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OPTICAL EMISSION SPECTROGRAPHIC ANALYSIS OF THULIUM OXIDE FOR
RARE EARTH IMPURITIES

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GOVERNMENT OF INDIA
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BHABHA ATOMIC RESEARCH CENTRE
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Descriptors

THULIUM OXIDES

IMPURITIES

EMISSION SPECTROSCOPY

QUANTITATIVE CHEMICAL ANALYSIS

ERBIUM

YTTERBIUM

LUTETIUM

YTTRIUM

SAMPLE PREPARATION

INTERFERING ELEMENTS

ACCURACY

CALIBRATION STANDARDS

SENSITIVITY

ABSTRACT

An optical emission spectrographic method has been developed for the analysis of high purity thulium oxide to determine rare earth elements Er, Yb, Lu and Y. A 1200 groove/mm grating blazed at 3300 Å is used to record the spectrum on Kodak SA-1 photographic plates after the excitation of the graphite-sample (1:1) mixture in a DC arc. The determination range is 0.008% to 0.1% and the relative standard deviation is 17.6%.

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I. INTRODUCTION

With the advent of high temperature ($T_c = 90^{\circ}$ K) superconductors, the rare earth (RE) elements have found a new use which might bring a revolution in the industry. These ceramic superconductors of the type RE-Ba-Cu-O, where RE is either Y or La or any other RE element, are being prepared and tested at many research centres throughout the world. With this development, the industrial production of high purity REs and their quick and sensitive testing methods have assumed higher importance.

Thulium (Tm) is a member of RE group of elements. Its abundance in rocks and ores is very small. Therefore, alongwith Eu, Ho and Lu, it is a high cost RE. Despite its high cost, Tm has found some industrial uses by virtue of its unique properties. An isotope of Tm viz. Tm-170 is used as a portable source of radiography. Its other use is as a blue primary phosphor in colour television cathode ray tubes. In high T_c superconductors Tm based superconductors are interesting in their magnetic behaviour.

Pure Tm is prepared by ion-exchange techniques and is likely to contain the neighbouring elements in the periodic table and also yttrium (Z=39) which occurs with heavy REs, as impurities in it. Our Division has a continuing programme of developing quick and sensitive methods of analysis for high purity REs by optical emission spectrographic (OES) methods¹⁻¹².

Earlier an X-ray fluorescence (XRF) spectrometric method was developed for the determination of Dy, Ho, Er, Yb, Lu and Y in thulium oxide¹³. The XRF method needs about 500 mg sample but at times, for costly REs like Tm, it is not possible to spare this high amount of sample. An alternate optical emission spectrographic (OES) method is therefore developed which requires less than 10 mg sample. The method can determine four elements viz. Er, Yb, Lu and Y with detection limits of 0.008%.

There is one OES method developed by Kniseley et al¹⁴ for the analysis of thulium oxide which determines these elements with a detection limit of 0.02%. The limits of determination being reported by us are better than the earlier work.

II. EXPERIMENTAL

II.1. Preparation of Standards and Samples

The standards are prepared synthetically in solution form initially. These are then precipitated as hydroxides and ignited to oxide. The details are given below.

Oxides of Er, Yb, Lu and Y obtained from Rare Earth Products Ltd., Cheshire, England, are heated for one hour in platinum crucibles to remove any moisture and known weights are dissolved in high purity nitric acid (Merck, G.R.) individually. Three standard solutions named A, B and C are prepared for each RE oxide which contain 1000 γ /ml, 100 γ /ml and 10 γ /ml of individual RE oxides. Thulium oxide is heated to remove moisture, appropriate amounts weighed out and dissolved separately in beakers for the five standards. To the thulium oxide solutions, the individual RE oxide solutions are added, as shown in Table I, to prepare standards which contain 50, 100, 200, 500 and 1000 ppm of each RE oxide on thulium oxide. The standards in solution form are precipitated as hydroxides by the addition of ammonium nitrate and an excess of ammonium hydroxide. The precipitates are allowed to settle down overnight and filtered. The filter paper containing the precipitate is dried and transferred to a platinum dish, charred over a low flame initially and then ignited in a furnace at 800^o C for about four hours. The resulting thulium oxide powders containing known amounts of impurities are ground with pure graphite powder in the weight ratio 1:1 in an agate mortar. The samples in oxide form are also mixed with graphite powder in the same 1:1 ratio. The graphite mixture of standards and samples are loaded in electrodes and their spectra recorded under conditions given in Table II.

It was later found that the starting material contained 30 ppm each of the analyte elements and the concentration of the standards prepared by us was 80, 130, 230, 530 and 1030 ppm with the addition of the blank. The concentration of these elements was found by the method

of standard additions to the working curves.

III. RESULTS AND DISCUSSION

III.1. Selection of Analysis Lines

The lines selected for the analyte elements viz. Er, Tm, Lu and Y, are the most sensitive lines available in the region 2875 - 3500 Å. These are also as far as possible free from interference of lines from other analyte elements and matrix element lines. These lines alongwith the internal standard Tm line are shown in the identification chart in Fig. 1.

