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HIGH PURITY RARE EARTHS

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60 Abstract : Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a technique capable of giving high sensitivity in trace elemental analysis. While the technique possesses high sensitivity, it lacks high selectivity. Selectivity is important where substances emitting complex spectra are to be analysed for trace elements. Rare earths emit highly complex spectra in a plasma source and the determination of adjacent rare earths in a high purity rare earth matrix, with high sensitivity, is not possible due to the inadequate selectivity of ICP-AES. One approach that has yielded reasonably good spectral selectivity in the high purity rare earth analysis by ICP-AES is by employing a combination of wavelength modulation technique and high resolution echelle grating. However, we found that by using a high resolution monochromator sensitivities either comparable to or better than those reported by the wavelength modulation technique could be obtained.

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## SOME ASPECTS OF ICP-AES ANALYSIS OF HIGH PURITY RARE EARTHS

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### INTRODUCTION

Rare earths (REs) emit complex spectra primarily due to the  $4f^n$  valence electron configuration. The spectra of La, Yb and Lu are less complex since there are no 4f electrons in La and the 4f shell is full in Yb and Lu. The ionization energy of the 6s electron of the REs varies between 5.4 eV and 6.2 eV. The removal of a 6s electron leaves the singly charged RE ion with an electron configuration of  $4f^n 6s$ . This configuration results in more spectral terms than the  $4f^n$  configuration of the neutral RE atom. As a consequence, the spectrum of a singly charged RE ion becomes more complex. Even in a d.c. arc source which has a  $T_{exc}$  of about  $5000^\circ K$ , ionization energy of 6 eV will be available and REs get easily ionized, resulting in the emission of complex ionic spectra. In an ICP source which has a higher  $T_{exc}$  than the d.c. arc, the spectra emitted will be much more complex. Therefore the high sensitivity that the ICP is capable of cannot be realized when traces of REs are to be determined in a high purity RE matrix. In such cases selectivity is also important. In ICP-AES selectivity, to certain extent, can be achieved through the choice of a suitable spectrometer/monochromator and by fixing optimum matrix concentration for nebulization. In this paper, some of these aspects will be considered, based on our experience with the analysis of some high purity REs.

## EXPERIMENTAL

### ICP-AES equipment

A Jobin-Yvon polychromator (Model No JY-48) and scanning monochromator (Model No. JY-38 THR 1000) system was employed in the present work. A 56 MHz RF generator (Model No. R-C DURR JY ICP-2255) was operated at a forward power of 1.5 kW with a three piece demountable quartz torch. The entrance slits of the polychromator, the monochromator and the plasma (region 15 mm above the top of load coil) are on the same optic axis. Complete experimental parameters are given in Table 1.

### Calibration standards

Using 'Specpure' grade (supplied by Johnson Matthey & Co) RE oxides, calibration standards in the required concentration range were prepared. The standards contained the RE matrix at a chosen concentration. In the case of La matrix the standards contained 2 mg/ml of La while 1 mg/ml of the matrix was incorporated in the calibration standards used for Eu, Gd, Tb and Dy analysis.

## RESULTS AND DISCUSSION

### Which one to choose, a polychromator or monochromator?

In ICP-AES, the selectivity can, to some measure, come from a polychromator or a scanning monochromator. Although a polychromator is suitable for rapid and simultaneous multielement analysis, it cannot offer the dispersion and resolution required for high purity RE analysis. In addition to the grating, better dispersion can come from the focal length (in case of a plane grating-concave mirror spectrometer) or the radius of curvature (in case of a concave grating spectrometer) of the instrument. A spectrometer either with larger focal length or radius of curvature will involve larger space for temperature control (climatisation). If a polychromator has to be used for the determination of adjacent REs in several high purity REs, many secondary slits for various RE lines chosen to be mutually interference-free can be mounted on the Rowland circle. But, this amounts to spending a lot of money and also to using lines of lesser sensitivity. A polychromator, costing a moderate sum,

can at best be programmed for the analysis of traces of REs in RE matrices which give relatively less complex spectra, viz. La, Yb, Lu and Y (which occurs along with heavier REs). Most REs have their sensitive lines in the spectral region above 300 nm. Therefore, it will be possible to choose a grating with appropriate grooves/mm so that the wavelength region above 300 nm can be employed in the second order with better dispersion and resolution.

In the light of above discussion, a scanning monochromator will be a better choice for RE analysis. The J-Y 38 THR-1000 scanning monochromator available with us gives a dispersion of 0.26 nm/mm in the first order. Using this monochromator, we have developed methods for the determination of adjacent REs in La, Eu, Gd, Tb, Dy and Y matrices.

