Studies on the Spectral Interference of Gadolinium on Different Analytes by Inductively Coupled Plasma Atomic Emission Spectrometry

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INTRODUCTION

Among spectroscopic methods, which are most commonly used for trace metal characterization, inductively coupled plasma atomic emission spectrometry (ICP-AES) scores over other techniques due to its simplicity and simultaneous multi-element determination capability coupled with adequate sensitivity, analytical range, and good precision of the determinations (1-5). Apart from these advantages, ICP-AES suffers severely from spectral interference in trace level determinations of the analytes in the presence of emission-rich matrix elements (6-8). Different kinds of interferences in ICP-AES including chemical, nebulization, atomization, and spectral interferences are also reported in the literature (9-11). Quantitative chemical separation of an emission-rich major matrix, followed by the analysis of the raffinate, is the general methodology used in ICP-AES to minimize spectral interferences (12-17). This requires not only selective ligands for preferential extraction of the matrix, leaving the analytes in the raffinate without any loss even at trace levels, but is time-consuming with the chance of contamination during processing of the samples. Therefore, an ICP-AES-based method is necessary for the direct determination of analytes without any chemical separation which requires a detailed study on the spectral interference of the emission-rich matrix elements of the analytes.

ABSTRACT

An attempt was made to understand the spectral interference of Gd on 29 common analytes (Ag, Al, B, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Dy, Fe, Ga, Gd, In, La, Li, Lu, Mg, Mn, Na, Nd, Ni, Pb, Pr, Sr, Tl, and Zn) using inductively coupled plasma atomic emission spectrometry (ICP-AES) with a capacitive charge-coupled device (CCD) as the detector. The present study includes identification of suitable interference-free analytical lines of these analytes, evaluation of the correction factor of each analytical line, and determination of the tolerance levels of these analytical lines along with the ICP-AES-based methodology for the simultaneous determination of Gd. Based on the spectral interference study, an ICP-AES-based method was developed for the determination of these analytes at trace levels in the presence of a Gd matrix without chemical separation. Furthermore, the developed methodology was validated using synthetic samples prepared from commercially available standard reference material solutions of individual elements; the results were found to be satisfactory. The method was also compared with other techniques.

The line-rich emission spectra of rare earth elements (REEs) and their multi-electron nature leads to the erroneous determination of analytes at trace levels owing to spectral interferences. Several studies reported on the mutual spectral interference of rare earth elements

(18-25). Gadolinium (Gd), being one of the important rare earth elements used in industry, is under consideration for studying its spectral interference on other analytes. It finds application as gadolinium yttrium garnets in microwaves, catalysts in petroleum cracking, phosphors for color TV tubes, and as alloy constituents for improving resistance to high temperatures and oxidation. The excellent neutron capture ability of ¹⁵⁵Gd and ¹⁵⁷Gd is utilized in the nuclear industry as urania-gadolinia fuel in nuclear control rods (26-28).

The advancement of the capacitive charge-coupled device (CCD) detector, which not only improves the analytical performance of the analytical lines, but also provides more options in choosing alternative interference-free analytical lines compared to the photomultiplier tube-based detector system (29-31).

In the present study, the spectral interference of Gd on 29 common analytes was studied in detail. Since the spectral interference is highly dependent on the concentration of Gd, an ICP-AES-based method was also developed for the simultaneous determination of Gd along with other analytes. Based on the spectral interference study and the analytical performance of the different analytical lines of the analytes, a new methodology was developed for the direct determination of these analytes without chemical separation. It was validated by using synthetic samples prepared from commercially available standard reference material of individual elements.

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EXPERIMENTAL

Instrumental and Operating Conditions

The analysis was carried out using a simultaneously multi-elemental atomic emission spectrometer (Spectro-Arcos, Germany) with a high-performing charge-coupled device (CCD) as the detector and inductively coupled plasma (ICP) as the source of excitation. The spectral interference as well as the overall analytical performance is highly dependent on the operating conditions. The plasma is operated at a frequency of 27.12 MHz. At a lower frequency, the skin depth will be more and the shape of the plasma changes to tear-shape which makes the sample introduction difficult. The power is optimized at 1.2 kW to sustain the plasma. Even though more power increases the signal intensity, the background also increases and as a result, the overall signal-to-noise ratio does not improve. Since in this case a pneumatic nebulizer is used, the nebulizer gas flow was optimized such that the aerosol of required diameter is generated and carried to the plasma. If the velocity for sample introduction is very low, the sample cannot be injected into the analytical zone of the plasma while high speed leads to the fact that the time of residence of the sample inside the plasma becomes small and the intensity of the analytical lines go down. In case of the present instrument, based on the overall performance of the analytes, the instrumental parameters were optimized in accordance with the recommendations of the manufacturer. There is very little flexibility in modifying the instrumental parameters. With the limited flexibility, an attempt was made to study (a) the input power vs net signal intensity, (b) nebulizer flow rate vs. net signal intensity for optimization of these parameters. The operating condi-

tions and instrumental specifications are listed in Table I. 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 the alternate analytical lines (see Figure 1).

Standard Solutions and Reagents

Standard solutions for all of the elements were prepared from CertiPUR® ICP multi-standard solutions (E-Merck, Darmstadt, Germany) by proper dilution. Suprapur® HNO₃ (E-Merck, Darmstadt, Germany) and quartz double-distilled water were used through-

out the study. 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 each line after proper peak search.

Methods

A series of SpecPure® Gd solutions (standard reference material elemental solution from E-Merck, Darmstadt, Germany) of concentrations between 0.05 to 1000 mg/L were prepared and fed into the argon plasma. The spectral interference of Gd was monitored by observing its contribution in different channels of the specified analytes. For each analyte, the least

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 130-450 nm 0.02 nm from 450-800 nm
Thermal regulation	Controlled to 30 ± 1 °C
Frequency	27.12 MHz
Pump	Dual channel peristaltic pump (12 roller)
Detector	Linear arrays of CCD (3648 pixels/array)
Nebulizer	Cross-flow nebulizer
ICP-torch	Demountable, radial viewing
Operating Conditions	
Coolant flow	13 L/min
Auxiliary flow	0.8 L/min
Nebulizer gas flow	0.8 L/min
Total time of measurement	28 s
Pump speed	30 rpm
Nebulizer pressure	3 bars
Pressure on manometer	6 bars
RF power out put	1.2 kW
Reflected power	< 10 W
Input power	230 V AC

interfered analytical lines were identified along with evaluation of the correction factor. The tolerance levels of Gd on these lines were also studied. The analytical performance such as detection limits, sensitivity, and linear dynamic range were studied for all of the analytical lines. Since the correction factor arising due to the spectral interference of Gd is a function of Gd concentration, an ICP-AES-based method was developed for the simultaneous determination of Gd along with the analytes. Based on the spectral interference of Gd as well as the analytical performance, an ICP-AES-based method was developed for the determination of these analytes at trace levels without any separation in the Gd matrix and validated by using synthetic samples prepared from commercially available standard reference materials.