The selected lines are given in column 1 of Table III. The Table III also gives in column 4 the probable interfering RE lines as given in M.I.T. Wavelength Tables¹⁵. It is found that most of the interfering elements are either not expected in thulium (due to the ion-exchange technique employed for its purification) or their intensities are too weak to give any substantial interference. In the case of Yb 2891.38 Å line there could be interference from an Er 2891.387 Å line with a listed intensity of 20 in M.I.T. tables¹⁵. This interference was checked by taking the spectrum of pure Er with a spectrum of a standard of thulium containing Yb impurity. It was found that even in pure Er spectrum, this line appears with a very weak intensity as shown in Fig. 2. From experiments it was further confirmed that even at 5% level of Er₂O₃ in Tm₂O₃, the line Er 2891.387 Å does not appear in the spectrum under our conditions. Since Er is expected as an impurity at ppm levels in thulium, this interference can be neglected.

A weak line of the matrix thulium at 3128.11 Å has been chosen as an internal standard because of its proximity to analyte element lines and suitable density for photometric evaluation. This weak line is not listed in wavelength tables¹⁵ and its wavelength has been computed by us from a Hartmann spectrum of Tm and Fe.

Earlier workers Kniseley et al¹⁴ have used a higher spectral region of 3300 - 4500 Å as against the region 2900 - 3500 Å used by us. The region used by the earlier workers is full of cyanogen (CN) bands resulting in high background to analyte lines whereas the region used by us is free of CN bands and is of a low background which is more amenable to quantitative analysis. In our method the selected lines can be accommodated in one plate of 10 inch length thus economising the analysis cost.

III.2. Volatilisation Studies

Volatilisation studies were done by the moving photographic plate method with a standard containing 1000 ppm impurities in thulium oxide. A 15 mg charge was excited in a DC arc under conditions given in Table II and the plate was racked every 10 seconds. The arcing was continued till 60 seconds. The densities of the lines of analyte elements and the internal standard element were obtained from the spectra for each time interval. The intensity ratios were obtained for different time intervals and plotted against time as shown in Fig.3.

The exposure time was fixed at 20 seconds since this exposure time gives a suitable density for the analyte lines. It is realised that an exposure of 20 seconds does not give a complete burn of the sample and also the intensity ratios vary to some extent during the exposure time but the integrated intensities show a good reproducibility. The internal standard provides only a partial compensation for the volatilisation differences but gives compensation for weight of the sample, development of the photographic plate, adjustments of the spectrograph etc.

III.3. Precision

The precision has been assessed in terms of percent relative standard deviation (RSD) from 11 values of intensity ratios of analyte elements at every concentration of the standards. The RSD so obtained is given in Table IV. The average RSD over entire concentration range for each element has been named as precision for the particular element and the elemental precision averaged for 4 elements has been named as the precision of the method.

III.4. Working Curves

The working curves relating log concentration with log intensity ratio are given in Figs. 4 and 5. Each intensity ratio point for every element at different concentrations is an average value of 11 individual values obtained from three different plates. The average intensity ratio values for each concentration of the element are given in Table V. The curves are drawn with the actual concentration in the

standards i.e. the amount added by us in the preparation of the standards plus the amount present in the blank as found by us from our studies.

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REFERENCES

1. S.V.Grapurohit, P.S.Murty and T.R.Saranathan,
Spectrographic Determination of Ce, Pr and Nd in Lanthanum Oxide
Report AEE/Spec/6 (1964)
2. S.V.Grapurohit and V.P.Bellary,
Determination of Rare Earth Impurities in Purified Lanthanum Oxide
Using the Stallwood Jet
Report BARC-472 (1970)
3. P.S.Murty and I.J.Machado,
Spectrographic Determination of La, Pr, Nd and Sm in Cerium Oxide
Report AEE/Spec/7 (1964)

4. S.V.Grampurohit and V.N.P.Kaimal,
Spectrographic Determination of Rare Earth Impurities in Purified
Samarium Oxide
Report BARC-710 (1973)

5. P.S.Murty and P.P.Khanna,
Spectrographic Analysis of High Purity Europium Oxide
Report BARC-532 (1971)

6. S.V.Grampurohit and K.Swamy,
Spectrographic Analysis of High Purity Gadolinium Oxide and
Dysprosium Oxide for Trace Amounts of Other Rare Earths
Report AEET/Spec/14 (1964)

7. S.V.Grampurohit and A.Sethunadhavan,
Spectrographic Determination of Rare Earth Impurities in Purified
Terbium Oxide and Holmium Oxide
Report AEET/Spec/16 (1966)

8. G.S.Ghodgaonkar, P.P.Khanna and A.Venugopalan,
Spectrographic Analysis of High Purity Dysprosium Oxide
for Trace Amounts of Er, Gd, Ho, Tb and Y
Report BARC-536 (1971)

9. S.V.Grampurohit and K.Swamy,
Spectrographic determination of Rare Earth Impurities in Erbium
Oxide and Ytterbium Oxide
Report BARC-471 (1970)

10. L.C.Chandola and P.P.Khanna,
An Optical Emission Spectrographic Method for Determination of
Ho, Er, Tm, Lu and Y in Ytterbium Oxide
Spect. Div. Prog. Rep. for Jan.85 - Dec.86, Report BARC-1368
(1987) pp.58-59.