Spectral selectivity in ICP-AES can be improved by using high resolution echelle gratings and employing wavelength modulation referred as second derivative spectrometry. Ishii and Satoh<sup>1</sup> applied such an approach and determined trace REs in La. They reported a detection limit of 10 ppm each for Ce, Pr, Nd and Sm when 10 mg/ml of La solution was nebulized into the plasma. We have obtained a detection limit of 5 ppm for the above 4 REs by nebulizing only 2 mg/ml of La solution and using JY-38 THR-1000 monochromator. Another more promising approach for improving selectivity in the analysis of REs is by combining ICP with atomic fluorescence spectrometry (ICP-AFS). ICP-MS also offers high selectivity in addition to excellent sensitivity.

#### Choice of matrix concentration in the solution used for nebulization

Nowadays we can get nebulizers which can tolerate high amount of dissolved solids. However, a solution containing a high concentration RE matrix, will give rise to a highly complex spectrum in the ICP. In the atlas of spectral of information Winge et al<sup>2</sup> reproduced the spectra of pure REs in the wavelength region 190-510 nm. These spectra consist of many lines accompanied by high background continuum. In recording these

spectra a concentration ranging between 5 and 100  $\mu\text{g/ml}$  only was employed. Therefore one can visualize the extent to which the spectrum becomes complex when higher amount of RE matrix is nebulized into the plasma. In our work, we considered this aspect and then decided upon the RE concentration. Since the spectrum of La is relatively simpler, we chose its concentration at 2 mg/ml. For Eu, Gd, Tb and Dy, we used a solution containing 1 mg/ml. Even at these concentrations, the spectral background was high. The enhanced background resulted in higher detection limits compared to those obtained with aqueous solutions. In Table 2, the data for La, Eu and Tb matrices are given. Although we have employed a low concentration ( 1 or 2 mg/ml) of the RE matrix in the solution nebulized, the detection limits obtained for the trace REs were either comparable to or better than those obtained by OES and XRF methods previously employed in our laboratory.

#### Selection of interference-free lines and background correction

The sequential monochromator used in this work offered sufficient dispersion and resolution so that lines free of spectral interference could be chosen for the various RE analytes. Each line was checked for freedom from spectral interference by recording the spectrum of 1 or 2 mg/ml RE matrix solution as well as the spectrum of the solution containing the RE matrix and 1  $\mu\text{g/ml}$  RE analyte solution. Figure 1 illustrates the procedure followed for Eu 393.048 nm line in Tb matrix.

The intense background continuum that is emitted during the excitation of REs in ICP necessitates application of background correction. The background intensities are measured at appropriate positions on either side of the analyte line and the average background intensity is subtracted from the gross intensity of the RE analyte line. In Figs.1 and 2 the positions where background intensities are measured are shown by arrow marks for Eu and Y in Tb matrix.



Table 1: ICP-AES experimental details

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Spectrometer	:	JY 48 Spectroanalyser (polychromator-Paschen-Runge mount) having 1m concave grating with 2550 grooves/mm.
Wavelength	:	130-415 nm; I order
Dispersion	:	0.39 nm/mm
Monochromator	:	JY 38 THR 1000 sequential, 1m monochromator (Czerny-Turner mount) having a grating with 3600 grooves/mm
Wavelength range	:	160-500 nm; I order
Dispersion	:	0.26 nm/mm
RF generator frequency forward power	:	Model No. R.C. DURR-JY ICP-2255, 56 MHz, 1.5 KW
Coolant argon flow rate	:	16 l/min
Aerosol argon flow rate	:	0.4 l/min
Sheathing argon flow rate	:	0.45 l/min
Plasma torch	:	quartz demountable type
Nebulizer	:	pneumatic, concentric type Model No. JY 31-021-975
Solution uptake rate	:	1.6 ml/min, without peristaltic pump
Observation height	:	15 mm above top of load coil
Data acquisition and processing.	:	through APPLE-IIe Computer

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Table 2: RE wavelengths, background factors and detection limits

Matrix	Element Wavelength (nm)	Background Factor <sup>a</sup>	Detection Limits	
			Aqueous Solution (ng/ml)	Matrix Solution (ng/ml)
La	Ce 413.380	1.36	7	10
	Pr 414.311	1.80	8	16
	Nd 406.109	1.39	4	6
	Sm 442.434	1.28	5	6
Eu	Pr 422.293	1.61	28	38
	Nd 406.109	1.28	8	18
	Sm 446.734	1.28	8	15
	Gd 303.284	2.15	7	15
	Tb 370.392	3.48	20	45
	Dy 364.540	2.64	8	30
Tb	Y 371.030	3.62	0.4	1.2
	Sm 446.734	1.80	4	5
	Eu 393.048	5.85	0.7	6
	Gd 310.050	3.67	3	12
	Dy 387.211	2.53	3	7
	Ho 345.600	3.30	2	8
	Er 390.631	1.83	6	8

<sup>a</sup> Background factor is expressed as the ratio of the average background intensities measured for the RE line scan of two solutions - one containing 1 $\mu$ g/ml RE with 1 or 2mg/ml, RE matrix and the other containing 1 $\mu$ g/ml RE only.