RESULTS AND DISCUSSION

Determination of Gd by ICP-AES

Though Gd exhibits line-rich emission spectra, four lines of Gd (335.047 nm, 335.862 nm, 336.223 nm, and 342.247 nm) were chosen to establish the calibration curves and to study the analytical performance (see Figure 2). It was found that these four lines can be used for the determination of Gd with less than 5% RSD (Table II). The sensitivity and detection limits of Gd with these 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 + three times the standard deviation of the above measurements, i.e., $\bar{x} + 3\sigma$. The description of the linear dynamic range for each line of Gd is listed in Table II. The sensitivity of these lines follows the order 335.047 nm < 335.862 nm < 336.223 nm < 342.247 nm, respectively, while the order for the detection limit is 335.047 nm < 342.247 nm < 336.223 nm < 335.862 nm (see Table II).

Fig. 1: Cross-sectional view of array of CCD-based detector.

Fig. 2: Calibration curves for different analytical lines of Gd.

TABLE II
Determination of Gd by ICP-AES
Using Different Analytical Lines

Gd (mg/L)	335.047 nm (mg/L)	335.862 nm (mg/L)	336.223 nm (mg/L)	342.247 nm (mg/L)
1	0.90 ± 0.02	0.95 ± 0.04	0.93 ± 0.07	0.90 ± 0.04
5	5.3 ± 0.3	4.8 ± 0.4	5.1 ± 0.4	4.9 ± 0.2
10	9.8 ± 0.8	9.9 ± 0.3	9.7 ± 0.4	9.9 ± 0.5
50	51.8 ± 1.1	49.3 ± 1.0	50.5 ± 1.0	50.2 ± 0.8
100	98.5 ± 2.5	102.1 ± 1.9	100.3 ± 1.6	101.6 ± 1.5
500	497 ± 2	499 ± 3	498 ± 2	502 ± 3
1000	1000 ± 3	999 ± 3	995 ± 6	1001 ± 6
D.L. (mg/L)	0.029	0.057	0.056	0.032
Sensitivity (counts/mg/L)	10.3 × 10 ⁴	6.6 × 10 ⁴	7.6 × 10 ⁴	9.9 × 10 ⁴
Linear Dynamic range (mg/L)	0.02–1000	0.057–1000	0.056–1000	0.032–1000
% RSD	~1%	~4%	~3%	~2%

Spectral Interference of Gd on Different Analytes

The ground state electronic configuration for Gd is [Xe].4f⁷.5d¹.6s² with the ground state term symbol of ⁹D₂. Due to the various possible transitions in Gd, it interferes in the spectra of other analytes making their determination erroneous, especially when the analytes are present in a Gd matrix at trace levels.

Ag, Ba, Bi, Cd, Cr, Cu, Dy, Li, Lu, Mg, Mn, Na, Nd, Sr, Zn.

The spectral interference of Gd on the determination of Ag, Ba, Bi, Cd, Cr, Cu, Dy, Li, Lu, Mg, Mn, Na, Nd, Sr, and Zn was studied as a function of Gd concentration. It was observed that the interference is linear with a Gd concentration. The spectral interference of Gd on these analytes is listed in Table III, while the analytical performance of these lines is summarized in Table IV.

Silver (Ag)

Four analytical lines of Ag were chosen for the present purpose: 338.289 nm, 328.068 nm, 224.641 nm, and 243.779 nm. The 224.641 nm line was found to be enormously interfered by Gd and is therefore not recommended for the direct determination of Ag in a Gd matrix. Practically no interference from Gd was observed for Ag at 328.068 nm with a 1000 mg/L tolerance level. The Gd tolerance levels for the 338.289 nm, 224.641 nm, and 243.779 nm analytical lines of Ag are 100 mg/L, 50 mg/L, and 50 mg/L, respectively. The analytical performance for 328.068 nm was 0.011 mg/L (detection limit) and 1359 counts/mg/L (sensitivity). Based on both of these factors, Ag at 328.068 nm was chosen as the best line for Ag determination in a Gd matrix.

Barium (Ba)

Three different analytical lines of Ba (230.424 nm, 233.527 nm, and 455.404 nm) were investigated. The contribution due to the spec-

tral interference of Gd for these lines followed the trend 455.404 nm < 230.424 nm < 233.527 nm. For Ba, the least interfered line of 455.404 nm showed the best analytical performance (detection limit 0.027 mg/L, sensitivity 2900.1 counts/mg/L), and hence should be the ideal choice for Ba estimation in the presence of a Gd matrix.

Bismuth (Bi)

Of the five analytical lines of Bi chosen for the present study (190.241 nm, 206.170 nm, 222.825 nm, 223.061 nm, and 306.772 nm), the 222.825 nm, 190.241 nm, and 206.170 nm lines showed significant interference from Gd and were not considered for further studies. The detection limit of the remaining two lines follows the order of 223.061 nm < 306.772 nm and the sensitivities are 263.7 counts/mg/L and 1117.95 counts/mg/L, respectively. Thus, for Bi the 306.772 nm line was chosen.

Cadmium (Cd)

Of the four lines for Cd (214.438 nm, 226.502 nm, 228.802 nm, and 361.051 nm), the 361.051 nm line was highly interfered by Gd, while the 214.438 nm and 228.802 nm lines showed moderate interference. The 226.502 nm line (tolerance level, 1000 mg/L) and the 214.438 nm line (tolerance level, 500 mg/L) have comparable detection limits of 0.0069 mg/L and 0.007 mg/L, respectively. The sensitivities of these lines are 8971.8 counts/mg/L and 4083.7 counts/mg/L, respectively. Thus, the best line which can serve our purpose is 226.502 nm.

