Determination of Strontium and Cerium in Aqueous Solution by X-ray Fluorescence Spectrometry

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Summary: An analytical method for the determination of strontium and cerium in aqueous solution using X-ray fluorescence spectrometer has been developed, where samples were introduced to the XRF spectrometer directly in simple polyethylene bottles. Statistical evaluation helped to establish an analytical application of the method. Effect of various cations and anions on strontium and cerium intensity has been studied. Matrix effect due to these cations and anions have been rectified using standards of similar composition.

Introduction

The present study was carried out to develope a precise, accurate and reliable X-ray fluorescence (XRF) spectrometric method for the determination of strontium (Sr) and cerium (Ce) in aqueous solution. XRF spectrometric technique have been used to determine the above mentioned elements in varied matrices [1-18]. The sample presentation techniques to the spectrometer were pelletization [2,5,6,10], fusion bead [3,13], preconcentration through solvent extraction [8] and deposition on filter paper and on mylar film as a thin sample [4,11,14,18]. Wavelength dispersive X-ray fluorescence spectrometer was used in present study where samples were introduced to the XRF spectrometer directly in a 0.1 mm thick walled polyethylene bottle [19-22]. This is unlike the above mentioned presentation techniques. High voltage (50 kV) and current (50 mA) were used to increase the intensity and to improve lower limit of detection. The effect of various cations and anions on Sr and Ce intensities were studied. The matrix 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 Sr and Ce to determine their concentration in solutions. The values determined match fairly well with the known concentration as is evident from Table 1.

In the spectra, given in Fig. 1, Sr Kα (25.18) line in first order and Ce Kα (20.475) line in the second order spectrum are selected as an analyte line. Ce Kα (6.75) line in first order spectrum could not be observed. Mo Kα (20.33) line in the spectrum of Sr is from the sample chamber and

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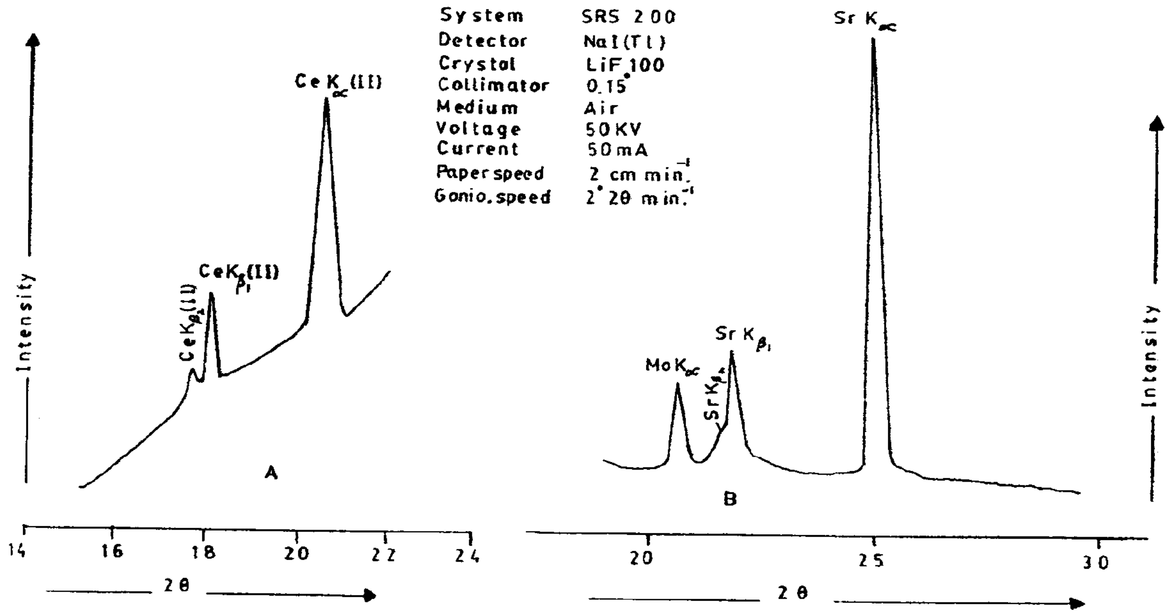
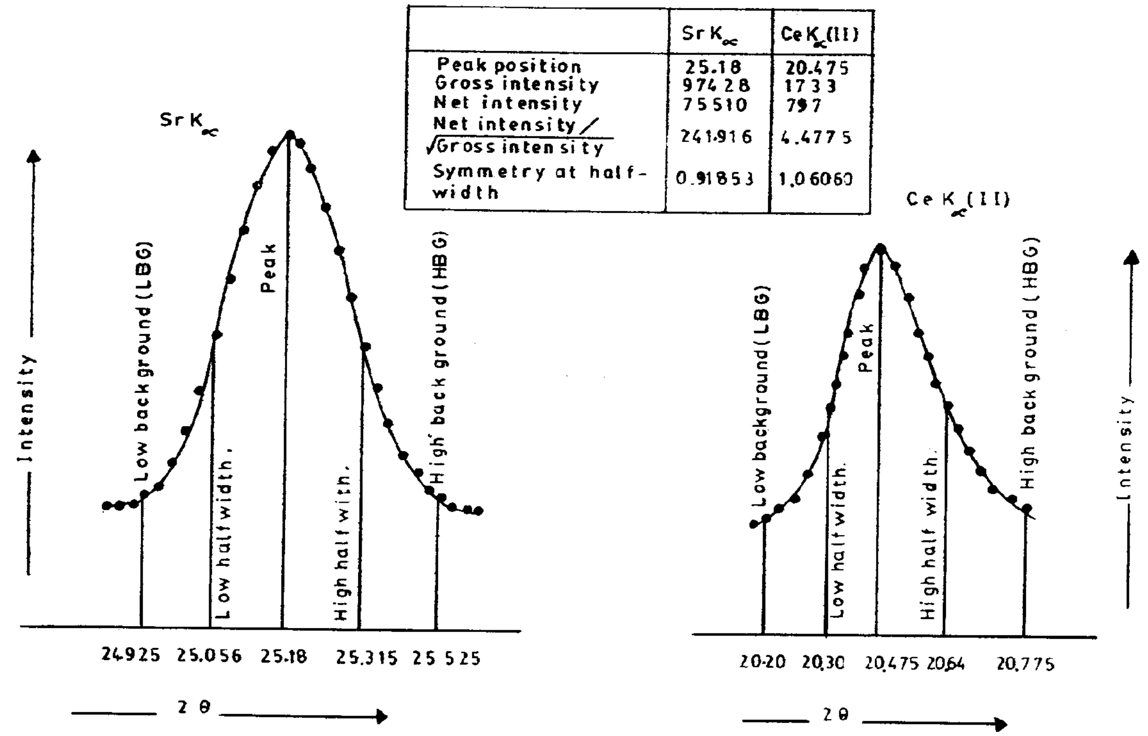


