

Determination of Gadolinium and Samarium in Aqueous Solution by X-Ray Fluorescence Spectrometry

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Summary: A simple X-ray fluorescence (XRF) spectrometric method for the determination of gadolinium and samarium in aqueous solution has been developed. The sample solution was introduced to the XRF spectrometer directly in simple polyethylene bottle. Statistical evaluation helped to establish an analytical application of the method. Effects of various cations and anions on gadolinium and samarium intensity have been studied. Matrix effects due to these cations and anions have been rectified using standards of similar composition.

Introduction

In continuation of our previous work [1], the present study was carried out to establish a rapid, accurate and non-destructive method to determine gadolinium (Gd) and samarium (Sm) in aqueous solution using X-ray fluorescence (XRF) spectrometry. In the past, XRF has been applied successfully for the determination of Gd and Sm in different matrices [2-20]. The inter element effects or spectral interferences from the matrix were minimized by use of internal standards [15,19,21]. In our studies, the sample solution was presented directly to the spectrometer in a 0.1 mm thick walled polyethylene bottle [22-24]. This is unlike the earlier presentation techniques such as pelletization [3-8,20], deposition on filter paper as a thin sample [15-16], solvent extraction [17] and bead formation [18]. High voltage (50 kV) and current (50 mA) were used to increase the intensity and to improve lower limit of detection. The effects of various cations and anions on Gd and Sm intensities were studied. The absorption-enhancement effects due to these cations and anions, if any, were eliminated by making the calibration curves in respective matrix.

Results and Discussion

The equations 2 and 3 were applied to the simulated mixture of Gd and Sm to determine their concentrations in solutions. The values determined match fairly well with the known concentrations as is evident from Table 1.

It is observed in Fig. 1 that the background is more prominent on lower 2θ -values. This background

Table 1: Determined Concentration of Gadolinium and Samarium in Simulated Blind Sample.

Known, $\mu\text{g/ml}$		Determined, $\mu\text{g/ml}$	
C_{Gd}	C_{Sm}	C_{Gd}	C_{Sm}
3000	50	2996	49
1000	100	998	101
500	500	502	497
100	1000	101	999
50	3000	48	3001

is due to inelastic collisions of the primary X-ray photons with the elements in the sample, its container and the environments [28]. The most prominent Gd $L_{\beta 1}$ and Sm ($L_{\beta 1} + L_{\beta 4}$) lines are well separated and do not interfere with each other and hence were selected as an analyte lines. The $\text{NiK}\beta$, $\text{CuK}\alpha$, $\text{NiK}\alpha$, $\text{FeK}\beta$, $\text{FeK}\alpha$ and $\text{CrK}\beta$ lines in the spectra are from the sample chamber and sample holder of stainless steel. Analysis shows that the peaks for Cd and Sm are symmetric. The calibration curves for Gd and Sm are drawn in Fig. 4 for conversion of intensity to concentration. The curves do not deviate from linearity and corresponding empirical relations (Eqs. 2 and 3) remain simple and linear. Precision was determined by making ten measurement each at optimized condition for Gd and Sm in the concentration range of 100-3000 $\mu\text{g/ml}$. The relative standard deviation (% RSD) are calculated using established statistical method. The variation of % RSD with concentration of Cd and Sm are given in Fig. 5. It is seen that % RSD is concentration dependent and is better at higher concentration.