Chromium (Cr)

Among the five lines of Cr (205.618 nm, 267.716 nm, 283.563 nm, 284.325 nm, and 284.984 nm), the 205.618 nm line showed no spectral interference from Gd up to a tolerance level of 1000 mg/L. This line also gives the best analytical performance, with a detection limit

TABLE III
Spectral Interference of Gd on Ag, Ba, Bi, Cd, Cr, Cu, Dy, Li, Lu, Mg, Mn, Na, Nd, Sr, and Zn Analytes

Element	Analytical Lines (nm)	Contribution from 1000 mg/L of Gd	Correction Factor	Tolerance Level (mg/L)	Element	Analytical Lines (nm)	Contribution from 1000 mg/L of Gd	Correction Factor	Tolerance Level (mg/L)
Ag	338.289	0.45	4×10^{-4}	100	Mg	279.553	0.02	2×10^{-5}	1000
	328.068	0.04	0	1000		280.270	0.02	2×10^{-5}	1000
	224.641	12.59	1.3×10^{-2}	50		285.213	0.07	7×10^{-5}	500
	243.779	2.1	2×10^{-3}	50		279.079	2.26	2.2×10^{-3}	50
Ba	455.404	*	-	1000	Mn	202.647	1.29	1.3×10^{-3}	5
	233.527	1.71	2×10^{-3}	50		257.611	0.04	4×10^{-5}	1000
	230.424	0.49	5×10^{-4}	100		259.373	0.03	3×10^{-5}	1000
Bi	223.051	1.47	2×10^{-3}	50	Na	260.569	0.09	9×10^{-5}	500
	190.241	7.46	8×10^{-3}	100		294.921	*	-	1000
	306.772	*	-	1000		403.076	1.69	1.7×10^{-3}	50
	222.825	#	Rejected	5		589.592	0.06	1×10^{-4}	1000
Cd	206.170	3.62	4×10^{-3}	50	Nd	588.995	0.17	2×10^{-4}	0.05
	214.438	0.1	1×10^{-4}	500		330.237	12.64	1.2×10^{-2}	50
	226.502	0.02	0	1000		330.298	#	Rejected	50
	228.802	0.49	5×10^{-4}	50		401.225	*	-	1000
Cr	361.051	#	Rejected	50	Zn	430.358	0.85	9×10^{-4}	100
	267.716	0.42	4×10^{-4}	50		406.109	15.82	1.6×10^{-2}	5
	205.618	0.03	0	1000		417.731	0.49	5×10^{-4}	500
	283.563	0.16	2×10^{-4}	500		213.856	0.04	0	1000
Sr	284.325	*	-	1000	Lu	206.200	2.05	2.1×10^{-3}	50
	284.984	1.32	1×10^{-3}	50		202.613	0.17	2×10^{-4}	50
	407.771	0.01	0	1000		334.502	3.96	4×10^{-3}	200
	421.553	0.03	0	1000		219.554	0.554	5.5×10^{-4}	50
Dy	460.733	0.15	1×10^{-4}	100	Cu	261.542	0.037	3.7×10^{-5}	1000
	353.170	0.06	1×10^{-4}	1000		291.139	0.151	1.5×10^{-4}	200
	394.468	*	-	1000		307.760	0.63	6.3×10^{-4}	50
	340.780	4.87	5×10^{-3}	5		324.754	0.03	0	1000
Li	353.602	0.37	4×10^{-4}	100		327.396	0.11	1×10^{-4}	200
	364.540	9.99	1×10^{-2}	5		224.700	0.68	7×10^{-4}	50
	670.780	*	-	1000		219.226	3.21	3.2×10^{-3}	50
	460.289	#	Rejected	50		219.958	1.15	1.2×10^{-3}	0.5
	323.261	#	Rejected	5					
	274.118	18.77	1.9×10^{-2}	50					

Note: * No interference, # significant interference.

TABLE IV
Analytical Performance of Ag, Ba, Bi, Cd, Cr, Cu, Dy, Li, Lu, Mg, Mn, Na, Nd, Sr, and Zn Analytes in the Presence of Gd

Ele - ments	Analytical Lines (nm)	D.L. (mg/L)	Sensitivity (counts/ mg/L)	Ele- ments	Analytical Lines (nm)	D.L. (mg/L)	Sensitivity (counts/ mg/L)
Ag	224.641	1.99	34.4	Mg	202.647	0.02	371
	243.779	0.155	360		279.079	0.14	302
	328.068	0.011	11359		279.553	0.0006	54115
	338.289	0.025	6258		280.270	0.001	41616
Ba	230.424	0.136	745	Mn	285.213	0.008	10846
	233.527	0.234	364		257.611	0.003	9189
	455.404	0.027	2900		259.373	0.0029	8067
Bi	190.241	1.09	29.2	Na	260.569	0.001	4193
	206.170	0.22	83.6		294.921	0.05	1454
	222.825	0.35	36.8		403.076	0.02	8572
	223.061	0.22	264		330.237	1.97	61.3
	306.772	4.47	1118		330.298	2.37	35.6
Cd	214.438	0.007	4084	Nd	588.995	0.026	47676
	226.502	0.0069	8972		589.592	0.013	27818
	228.802	0.042	1354		401.225	0.061	3206
	361.051	0.511	331		406.109	0.12	2168
Cr	205.618	0.004	5764	Zn	417.731	0.24	1795
	267.716	0.108	545		430.358	0.04	3467
	283.563	0.014	3220		202.613	0.03	1649
	284.325	0.347	1302		206.200	0.2	144
	284.984	0.22	385		213.856	0.002	14112
Sr	407.771	0.0005	369965	Lu	334.502	0.44	379
	421.553	0.0009	270567		219.554	0.02	986
	460.733	0.009	2054		261.542	0.004	7184
Dy	340.780	0.046	4283	Cu	291.139	0.026	2955
	353.170	0.0063	17002		307.760	0.066	3321
	353.602	0.065	4374		219.226	0.015	290
	364.540	0.032	4693		219.958	0.05	548
	394.468	0.05	4068		224.700	0.022	1310
Li	274.118	1.52	33.8		324.754	0.0019	41210
	323.261	0.222	147		327.396	0.005	27554
	460.289	0.528	176				
	670.780	0.002	175101				

of 0.004 mg/L and a sensitivity of 5764.5 mg/L. Hence, this line was chosen for further study.