System	SRS 200
Detector	NaI(Tl)
Crystal	LiF 100
Collimator	0.15°
Medium	Air
Voltage	50KV
Current	50mA
Paper speed	2 cm min^{-1}
Gonio. speed	2° 2θ min^{-1}

Fig.1: XRF spectra of Ce and Sr. a; IInd order spectrum of Ce. B; Ist order spectrum of Sr.



	Sr K$_\alpha$	Ce K$_\alpha$(II)
Peak position	25.18	20.475
Gross intensity	97428	1733
Net intensity	75510	797
Net intensity/ $\sqrt{\text{Gross intensity}}$	241.916	4.4775
Symmetry at half-width	0.91853	1.06060

Fig.2: Peak analysis of SrKα and CeKα(II) lines.

Table 1: Determined concentration of Sr and Ce in simulated blind sample

Known, C_{Sr}	μg/ml C_{Ce}	Determined C_{Sr}	μg/ml C_{Ce}
2000	70	2001	72
1000	100	998	102
500	300	499	298
100	500	101	500
50	1000	49	1002
10	3000	9.8	3002

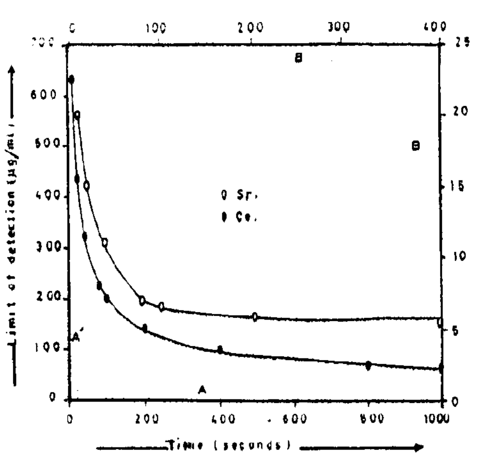


Fig.3: Limit of detection as a function of counting time A,A' = scales for Ce B,B' = scales for Sr