<sup>b</sup> Calculated from 3 times the standard deviation of the background using aqueous solution containing the REs (each 1  $\mu$ g/ml).

<sup>c</sup> Calculated from 3 times the standard deviation of the background using a solution containing the REs (each 1  $\mu$ g/ml) and RE matrix (1 or 2 mg/ml).

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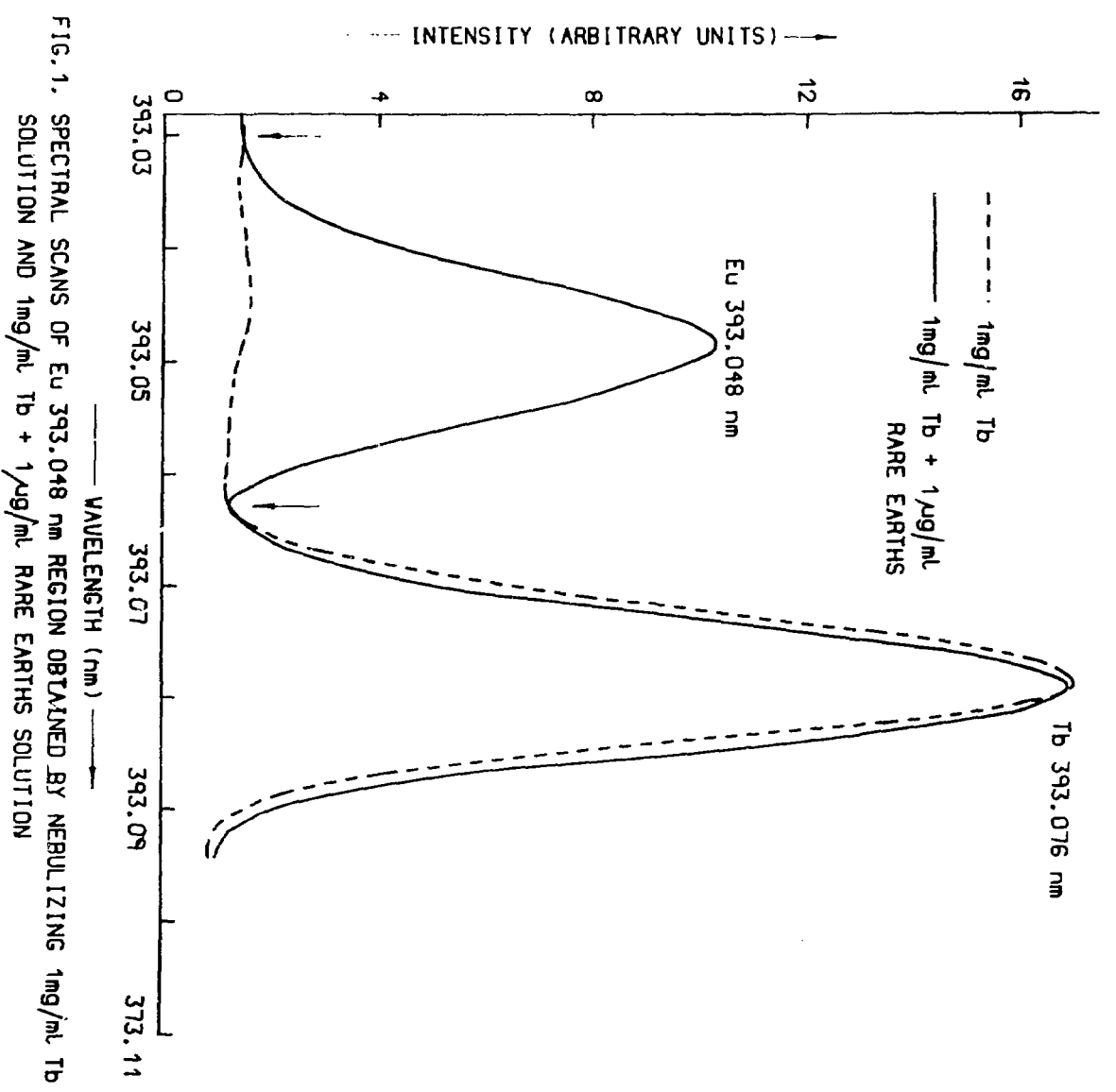