Copper (Cu)

Out of five analytical lines for Cu (219.226 nm, 219.958 nm, 224.700 nm, 324.754 nm, and 327.396 nm), the 324.754 nm line showed the best analytical performance with no spectral interference from Gd. Thus, the 324.754 nm line should be the best choice for the present study.

Dysprosium (Dy)

On the basis of analytical performance, both the 394.468 nm and 353.602 nm lines appeared to be good, but they showed significant spectral interference. Fortunately for Dy, the best performing analytical line is 353.170 nm which shows the least spectral interference.

Lithium (Li)

Among the chosen lines of Li (274.118 nm, 323.261 nm, 460.289 nm, and 670.780 nm), the only line which is not interfered by a Gd matrix is 670.780 nm, having a tolerance level of 1000 mg/L. The analytical performance (detection limit 0.002 mg/L, and sensitivity 175101.25 counts/mg/L), making it the best possible line for analysis.

Lutetium (Lu)

Among four lines of Lu (219.554 nm, 261.542 nm, 291.139 nm, and 307.760 nm), the 261.542 nm line showed practically no interference from 1000 mg/L of Gd. The 261.542 nm Lu line has lowest detection limit, while the other three lines have almost comparable detection limits. The sensitivity followed the trend 261.542 nm > 307.760 nm > 291.139 nm > 219.554 nm. Thus, the 261.542 nm line has best performance, shows no spectral interference, and should be the best choice of determining Lu in the presence of Gd even at trace levels.

Magnesium (Mg)

Out of five analytical lines of Mg (279.553 nm, 280.270 nm, 285.213 nm, 279.079 nm, and 202.647 nm), the 279.079 nm and 202.647 nm lines were found to suffer from severe spectral interference from Gd. No interference was observed from Gd up to 1000 mg/L for the analytical lines of 280.270 nm, 297.553 nm, and 285.213 nm. The detection limit values followed the trend $279.553 < 280.270 \text{ nm} < 285.213 \text{ nm} < 279.079 \text{ nm}$, while the trend was completely reversed for sensitivity. In view of spectral interference as well as analytical performance, the Mg 279.553 nm line was thought to be the best choice in the presence of Gd with a detection limit of 0.0006 mg/L and a sensitivity of 54115.05 counts/mg/L.

Manganese (Mn)

Of the five different analytical lines of Mn (257.611 nm, 259.373 nm, 260.569 nm, 294.921 nm, and 403.076 nm), the 403.076 nm line was interfered by Gd and hence was not taken into account. There was practically no interference observed from Gd on the 257.611 nm line up to 1000 mg/L. The sensitivity for the remaining four lines follows the order $257.611 \text{ nm} > 259.373 \text{ nm} > 260.569 \text{ nm} > 294.921 \text{ nm}$, with a detection limit of 0.003 mg/L, 0.0029 mg/L, 0.001 mg/L and 0.05 mg/L, respectively. Thus the 257.611 nm line should be the better choice for the present investigation.

Sodium (Na)

Among four lines of Na (330.237 nm, 330.298 nm, 589.592 nm, and 588.995 nm), the 330.237 nm and 330.298 nm lines were highly interfered by Gd and hence were not chosen for further studies. Of the remaining two lines, only 589.592 nm was found to be unaffected by Gd. Furthermore, the analytical performance of this line was found to

be superior to the rest and was thus considered the best choice for the present study.

Neodymium (Nd)

Of the four lines of Nd (401.225 nm, 406.109 nm, 417.731 nm, and 430.358 nm), the 401.225 nm and 430.358 nm lines have almost comparable analytical performance (detection limit and sensitivity). However, the 401.225 nm line shows no spectral interference from Gd and was considered to be the ideal line for trace level determination of Nd in a Gd matrix.

Strontium (Sr)

Of three analytical lines for Sr (407.771 nm, 421.553 nm, and 460.733 nm), the 460.733 nm line was found to be significantly interfered by Gd, while the other two lines were free of spectral interference. The 407.771 nm line showed slightly better analytical performance (detection limit 0.0005 mg/L and sensitivity 369964.95 counts/mg/L) compared to the 421.553 nm line (detection limit 0.0009 mg/L and sensitivity 270567.2 counts/mg/L), and was thus considered the best choice for Sr determination in the presence of Gd.

Zinc (Zn)

Four different analytical lines for Zn (202.613 nm, 206.200 nm, 213.856 nm, and 334.502 nm) were chosen in the present study. The only line which is not interfered by Gd was 213.856 nm, with a tolerance level of 1000 mg/L of Gd and the lowest detection limit. The sensitivity of the lines followed the trend $213.856 \text{ nm} > 202.613 \text{ nm} > 334.502 \text{ nm} > 206.220 \text{ nm}$. The analytical performance and interference results revealed that the Zn 213.856 nm line is the best for the determination in a Gd matrix.

Ca, B, Co, Fe, Ga, La, Ni, Pr, Tl, Ce, Pb, Al, and In

The results of the spectral interference study for these analytes are summarized in Table V and the analytical performance results in Table VI.

Calcium (Ca)

For Ca, five lines (183.801 nm, 315.887 nm, 317.933 nm, 393.366 nm, and 396.847 nm) were under investigation. The 183.801 nm and 315.887 nm lines showed interference from Gd, and were not suitable for trace determination of Ca in the presence of a Gd matrix. The 393.366 nm line showed moderate spectral interference from Gd, while the analytical performance was found to have the lowest detection limit (0.0009 mg/L) and the highest sensitivity (586501.5 counts/mg/L). Thus, Ca at the 393.366 nm line was found to be best for its trace level determination in the presence of large amounts of Gd.