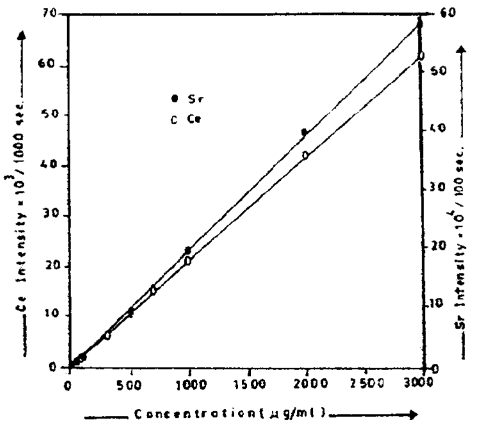


Fig.4: Calibration curves for Ce and Sr.

sample holder of stainless steel. Analysis shows that the peaks for Sr and Ce are symmetric. The calibration curves for Sr and Ce are drawn in Fig. 4 for conversion of net intensity to concentration. The curves do not deviate from linearity and corresponding empirical relations (equations 2 and 3) remains simple and linear. Precision was determined by making ten measurement each at optimized conditions for Sr and Ce for different concentration solutions. The relative standard deviation (% RSD) are calculated using established statistical method. The variation of % RSD with concentration for Sr and Ce are given in Fig. 5.

The effect of various cations (K^{+1}, Na^{+1}, Rb^{+1}, Cs^{+1}, Li^{+1}, Co^{+2}, Zn^{+2} Ce^{+3}, Cr^{+3}) and anions (CH_3COO^-, $S_2O_3^{--}$, Cl^- Br^-, I^-, NO_3^- and EDTA) on Sr and Ce intensities have been studied with their composition fixed at 1000 μg/ml and 2000 μg/ml respectively. The results are shown in Fig. 6. It is clear that cations increase the intensity of Ce in the order of $Zn^{+2} > Co^{+2} > Cr^{+3} > Na^{+1} > K^{+1} > Rb^{+1} > Cs^{+1} > Li^{+1}$. Similarly, Cr^{+3}, K^{+1}, Na^{+1} increases the Sr intensity where as Li^{+1} reduces the Sr intensity. Anions increase the Ce intensity in the order of $NO_3^- > Cl^- > Br^- > S_2O_3^{--} > I^- >$ EDTA $> CH_3COO^-$. Thiosulphate decreases the Sr intensity while others anions increase Sr intensity in the order of $NO_3^- > Cl^- > Br^-. > I^- >$ EDTA $> CH_3COO^-$. For reasons cited above, calibration curves for Ce and Sr in presence of these cations and anions were obtained and the best fitting equations got through regression corresponding to the calibration curves were used to determine Sr and Ce concentration. These equations are given in Table 2 and 3.

Table 2: Best fitting equations for Sr in presence of various cations and anions

Strontium in presure of	Equation of Line*	Variance
Cr^{+3}	$N_{Sr} = 2.196x10^2\ C_{Sr} + 1.947x10^3$	$4.266x10^2$
K^{+1}	$N_{Sr} = 2.026x10^2\ C_{Sr} - 4.150x10^{+3}$	$1.49x10^4$
Na^{+1}	$N_{Sr} = 1.950x10^2\ C_{Sr} - 2.665x10^3$	$3.382x10^3$
Sr (Pure)	$N_{Sr} = 1.842x10^2\ C_{Sr} + 4.598x10^3$	$7.247x10^3$
Li^{+1}	$N_{Sr} = 1.669x10^2\ C_{Sr} + 1.293x10^3$	$8.489x10^3$
NO_3^-	$N_{Sr} = 3.051x10^2\ C_{Sr} + 3.815x10^{-1}$	$2.45x10^{-2}$
Cl^-	$N_{Sr} = 2.829x10^2\ C_{Sr} + 1.331x10^1$	$1.335x10^1$
Br^-	$N_{Sr} = 2.753x10^2\ C_{Sr} + 2.686x10^1$	$3.070x10^1$
I^-	$N_{Sr} = 2.468x10^2\ C_{Sr} + 2.686x10^1$	$3.087x10^1$
EDTA	$N_{Sr} = 2.224x10^2\ C_{sr} + 8.101x10^2$	$9.486x10^2$
CH_3COO^-	$N_{Sr} = 2.155x10^2\ C_{Sr} - 7.057$	$2.785x10^{-2}$
$S_2O_3^{--}$	$N_{Sr} = 1.992x10^2\ C_{Sr} - 7.277x10^3$	$1.653x10^4$