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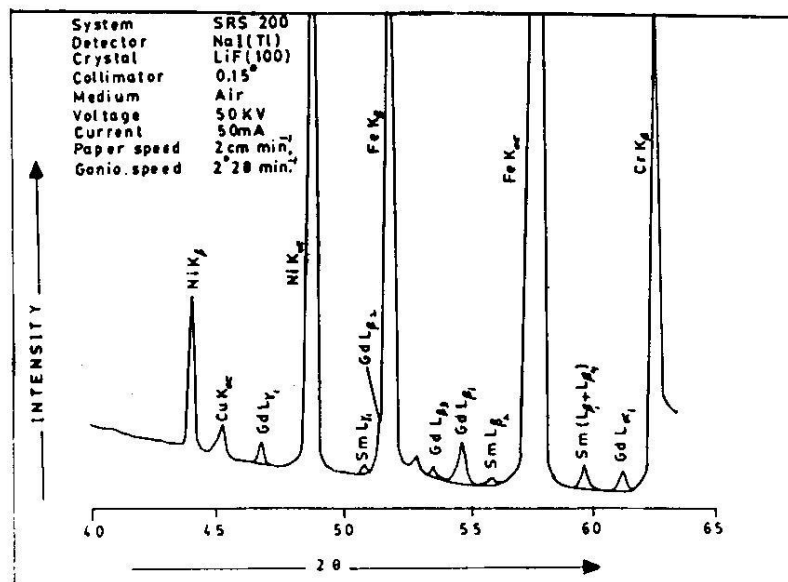
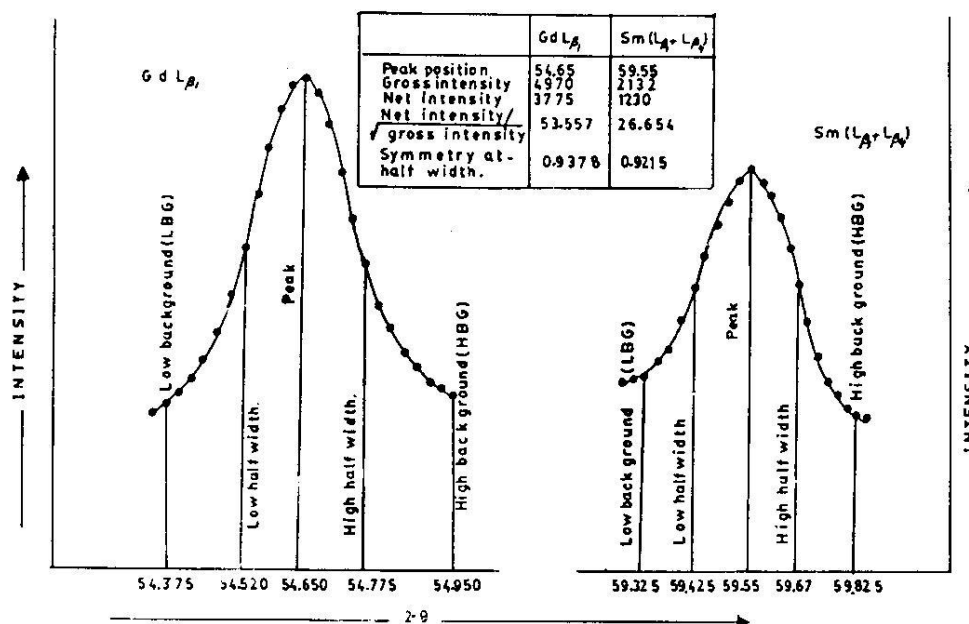


Fig. 1: XRF spectra of gadolinium and samarium.

Fig. 2: Peak analysis of Gd L_{β_1} and Sm ($L_{\beta_1} + L_{\beta_2}$) lines.

The effects of various cations (K^+ , Na^+ , Cs^+ , Rb^+ , Li^+ , Zn^{+2} , Co^{+2} , Ce^{+3} , and Cr^{+3}) and anions (CH_3COO^- , $S_2O_3^{2-}$, Cl^- , Br^- , I^- , NO_3^- and EDTA) on Gd and Sm intensities have been studied with their

composition fixed at 1000 $\mu g/ml$ and 2000 $\mu g/ml$ respectively. The results are shown in Fig. 6. It is clear that K^+ enhances the Gd intensity, while other cations reduce the Gd intensity. Similarly, Zn^{+2} ,

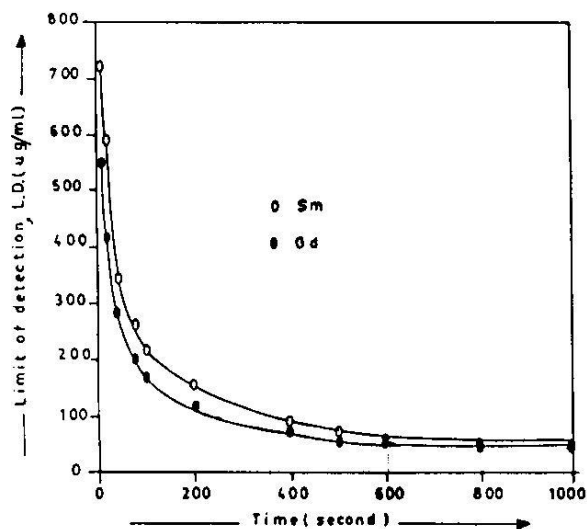


Fig. 3: Limit of detection as a function of counting time.