Boron (B)

For B, five analytical lines (136.246 nm, 182.641 nm, 208.959 nm, 249.677 nm, and 249.773 nm) were chosen to study the spectral interference of Gd. The 136.246 nm line showed a significant contribution from Gd. The correction factors due to the spectral interference of Gd for the other analytical lines of B follow the trend: $208.959 \text{ nm} < 182.641 \text{ nm} < 249.773 \text{ nm} < 249.677 \text{ nm}$. The detection limits of the analytical lines follow the order: $208.959 \text{ nm} (0.019 \text{ mg/L}) < 249.773 \text{ nm} (0.024 \text{ mg/L}) < 182.641 \text{ nm} (0.032 \text{ mg/L}) < 249.677 \text{ nm} (0.054 \text{ mg/L}) < 136.246 \text{ nm} (14.57 \text{ mg/L})$. The sensitivity of these lines followed the trend: $208.959 \text{ nm} > 249.773 \text{ nm} > 249.677 \text{ nm} > 182.641 \text{ nm} > 136.246 \text{ nm}$. Considering all of these facts, B at the 208.959 nm line was believed to be the best choice.

TABLE V
Spectral Interference of Gd on Ca, B, Co, Fe, Ga, La, Ni, Pr, Tl, Ce, Pb, Al and In Analytes

Element	Analytical Lines (nm)	Contribution from 1000 mg/L of Gd	Correction Factor	Tolerance Level (mg/L)	Element	Analytical Lines (nm)	Contribution from 1000 mg/L of Gd	Correction Factor	Tolerance Level (mg/L)
Ca	396.847	0.23	2×10^{-4}	5	Pr	411.846	0.28	3×10^{-4}	200
	393.366	0.24	2×10^{-4}	5		417.939	0.44	4×10^{-4}	500
	317.933	0.67	7×10^{-4}	50		422.535	4.98	5×10^{-3}	50
	315.887	2.22	2.2×10^{-3}	500		414.311	*	-	1000
	183.801	8.43	8.4×10^{-3}	50	Tl	190.864	0.32	3×10^{-4}	50
	422.673	0.28	3×10^{-4}	100		276.787	#	Rejected	50
B	249.773	0.76	8×10^{-4}	0.05	Cs	418.660	0.72	7×10^{-4}	200
	249.677	3.03	3×10^{-3}	0.05		448.691	#	Rejected	50
	182.641	0.28	3×10^{-4}	0.05		413.765	1.36	1.4×10^{-3}	100
	208.959	0.08	1×10^{-4}	0.05		413.380	0.81	8×10^{-4}	200
	136.246	#	Rejected			393.373	17.11	1.7×10^{-2}	0.05
Co	228.616	0.56	6×10^{-4}	50	Pb	220.353	4.76	4.8×10^{-3}	50
	238.892	0.23	2×10^{-4}	100		405.778	4.19	4.2×10^{-3}	200
	230.786	1.1	1.1×10^{-3}	50		283.305	5.8	5.8×10^{-3}	50
	237.862	0.45	4×10^{-4}	50		261.418	19.06	1.9×10^{-2}	50
Fe	259.941	0.24	2×10^{-4}	50	Al	167.078	#	Rejected	
	238.204	1.37	1.4×10^{-3}	50		396.152	0.1	1×10^{-4}	200
	239.562	0.18	2×10^{-4}	50		394.401	4.22	4.2×10^{-3}	5
	244.451	3.12	3.1×10^{-3}	50		308.215	#	Rejected	5
	261.187	0.51	5×10^{-4}	50		309.271	*	-	1000
	262.567	3.56	3.6×10^{-3}	50	In	230.606	0.68	7×10^{-4}	100
	262.829	2.62	2.6×10^{-3}	100		325.609	2.35	2.4×10^{-3}	50
	275.573	0.86	9×10^{-4}	50		451.131	*	-	1000
	241.331	6.48	6.5×10^{-3}	50	Ni	303.936	1.88	1.9×10^{-3}	50
	373.486	0.49	5×10^{-4}	200		231.604	0.67	7×10^{-4}	50
						221.648	0.42	4×10^{-4}	0.05
Ga	417.206	0.14	1×10^{-4}	500		232.003	1.89	1.9×10^{-3}	50
	294.364	0.53	5×10^{-4}	50		227.021	1.01	1×10^{-3}	100
	287.424	17.12	1.7×10^{-2}	50		174.828	#	Rejected	100
La	408.672	0.26	3×10^{-4}	200		300.249	13.25	1.3×10^{-3}	100
	333.749	0.25	3×10^{-4}	500		341.476	0.34	3×10^{-4}	500
	379.478	0.81	8×10^{-4}	100					

* No interference, # significant interference.

TABLE VI
Analytical Performance of Ca, B, Co, Fe, Ga, La, Ni, Pr, Tl, Ce, Pb, Al, and In Analytes the Presence of Gd

Ele - ments	Analytical Lines (nm)	D.L. (mg/L)	Sensitivity (counts/ mg/L)	Ele- ments	Analytical Lines (nm)	D.L. (mg/L)	Sensitivity (counts/ mg/L)
Ca	183.801	0.799	18.7	Pr	411.846	0.06	2705
	315.887	0.15	972		414.311	0.06	3394
	317.933	0.04	2936		417.939	0.244	2958
	393.366	0.0009	586502		422.535	0.1	2628
	396.847	0.002	442492	Tl	190.864	0.055	674
B	422.673	0.008	21893		276.787	1	19
	136.246	14.57	0.6	Ce	393.373	0.26	2821
	182.641	0.032	554		413.38	0.067	2413
	208.959	0.019	3080		413.765	0.058	2406
	249.677	0.054	787		418.66	0.327	1968
Co	249.773	0.024	1240	Pb	448.691	2	59.6
	228.616	0.052	588		220.353	0.17	219
	230.786	0.076	506		261.418	0.9	53
	237.862	0.025	1005		283.305	0.08	547
Fe	238.892	0.047	1459	Al	405.778	0.27	707
	238.204	0.109	524		167.078	43.6	0.5
	239.562	0.019	1719		308.215	0.041	1338
	241.331	0.487	137		309.271	3.03	2539
	244.451	0.26	115	In	394.401	0.058	3141
	259.941	0.03	1223		396.152	0.023	9690
	261.187	0.05	651		230.606	0.181	517
	262.567	0.678	93.2		303.609	0.323	375
Ga	262.829	0.421	123	Ni	325.609	0.055	1115
	275.573	0.21	222		451.131	42	16.5
	373.486	0.09	2085		174.828	11.2	1.25
	287.424	0.427	155		221.648	0.175	679
	294.364	0.12	642		227.021	0.08	102
La	417.206	0.1	7204		231.604	0.02	651
	333.749	0.04	4104		232.003	0.04	548
	379.478	0.038	6022		300.249	0.36	440
	408.672	0.033	7071		341.476	0.01	4082

Cobalt (Co)

Of all analytical lines chosen for Co (228.616 nm, 230.786 nm, 237.862 nm and 238.892 nm), the least interfered line was found to be 238.892 nm. The detection limit of the lines were evaluated as 0.052 mg/L, 0.076 mg/L, 0.025 mg/L, 0.047 mg/L, respectively. The sensitivity followed the trend: 238.892 nm > 237.862 nm > 228.616 nm > 230.786 nm. Therefore, in view of both the spectral interference and the analytical performance, the best line for Co was found to be 238.892 nm.