*N_{Sr} = Strontium net intensity, counts
C_{Sr} = Strontium concentration, μg/ml

Table 3: Best fitting equations for Ce in presence of various cations and anions

Cerium in presence of	Equation of Line*	Variance
Zn^{+2}	$N_{Ce} = 26.39\,C_{Ce} - 13.69$	18.19
Co^{+2}	$N_{Ce} = 23.93\,C_{Ce} - 12.38$	28.90
Cr^{+3}	$N_{Ce} = 23.89\,C_{Ce} - 71.00$	12.40
Na^{+1}	$N_{Ce} = 23.01\,C_{Ce} - 407.20$	251.4
K^{+1}	$N_{Ce} = 22.40\,C_{Ce} + 0.003906$	1.702×10^{-5}
Rb^{+1}	$N_{Ce} = 21.44\,C_{Ce} - 5.805$	16.68
Cs^{+1}	$N_{Ce} = 21.40\,C_{Ce} + 0.00781$	2.103×10^{-5}
Li^{+1}	$N_{Ce} = 20.19\,C_{Ce} - 12.59$	16.36
Ce (Pure)	$N_{Ce} = 20.26\,C_{Ce} - 10.71$	24.04
NO_3^-	$N_{Ce} = 24.52\,C_{Ce} - 9.359$	27.05
Cl^-	$N_{Ce} = 24.41\,C_{Ce} + 85.30$	187.6
Br^-	$N_{Ce} = 23.11\,C_{Ce} - 12.58$	16.36
$S_2O_3^{--}$	$N_{Ce} = 23.06\,C_{Ce} - 10.71$	24.04
I^-	$N_{Ce} = 22.11\,C_{Ce} - 12.86$	12.40
EDTA	$N_{Ce} = 22.07\,C_{Ce} - 1.66$	27.37
CH_3COO^-	$N_{Ce} = 20.92\,C_{Ce} - 9.363$	27.05

*N_{Ce} = Cerium net intensity, counts.
C_{Ce} = Cerium concentration, μg/ml.

Experimental

Instrumentation

Sequential wavelength dispersive X-ray fluorescence spectrometer, SRS-200, (Siemens, West Germany) is used with the following attachment: Cr X-ray tube, Soller slit with angular divergence of 0.15°, LiF-100 crystal and NaI(TI) scintilation 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).

Calibration standards

Separate standards for Sr and Ce were prepared in the concentration ragne of 10-300 μg/ml and 100-3000 μg/ml respectively from their stock solutions. The stock solutions were prepared from cerium nitrate (99.999%), supplied by M/S Rare Earth Products and strontium nitrate (Merck, Item No. 7872).

Optimization of spectral line and measuring conditions

Spectra of Sr and Ce are recorded with 3.0 ml solution containing 10 g/l each of Sr and Ce. The spectra taken are shown in Fig. 1. The lines are identified from 2θ values given in literature [23]. Sr K (25.15) and CeK (II) (20.52) 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 substracting weighted average of background counts from the peak counts. Calculated limits of detection (L.D) were observed as a function of counting time for Sr and Ce. The results are shown in Fig. 3. The equation used to calculate L.D is given below [20].

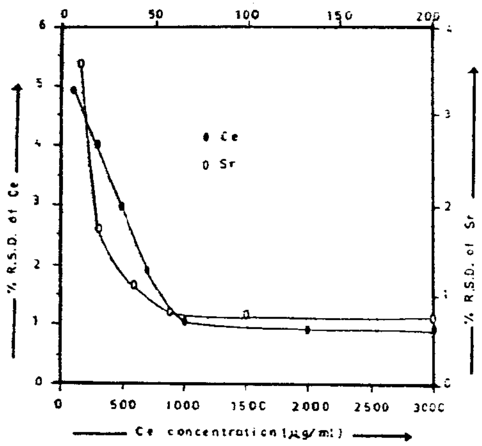


Fig.5: Variation of % RSD with concentration of Ce and Sr.

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

Where C = concentration of analyte in solution (μg/ml).

N = Peak counts.
N_b = Background counts.
T = Counting time.

