.8651E-006
	324.228	0.187	1.87×10^{-4}	6.811E-005	2.5883E-006
	360.073	0.087	8.7×10^{-5}	0.0002023	3.1694E-006
	362.871	0.209	2.09×10^{-4}	0.002476	2.9604E-005
	371.030	0.061	6.1×10^{-5}	9.471E-005	1.4163E-006
	377.433	0.027	2.7×10^{-5}	0.0006185	2.2761E-006
	442.259	0.104	1.04×10^{-4}	0.006534	4.0566E-005

Yb	222.446	0.042	4.2×10^{-5}	0.001962	2.5171E-005
	289.138	0.022	2.2×10^{-5}	0.0003137	7.7288E-006
	328.937	0.015	1.5×10^{-5}	0.0001766	5.13E-007
	369.419	0.023	2.3×10^{-5}	0.0001183	1.7341E-006

NA – Not applicable

TABLE 3: Comparison of types of spectral interference and analytical performance of various analytical lines for the elements under study

Element	Anal. Line (nm)	Level of spectral interference	Analytical Performance
Ba	230.424	Bad line, should not be used	D.L. 100 times higher than best line
	233.527	Negligible (correction factor not required)	Best
	455.404	Moderate (correction factor required)	D.L. comparable with best line
Bi	143.683	Bad line, should not be used	D.L. 100 times higher than best line
	153.317	Worst line, should not be used	D.L. 1000 times higher than best line
	190.241	Significant, should not be used	D.L. 100 times higher than best line
	222.825	Significant, should not be used	D.L. 10 times higher than best line
	223.061	Moderate (correction factor required)	Best
	306.772	Moderate (correction factor required)	D.L. 100 times higher than best line
Ce	413.38	Moderate (correction factor required)	D.L. comparable with best line
	413.765	Negligible (correction factor not required)	Best
	418.66	Bad line, should not be used	D.L. comparable with best line
	448.691	Significant, should not be used	D.L. 10 times higher than best line
Er	323.058	Moderate (correction factor required)	D.L. 10 times higher than best line
	326.478	Significant, should not be used	D.L. 10 times higher than best line
	337.271	Negligible (correction factor not required)	Best
	349.91	Moderate (correction factor required)	D.L. 10 times higher than best line
La	333.749	Moderate (correction factor required)	D.L. comparable with best line
	379.478	Negligible (correction factor not required)	D.L. 10 times higher than best line

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	408.672	Negligible (correction factor not required)	Best
Lu	219.554	Negligible (correction factor not required)	D.L. 100 times higher than best line
	261.542	Negligible (correction factor not required)	Best
	291.139	Negligible (correction factor not required)	D.L. 10 times higher than best line
	307.76	Negligible (correction factor not required)	D.L. 10 times higher than best line
Mo	202.095	Negligible (correction factor not required)	D.L. 10 times higher than best line
	203.909	Negligible (correction factor not required)	D.L. 10 times higher than best line
	204.664	Negligible (correction factor not required)	D.L. 10 times higher than best line
	281.615	Negligible (correction factor not required)	Best
Nd	401.225	Significant, should not be used	D.L. comparable with best line
	406.109	Moderate (correction factor required)	Best
	417.73	Moderate (correction factor required)	D.L. 10 times higher than best line
	430.358	Moderate (correction factor required)	D.L. comparable with best line
Pr	411.846	Negligible (correction factor not required)	Best
	414.311	Moderate (correction factor required)	D.L. comparable with best line
Sb	187.115	Moderate (correction factor required)	D.L. 10 times higher than best line
	206.833	Moderate (correction factor required)	Best
	217.581	Moderate (correction factor required)	D.L. comparable with best line
Sc	335.373	Negligible (correction factor not required)	D.L. comparable with best line
	356.770	Moderate (correction factor required)	D.L. 100 times higher than best line
	361.384	Negligible (correction factor not required)	D.L. comparable with best line
	424.683	Very much insignificant, correction factor not required	Best
Ti	334.187	Negligible (correction factor not required)	D.L. comparable with best line

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	336.121	Negligible (correction factor not required)	Best
Tl	190.864	Moderate (correction factor required)	Best
	276.787	Significant, should not be used	D.L. 30 times higher than the best line
U	279.394	Significant (to be used after incorporating correction factor)	D.L. comparable with best line
	367.007	Significant (to be used after incorporating correction factor)	D.L. comparable with best line
	385.958	Moderate (correction factor required)	Best
	409.014	Major (cannot be used)	D.L. comparable with best line
W	207.911	Negligible (correction factor not required)	Best
	220.448	Moderate (correction factor required)	D.L. comparable with best line
	224.875	Negligible (correction factor not required)	D.L. comparable with best line
	239.709	Moderate (correction factor required)	D.L. comparable with best line
Y	224.306	Moderate (correction factor required)	D.L. 10 times higher than best line
	320.332	Negligible (correction factor not required)	D.L. 10 times higher than best line
	324.228	Moderate (correction factor required)	D.L. 10 times higher than best line
	349.609	Worst line, should not be used	D.L. 10 times higher than best line
	360.073	Negligible (correction factor not required)	Best
	362.871	Moderate (correction factor required)	D.L. 10 times higher than best line
	371.030	Negligible (correction factor not required)	D.L. 10 times higher than best line
	377.433	Negligible (correction factor not required)	D.L. comparable with the best line
	442.259	Moderate (correction factor required)	D.L. 10 times higher than best line
Yb	222.446	Negligible (correction factor not required)	D.L. 10 times higher than best line
	289.138	Negligible (correction factor not required)	Good and comparable with best line
	328.937	Negligible (correction factor not required)	Good and comparable with best line
	369.419	Negligible (correction factor not required)	Best

TABLE 4: Detection limits for various analytes on ppm ($\mu\text{g/g}$) basis

Element	Wavelength (nm)	Detection Limit ($\mu\text{g/g}$)
Ba	233.527	1.5
Bi	223.061	5.23
Ce	413.765	3.57
Er	337.271	1.6
La	408.672	0.27
Lu	261.542	0.048
Mo	281.615	0.68
Nd	406.109	3.70
Pr	411.846	5.51
Sb	206.833	5.7
Sc	424.683	0.3
Ti	336.121	1.75
Tl	190.864	27
U	385.958	15
W	207.911	3.3
Y	360.073	0.20
Yb	369.419	0.12

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