Iron (Fe)

Unfortunately, all 10 lines chosen for Fe (238.204 nm, 239.562 nm, 241.331 nm, 244.451 nm, 259.941 nm, 261.187 nm, 262.567 nm, 262.829 nm, 275.573 nm, and 373.486 nm) showed spectral interference from Gd. The least interfered line was 239.562 nm, and with a tolerance level of 50 mg/L showed comparable analytical performance with rest of the analytical lines and was chosen for the present study.

Gadolinium (Ga)

The tolerance levels for the analytical lines of Ga (417.206 nm, 287.424 nm, and 294.364 nm) were found to be 500 mg/L, 50 mg/L, and 50 mg/L, respectively. In the case of Ga, the least interfered and best performing analytical line was 417.206 nm, with a detection limit of 0.1 mg/L, and a sensitivity of 7203 counts/mg/L. It is, therefore, recommended as the best line for Ga in the presence of a Gd matrix.

Lanthanum (La)

Since the three analytical lines for La (333.749 nm, 379.478 nm, and 408.672 nm) were interfered by Gd, the analytical performance is the determining factor for choosing the analytical line for trace level determination of La in a Gd matrix. The detection limit of the three

lines was found to be comparable and the sensitivity followed the trend: 408.672 nm > 379.478 nm > 333.749 nm, respectively. Thus, the 408.672 nm line is considered best to serve the purpose for this study.

Nickel (Ni)

Nickel, having line-rich emission spectra, therefore offers more options for choosing alternative interference-free analytical lines. All seven analytical lines of Ni (174.828 nm, 221.648 nm, 227.021 nm, 231.604 nm, 232.003 nm, 300.249 nm, and 341.476 nm) were interfered by Gd. The 174.828 nm line interfered most and, hence, was ignored for further investigation. However, the least interfered line was 341.476 nm. It has a tolerance level of 500 mg/L and a detection limit of 0.01 mg/L. The sensitivity of the lines followed the order: 341.476 nm > 221.648 nm > 231.604 nm > 232.003 nm > 300.249 nm. The best line selected for this study is 341.476 nm.

Praseodymium (Pr)

The spectral interference of Gd on the four different analytical lines of Pr (411.846 nm, 414.311 nm, 417.939 nm, and 422.535 nm) revealed that the 411.311 nm line was not interfered by Gd; however, the analytical performance was not satisfactory. The second least interfered line (414.311 nm) of Pr also showed similar analytical performance. Therefore, the only option was to choose the 414.311 nm line for further investigation.

Tellurium (Tl)

The 276.787 nm line of Tl was found to be more interfered by Gd than the 190.864 nm line. The analytical performance of these lines revealed that better performance was obtained with the 190.864 nm line and was chosen for further investigation.

Cesium (Cs)

Of the five lines of Cs (393.373 nm, 413.380 nm, 413.765 nm, 418.660 nm, and 448.691 nm), the 448.691 nm and 393.373 nm lines were significantly interfered from Gd. Though the spectral interference of the other three lines showed similar contribution, the detection limit of these lines (413.380 nm, 413.765 nm, and 418.66 nm) was evaluated as 0.067 mg/L, 0.058 mg/L, and 0.327 mg/L, respectively. The sensitivity of these lines followed the trend: 413.380 nm > 413.765 nm > 418.66 nm. Based on the analytical performance of the 413.380 nm Cs line, it was chosen best for further study.

Lead (Pb)

Four lines of Pb (220.353 nm, 405.778 nm, 283.305 nm, and 261.418 nm) were chosen for the present study. All of the lines were found to have prominent spectral interference from Gd. The least interfered line (405.778 nm) was also found to be the most sensitive and, therefore, chosen as the best line for trace level determination of Pb in a Gd matrix.

Aluminum (Al)

Of the five analytical lines of Al (167.078 nm, 308.215 nm, 309.271 nm, 394.401 nm, and 396.152 nm), the least interfered with Gd was 396.152 nm. The tolerance level of 200 mg/L and a correction factor of 0.000104 mg/L per 1000 mg/L of Gd showed the best analytical performance (detection limit 0.023 mg/L and sensitivity 9690.35 counts/mg/L). Hence, it was found to be suitable for Al determination in the presence of a Gd matrix.

Indium (In)

Of the four analytical lines of In (230.606 nm, 325.609 nm, 451.131 nm, and 303.609 nm), the 451.131 nm line showed no spectral inter-

ference from Gd, but had the worst analytical performance (detection limit and sensitivity). Therefore, for this study, the 325.609 nm line is the best.

The typical spectral interference from different concentrations of Gd on the Nd 406.109 nm, Al 308.215 nm, Ce 448.691 nm, and Dy 364.540 nm lines are shown in Figure 3 (a), (b), (c), (d), respectively.