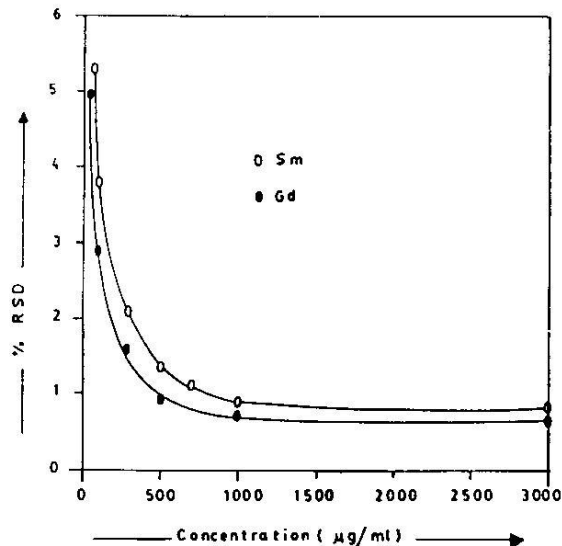


Fig. 5: Variation of % RSD with concentration of Gd and Sm.

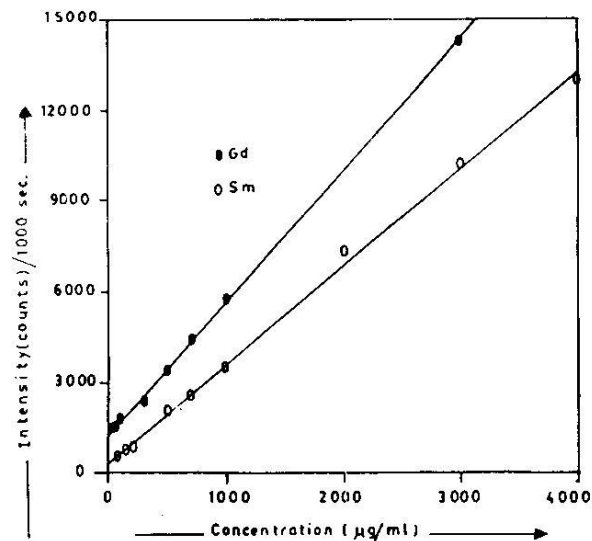


Fig. 4: Calibration curves of Gd and Sm.

Cs⁺, Rb⁺, Co²⁺, K⁺ increase the Sm intensity while Na⁺ and Ce²⁺ reduces the Sm intensity. Cr³⁺ and Li⁺ have no effect on Sm intensity. Anions reduce the Gd intensity in the order of EDTA > CH₃COO⁻ > I⁻ > Br⁻ NO₃⁻ > Cl⁻ > S₂O₃²⁻. Similarly S₂O₃²⁻, EDTA, I⁻, CH₃COO⁻ increase the Sm intensity while Br⁻ reduces the Sm intensity. Cl⁻ and NO₃⁻ have no effect on Sm intensity. For reasons cited above, calibration curves for Gd and Sm in the presence of various cations and anions were obtained and the best fitting equations got through regression

corresponding to the calibration curves were obtained. The equations are given in Table 2 and 3.

Table 2: Best fitting equations for gadolinium in presence of various cations and anions in the concentration range of 100-3000 µg/ml

Gadolinium in presence of	Equation of Line	Regression Coefficient, r
K ⁺	N _{Gd} = 4.270 C _{Gd} + 323.5	0.9942
Gd (Pure)	N _{Gd} = 4.141 C _{Gd} + 296.9	0.9999
Li ⁺	N _{Gd} = 4.121 C _{Gd} + 175.7	0.9993
Rb ⁺	N _{Gd} = 3.933 C _{Gd} + 437.3	0.9907
Ce ³⁺	N _{Gd} = 3.905 C _{Gd} + 234.0	0.9983
Co ²⁺	N _{Gd} = 3.841 C _{Gd} + 106.7	0.9962
Zn ²⁺	N _{Gd} = 3.828 C _{Gd} + 229.9	0.9967
Cs ⁺	N _{Gd} = 3.655 C _{Gd} + 471.6	0.9986
Na ⁺	N _{Gd} = 3.630 C _{Gd} + 430.1	0.9963
Cr ³⁺	N _{Gd} = 3.011 C _{Gd} + 617.1	0.9889
S ₂ O ₃ ²⁻	N _{Gd} = 3.568 C _{Gd} + 92.2	0.9992
Cl ⁻	N _{Gd} = 3.345 C _{Gd} + 116.6	0.9965
NO ₃ ⁻	N _{Gd} = 3.208 C _{Gd} + 455.2	0.9908
Br ⁻	N _{Gd} = 2.861 C _{Gd} + 452.9	0.9996
I ⁻	N _{Gd} = 2.829 C _{Gd} + 361.4	0.9899
CH ₃ COO ⁻	N _{Gd} = 2.775 C _{Gd} + 613.6	0.9896
EDTA	N _{Gd} = 2.737 C _{Gd} + 634.6	0.9946