The equation bears a confidence level above 99% specified by 3 in it [24]. The counting time selected for the Sr and Ce are 100 seconds and 1000 seconds respectively.

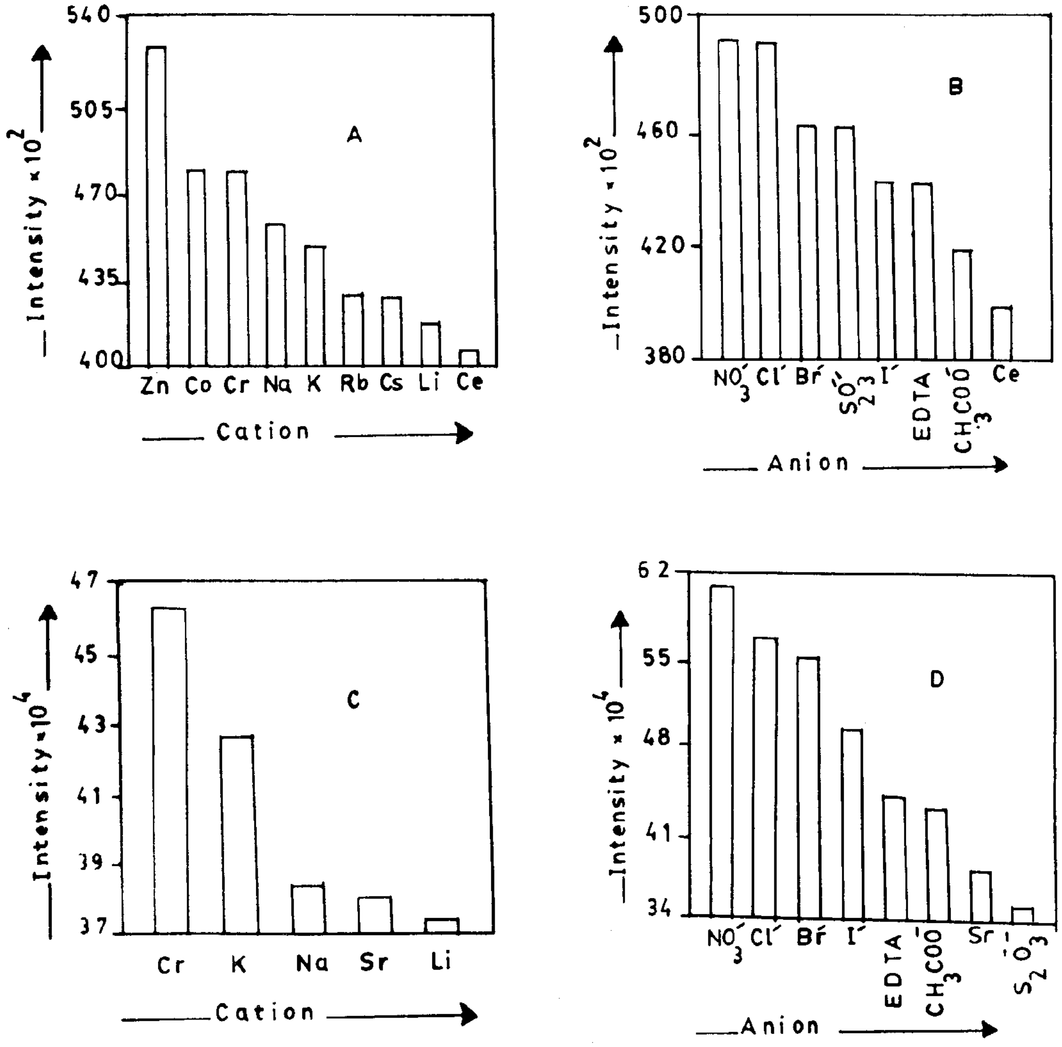


Fig.6: A - Effect of different cations on Ce intensity.
B - Effect of different anions on Ce intensity.
C - Effect of different cations on Sr intensity.
D - Effect of different anions on Sr intensity.

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 Sr and Ce. The data of these lines are subjected to regression analysis. The best empirical relationship between net intensity and concentration for Sr and Ce are

$$N_{Sr} = 1.951\text{x}10^2\, C_{Sr} + 6.138\text{x}10^2 \qquad (2)$$

and $$N_{Ce} = 2.046\text{x}10^1\, C_{Ce} + 4.518\text{x}10^2 \qquad (3)$$

Where N = Net counts and C = concentration (μg/ml)

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