Direct Determination of Analytes Without Chemical Separation

Based on the spectral interference of Gd on the different analytical lines mentioned above and their analytical performance, a methodology was developed for the determination of these analytes in a Gd matrix without chemical separation. This not only saves time, but also decreases the chance of contamination and sample handling which is very important for trace impurity analyses. On this basis, the analytical performance (detection limit, sensitivity) and spectral interference data, the suitable lines for all of the analytes in this study obtained were as follows: Ag 328.068 nm, Ba 455.404 nm, Bi 306.772 nm, Cd 226.502 nm, Cr 205.618 nm, Cu 324.754 nm, Dy 353.170 nm, Li 670.780 nm, Lu 2611.542 nm, Mg 279.553 nm, Mn 257.611 nm, Na 589.592 nm, Na 401.225 nm, Sr 407.771 nm, Zn 213.856 nm, Ca 393.366 nm, B 208.959 nm, Co 205.618 nm, Fe 239.562 nm, Ga 417.206 nm, La 408.672 nm, Ni 341.476 nm, Pr 411.846 nm, Pb 405.778 nm, Al 396.152 nm, and In 325.609 nm. For all of the analytes, the contributions due to the spectral interference of Gd were found to be linear with the concentrations of Gd fed into the plasma. The correction factors (C.F.) were calculated as a ratio of contribution (mg/L) on the analytical line due to a pure Gd solution

Fig. 3(a). Spectral interference of Gd on Nd 406.109 nm.

Fig. 3(b). Spectral interference of Gd on Al 308.215 nm.

(C*) to the concentration of Gd (mg/L) solution (CGd):

$$C.F. = C^*/C \text{ Gd} \quad (1)$$

In view of the above studies, two synthetic samples (S1 and S2) were prepared for Ag, Ba, Bi, Cd, Cr, Cu, Dy, Li, Lu, Mg, Mn, Na, Nd, Sr, and Zn. Sample S1 contained all of the above analytes at 0.1 mg/L and Gd at 1000 mg/L, while the second sample, S2, contained 1.0 mg/L of the above-mentioned analytes along with 1000 mg/L of Gd. The results, listed in Table VII, reveal that Ag, Ba, Bi, Cd, Cr, Cu, Dy, Li, Lu, Mg, Mn, Na, Nd, Sr, and Zn can be determined even at the 0.1 mg/L level in the presence of a Gd matrix (1000 mg/L) without chemical separation.

Two synthetic samples were prepared for Ca, B, Co, Fe, Ga, La, Ni, Pr, and Tl. Sample S3 consisted of 0.2 mg/L of each specified analyte along with 1000 mg/L of Gd, while sample S4 consisted of 2 mg/L of these analytes along with 1000 mg/L of Gd. The results for these samples are summarized in Table VIII which revealed that these analytes can be estimated as low as 0.2 mg/L of concentration in a Gd matrix.

A similar study of Ce and Pb with synthetic samples S5 and S6 revealed that these two analytes can be estimated as low as 2 mg/L concentration in a Gd matrix (see Table IX). The synthetic sample S5 contained 2.0 mg/L of Ce and Pb along with 1000 mg/L of Gd, while sample S6 contained 10 mg/L of Ce and Pb in 1000 mg/L of Gd matrix.

Comparison of Present Method With Other Analytical Methods

An attempt was made to compare the analytical results of the synthetic samples using the proposed methodology with that of other existing analytical methods. The synthetic samples contained 0.5 mg/L of Ag, Ba, Bi, Cd,

Fig. 3(c). Spectral interference of Gd on Ce 338.691 nm.

Fig. 3(d). Spectral interference of Gd on Dy 364.540 nm.

Cr, Cu, Dy, Li, Lu, Mg, Mn, Na, Nd, Sr, and Zn; 1 mg/L concentration of Ca, B, Co, Fe, Ga, La, Ni, Pr, Tl; and 5 mg/L of Ce and Pb in 1000 mg/L of Gd. The synthetic sample was directly fed to the plasma for analysis without any chemical separation. The results were corrected for spectral interference of Gd using the correction factors evaluated previously. The analytical results thus obtained were compared with existing analytical techniques. For Ag, the atomic absorption spectroscopic technique was used for comparison purposes (32). For Ba, Bi, Cd, Cr, Cu, Li, Mg, Mn, Na, Sr, Zn, Ca, B Co, Fe, Ga, Ni, Tl and Pb, the D.C. arc carrier distillation technique (33–35) was used, while mainly for rare earth elements (Dy, Ce, Lu, Nd, La, and Pr), ion chromatography was employed (36). The results obtained by the present method were found to compare well with the existing methods.

CONCLUSION

A systematic study was performed on the spectral interference of Gd on Ag, Ba, Bi, Cd, Cr, Cu, Dy, Li, Mg, Mn, Na, Nd, Sr, Zn, Ca, B, Co, Fe, Ga, La, Ni, Pr, Tl, Ce, Pb, Al, and In. The analytical performance of the different analytical lines of these analytes revealed that the best lines for the determination of these analytes in a Gd matrix are as follows: Ag 328.068 nm, Ba 455.404 nm, Bi 306.772 nm, Cd 226.502 nm, Cr 205.618 nm, Cu 324.754 nm, Dy 353.170 nm, Li 670.780 nm, Lu 2611.542 nm, Mg 279.553 nm, Mn 257.611 nm, Na 589.592 nm, Na 401.225 nm, Sr 407.771 nm, Zn 213.856 nm, Ca 393.366 nm, B 208.959 nm, Co 205.618 nm, Fe 239.562 nm, Ga 417.206 nm, La 408.672 nm, Ni 341.476 nm, Pr 411.846 nm, Pb 405.778 nm, Al 396.152 nm, and In 325.609 nm. It was also observed that Ag, Ba, Bi, Cd, Cr, Cu, Dy, Li, Lu, Mg, Mn, Na, Nd, Sr, and Zn can be determined at the

0.1 mg/L level, while Ca, B, Co, Fe, Ga, La, Ni, Pr, and Tl can be determined at 0.2 mg/L in the presence of a Gd matrix.

The methodology developed for the direct determination of these analytes in the presence of a Gd matrix without any chemical separation was validated using synthetic samples prepared from a commercially available standard reference material solution of the individual elements. The newly developed methodology was also compared with current analytical techniques and the results were found to be in good agreement.