FIG. 1. SPECTRAL SCANS OF EU 393.048 nm REGION OBTAINED BY NEBULIZING 1mg/ml Tb SOLUTION AND 1mg/ml Tb + 1µg/ml RARE EARTHS SOLUTION

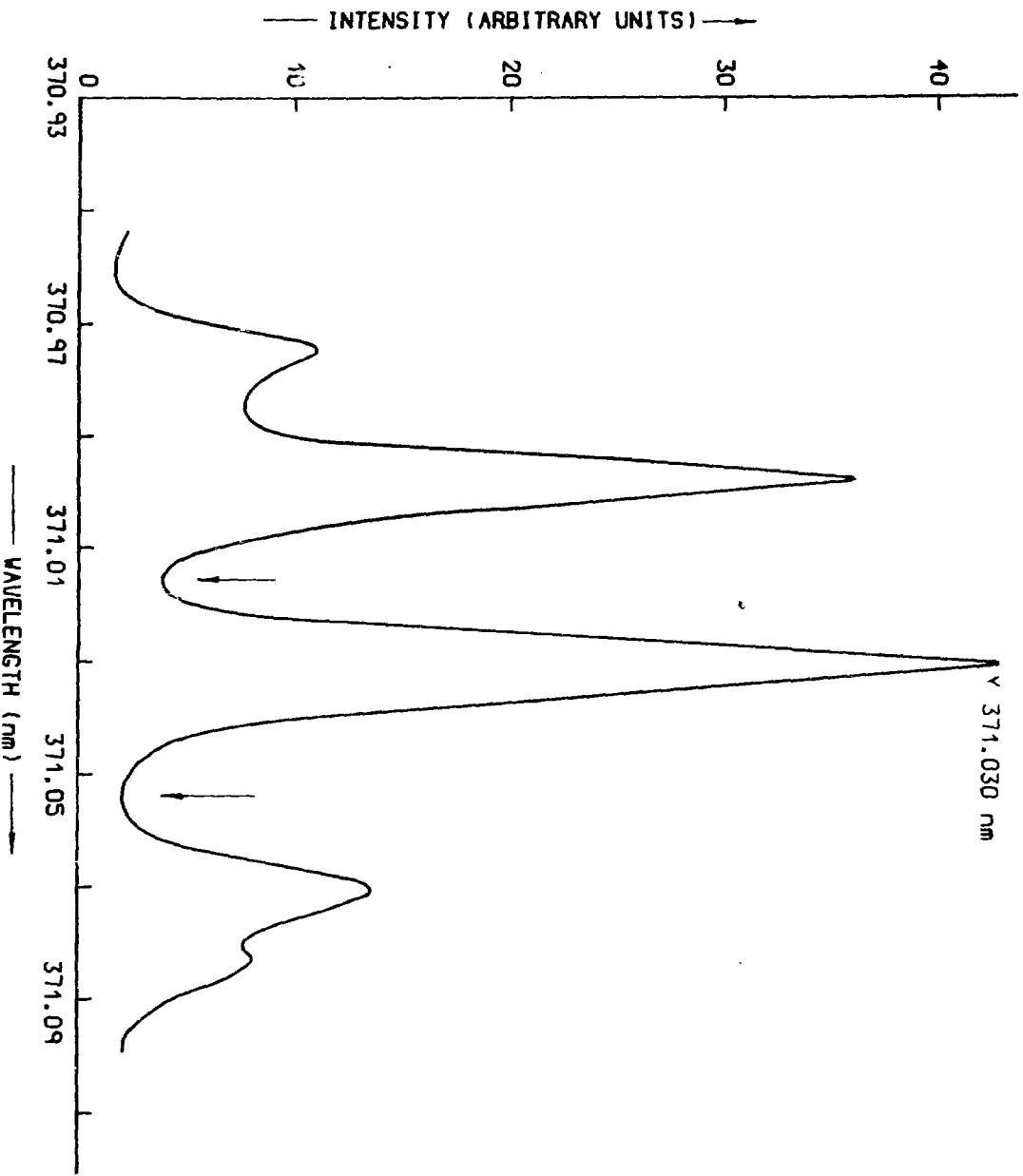


FIG. 2. SPECTRAL SCAN OF Y 371.03 nm LINE SHOWING THE POSITIONS (↓) FOR BACKGROUND INTENSITY MEASUREMENTS IN THE PRESENCE OF NEARBY MATRIX LINES.