*N_{Gd} = Gadolinium net intensity, counts.

C_{Gd} = Gadolinium concentration, µg/ml.

Experimental

Instrumentation

Sequential wavelength dispersive X-ray fluorescence spectrometer, SRS-200, (Siemens, West

Table 3: Best fitting equations for samarium in presence of various cations and anions in the concentration range of 100-3000 $\mu\text{g/ml}$

Samarium in presence of	Equation of Line	Regression Coefficient, r
Zn ⁺²	$N_{\text{Sm}} = 3.735 C_{\text{Sm}} - 12.71$	0.9909
Cs ⁺¹	$N_{\text{Sm}} = 3.570 C_{\text{Sm}} + 34.38$	0.9896
Rb ⁺¹	$N_{\text{Sm}} = 3.506 C_{\text{Sm}} + 65.07$	0.9979
Co ⁺²	$N_{\text{Sm}} = 3.406 C_{\text{Sm}} + 194.70$	0.9991
K ⁺	$N_{\text{Sm}} = 3.393 C_{\text{Sm}} + 131.50$	0.9906
Cr ⁺³	$N_{\text{Sm}} = 3.387 C_{\text{Sm}} + 274.60$	0.9896
Li ⁺¹	$N_{\text{Sm}} = 3.297 C_{\text{Sm}} + 151.70$	0.9889
Sm (Pure)	$N_{\text{Sm}} = 3.267 C_{\text{Sm}} + 168.50$	0.9998
Na ⁺¹	$N_{\text{Sm}} = 3.201 C_{\text{Sm}} + 46.07$	0.9983
Ce ⁺³	$N_{\text{Sm}} = 3.161 C_{\text{Sm}} + 139.30$	0.9978
S ₂ O ₃ ²⁻	$N_{\text{Sm}} = 4.565 C_{\text{Sm}} - 40.35$	0.9990
EDTA	$N_{\text{Sm}} = 4.341 C_{\text{Sm}} - 45.13$	0.9989
I ⁻	$N_{\text{Sm}} = 4.162 C_{\text{Sm}} + 73.57$	0.9993
CH ₃ COO ⁻	$N_{\text{Sm}} = 3.740 C_{\text{Sm}} + 169.80$	0.9998
Cl ⁻	$N_{\text{Sm}} = 3.632 C_{\text{Sm}} - 23.07$	0.9893
NO ₃ ⁻	$N_{\text{Sm}} = 3.401 C_{\text{Sm}} - 10.79$	0.9969
Br ⁻	$N_{\text{Sm}} = 3.307 C_{\text{Sm}} + 94.00$	0.9995

* N_{Sm} = Samarium net intensity, counts.

C_{Sm} = Samarium concentration, $\mu\text{g/ml}$.

Germany) is used with the following attachment: Cr X-ray tube, Soller slit with angular divergence of 0.15° , LiF-100 crystal and NaI(Tl) scintillation counter. The sample chamber is made of stainless steel. The instrument is coupled with a computer PDP-11/04 through an universal interface called logic controller (LC-200). The software OLD TV80 is in BASIC and is a modified version of RASBERRY-HEINRICH approach [25].

Calibration standards

Separate standards for Gd and Sm were prepared in the concentration range of 50-4000 $\mu\text{g/ml}$ from their stock solutions. The stock solutions were prepared from gadolinium nitrate (99.999%) and samarium nitrate (99.999%) supplied by M/S Rare Earth products. All dilutions were made with distilled water.