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TABLE VII
Analyses of Synthetic Samples Containing Analytes Ag, Ba, Bi, Cd, Cr, Cu, Dy, Li, Lu, Mg, Mn, Na, Nd, Sr, and Zn in Gd Matrix

Ele- ments	Analytical Lines (nm)	Actual Concen- tration (mg/L)	S1	Actual Concen- tration (mg/L)	S2
			Amount Estimated After Incorporating Correction Factor (mg/L)		Amount Estimated After Incorporating Correction Factor (mg/L)
Ag	328.068	0.1	0.099± 0.010	1	0.99± 0.099
Ba	455.404	0.1	0.089± 0.008	1	0.89± 0.089
Bi	306.772	0.1	0.11± 0.011	1	1.2 ± 0.120
Cd	226.502	0.1	0.13± 0.013	1	1.3± 0.130
Cr	205.618	0.1	0.098± 0.010	1	0.98± 0.098
Cu	324.754	0.1	0.091 ± 0.009	1	0.91± 0.091
Dy	353.17	0.1	0.099± 0.010	1	0.99± 0.099
Li	670.78	0.1	0.11± 0.011	1	1.1± 0.110
Lu	261.542	0.1	0.095± 0.009	1	0.95± 0.095
Mg	279.553	0.1	0.12± 0.012	1	1.2± 0.120
Mn	257.611	0.1	0.11± 0.011	1	1.1± 0.110
Na	589.592	0.1	0.13± 0.013	1	1.3± 0.130
Nd	401.225	0.1	0.098± 0.010	1	0.98± 0.098
Sr	407.771	0.1	0.12± 0.012	1	1.2± 0.120
Zn	213.856	0.1	0.093± 0.009	1	0.93± 0.093

TABLE VIII
Analyses of Synthetic Samples Containing Analytes Ca, B, Co, Fe, Ga, La, Ni, Pr, and Tl in Gd Matrix

Ele- ments	Analytical Lines (nm)	Actual Concen- tration (mg/L)	S3	Amount Estimated After Incorporating Correction Factor (mg/L)	Actual Concen- tration (mg/L)	S4	Amount Estimated After Incorporating Correction Factor (mg/L)
			Amount Estimated Before Incorporating Correction Factor (mg/L)			Amount Estimated Before Incorporating Correction Factor (mg/L)	
Ca	393.366	0.2	0.445 ± 0.022	0.203 ± 0.010	2	2.272 ± 0.113	2.03 ± 0.101
B	208.959	0.2	0.304 ± 0.015	0.226 ± 0.011	2	2.038 ± 0.101	1.96 ± 0.098
Co	238.892	0.2	0.427 ± 0.021	0.202 ± 0.010	2	2.345 ± 0.117	2.12 ± 0.106
Fe	239.562	0.2	0.400 ± 0.020	0.221 ± 0.011	2	2.289 ± 0.114	2.11 ± 0.105
Ga	417.206	0.2	0.348 ± 0.017	0.213 ± 0.010	2	2.115 ± 0.106	1.98 ± 0.099
La	408.672	0.2	0.447 ± 0.022	0.191 ± 0.0095	2	2.166 ± 0.108	1.91 ± 0.095
Ni	341.476	0.2	0.527 ± 0.026	0.187 ± 0.0093	2	2.310 ± 0.115	1.97 ± 0.098
Pr	411.846	0.2	0.470 ± 0.023	0.191 ± 0.0095	2	2.389 ± 0.119	2.11 ± 0.105
Tl	190.864	0.2	0.506 ± 0.025	0.185 ± 0.0092	2	2.271 ± 0.113	1.95 ± 0.097

TABLE IX
Analyses of Synthetic Samples Containing Ce and Pb in Gd Matrix

Ele- ments	Analytical Lines (nm)	Actual Concen- tration (mg/L)	S5		Actual Concen- tration (mg/L)	S6	
			Amount Estimated Before Incorporating Correction Factor (mg/L)	Amount Estimated After Incorporating Correction Factor (mg/L)		Amount Estimated Before Incorporating Correction Factor (mg/L)	Amount Estimated After Incorporating Correction Factor (mg/L)
Ce	413.38	2	2.921 ± 0.146	2.11 ± 0.105	10	10.931 ± 0.546	10.12 ± 0.506
Pb	405.778	2	6.151 ± 0.307	1.96 ± 0.098	10	14.101 ± 0.705	9.91 ± 0.495

TABLE X
**Analysis of Synthetic Samples by Present Method
and Its Comparison with Existing Method**

Elements	Analytical Lines (nm)	Estimated by Present Method (mg/L)	Comparison with Other Method (mg/L)
Ag	328.068	0.52 ± 0.03	0.47 ± 0.05#
Ba	455.404	0.48 ± 0.01	0.46 ± 0.06**
Bi	306.772	0.50 ± 0.03	0.51 ± 0.02**
Cd	226.502	0.53 ± 0.04	0.50 ± 0.05**
Cr	205.618	0.48 ± 0.03	0.53 ± 0.04**
Cu	324.754	0.49 ± 0.02	0.54 ± 0.06**
Dy	353.17	0.52 ± 0.03	0.46 ± 0.04*
Li	670.78	0.52 ± 0.02	0.48 ± 0.03**
Lu	261.542	0.48 ± 0.02	0.51 ± 0.03*
Mg	279.553	0.50 ± 0.04	0.52 ± 0.04**
Mn	257.611	0.50 ± 0.04	0.49 ± 0.04**
Na	589.592	0.47 ± 0.03	0.46 ± 0.04**
Nd	401.225	0.47± 0.02	0.52± 0.03*
Sr	407.771	0.51 ± 0.02	0.54 ± 0.04**
Zn	213.856	0.52 ± 0.03	0.47 ± 0.03**
Ca	393.366	1.11± 0.06	0.97 ± 0.08**
B	208.959	0.97± 0.07	1.2± 0.09**
Co	238.892	1.05± 0.06	0.98 ± 0.08**
Fe	239.562	0.99± 0.05	1.02± 0.06**
Ga	417.206	0.98 ± 0.07	1.2 ± 0.07**
La	408.672	1.08± 0.05	1.11± 0.06*
Ni	341.476	0.98± 0.06	0.97 ± 0.06**
Pr	411.846	1.12± 0.09	1.2 ± 0.09*
Tl	190.864	1.08± 0.07	0.94± 0.07**
Ce	413.38	5.2 ± 0.3	4.7 ± 0.4*
Pb	405.778	4.8 ± 0.2	5.1 ± 0.3**

Note: The Gd concentration in the synthetic sample is 1000 mg/L;

refers to the analysis by Atomic Absorption Spectrometry;

** refers to the analysis by D.C. Arc carrier distillation technique;

* refers to the analysis by chromatographic technique.

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