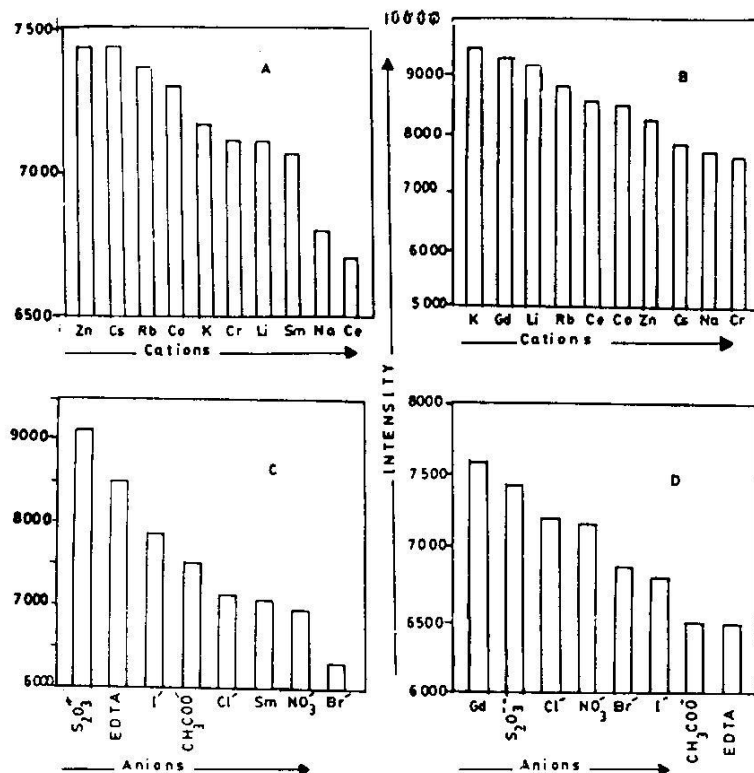


Fig. 6: A - Effects of different cations on Sm intensity.
 B - Effects of different cation on Gd intensity
 C - Effects of different anions on Sm intensity
 D - Effects of different anions on Gd intensity.

Optimization of spectral lines and measuring conditions

Spectra of Gd and Sm are recorded with 3.0 ml solution containing 10 g /l each of gadolinium and samarium. The spectra taken are shown in Fig. 1. The lines are identified from 2θ values given in literature [26]. Gd $L_{\beta 1}$ (54.69) and Sm ($L_{\beta 1} + L_{\beta 4}$) (59.50 - 59.59) were selected for the present studies. Peak analysis of these lines is performed to establish low background (LBG), peak and high background (HBG) angles after counting in steps of 0.025° 2θ values. The peak analysis is shown graphically in Fig. 2. To calculate the net intensities from gross intensities, measurements at the backgrounds and peak angles, were done in triplicate. Net intensities have been calculated after subtracting weighted average of back-ground counts from the peak counts. Calculated limits of detection (L.D.) were observed as a function of counting time for Gd and Sm. The results are shown in Fig. 3. The equation used to calculate L.D is given below [23].

$$L.D. = 3C/N (2N_b/T)^{-0.5} \quad 1$$

Where C = Concentration of analyte in solution ($\mu\text{g/ml}$).

N = Peak counts.

N_b = Background counts.

T = Counting time.

The equation bears a confidence level above 99% specified by 3 in it [27]. The counting time selected for the present work was 1000 seconds for Gd and Sm.

Intensity measurement and data processing

Equal volume (3.0 ml) of standard and sample solutions in the prescribed polyethylene bottles were presented to the spectrometer and integrals were evaluated under the conditions described above. Calibration curves shown in Fig. 4 were obtained by plotting the net intensities versus concentration for Gd and Sm. The data of these lines are subjected to regression analysis. The best empirical relationship between net intensity and concentration for Gd and Sm are

$$N_{Gd} = 1.217 \times 10^3 + 4.379 C_{Gd} \dots\dots \quad 2$$

$$\text{and } N_{Sm} = 2.680 \times 10^2 + 3.268 C_{Sm} \dots\dots \quad 3$$

Where N = Net Counts and C = Concentration ($\mu\text{g/ml}$)

Conclusion

The measurement of Gd and Sm in aqueous solutions can be carried out precisely and accurately using X-ray fluorescence spectrometer. The method does not require chemical separation or any special sample preparation technique. Solutions in simple polyethylene bottles can be used. The measurement in the concentration range of 100 - 3000 $\mu\text{g/ml}$ gave a precision of 5.5% to 0.9% for Sm and 5.0% to 0.8% for Gd.

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