11. L.C.Chandola and V.S.Dixit
Optical Emission Spectrographic Analysis of Lutetium Oxide for
Rare Earth Impurities
Report BARC-1329 (1986)

12. S.V.Grampurohit, R.C.Naik and S.B.Sindgikar,
A DC Arc Method for the Determination of Rare Earth Impurities
in Yttrium Oxide
Report BARC-521 (1971)

13. L.C.Chandola and P.P.Khanna,
X-ray Fluorescence Analysis of Thulium Oxide for Rare Earth
Impurities
J.Radioanal.Nucl.Chem., Articles 121, 53 (1988)

14. R.N.Kniseley, V.A.Fassel, R.W.Tabeling, B.G.Murd and B.B.Quinney,
Quantitative Spectrographic Analysis of Rare Earth Elements
Spectrochim. Acta 13, 300(1959)

15. G.Harrison,
M.I.T.Wavelength Tables
John Wiley, New York, 1939.

TABLE I

Preparation of Standards

Concentration of Std. ppm	Amount of Soln. Added ml	Total Weight of Impurities mg	Matrix Added mg
1000	1 ml of Soln.A	4	996
500	5 ml of Soln.B	2	998
200	2 ml of Soln.B	0.8	999.2
100	1 ml of Soln.B	0.4	999.6
50	5 ml of Soln.C	0.2	999.8

Solutions A,B and C refer to 1000 γ /ml, 100 γ /ml and 10 γ /ml respectively of each of Er_2O_3 , Yb_2O_3 , Lu_2O_3 and Y_2O_3 . It was later found that the starting material thulium oxide contained 30 ppm each of the analyte elements. The actual concentration of the standards was 1030, 530, 230, 130 and 80 ppm each.

TABLE II

Equipment and Experimental Conditions

Spectrograph	: 3.4 m Jarrel-Ash plane grating, Ebert mount.
Grating	: 1200 grooves/mm plane, blazed at 3300 Å; Reciprocal linear dispersion 2.5 Å/mm.
Wavelength Range	: 2875-3500 Å in first order.
Optical System	: An intermediate image of the source placed at 75 cm from slit is formed at 48 cm which is focussed on the slit by a cylindrical lens of 10 cm focal length.
Diaphragm	: Incandescent electrode tips are cut off at collimating mirror.
Slit Width	: 10 microns with zero error adjustment.
Excitation Source	: Jarrel-Ash Custom Vari-source; DC arc run at 10 amps.
Sample Electrode	: Anode; 3/16 in. graphite, neck type; Ultra Carbon (USA).
Counter Electrode	: Cathode; 1/8 in. graphite, pointed; Ultra Carbon (USA).
Sample Charge	: 15 mg; sample:graphite :: 1:1.
Analytical Gap	: 4 mm.
Exposure Time	: 20 seconds.
Photographic Emulsion	: Kodak SA-1, one glass plate of 10" length.
Photographic	: Developed in Kodak D-19 developer for 2 min.
Processing	: at 20 ⁰ C; fixed in Kodak F-5 fixer.
Emulsion	: A Fe spectrum is recorded at 3 amps. for 45 sec.
Calibration	: through a 7 step rotating sector with log ratio of 0.2 between two consecutive steps.
Photographic	: Hilger non-recording L.451 with a log scale.
Photometry	
Data processing	: Densities are converted to intensity ratios on a Norsk Data computer.

TABLE III

Analytical Data

Analyte Ele. Int. Std.		Concent.	Interfering	
Line	Line	Range	Line	Remarks
A	A	%	A	
			Eu 3230.58	Not expected in Tm
			Ho 3230.57	Too weak to interfere
Er 3230.58	Tm 3128.11	0.008-1	Sm 3230.54	Not expected in Tm
			Dy 3230.32	Too weak to interfere
			Ce 3230.29	Not expected in Tm
			Er 2891.39	Interference negligible
Yb 2891.38	"	"	Ho 2891.39	Too weak to interfere
			Tb 2891.41	Not expected in Tm
			Ho 3359.49	Too weak to interfere
Lu 3359.56	"	"	Dy 3359.48	Not expected in Tm
Y 3242.28	"	0.008-0.5	Dy 3242.29	Not expected in Tm

TABLE IV

Relative Standard Deviation Percent

Standard PPM	Y	Yb	Er	Lu
80	7.1	19.9	29.6	21.3
130	9.5	25.6	21.4	19.8
230	9.5	20.2	18.8	16.0
530	17.5	13.5	26.4	14.7
1030	-	15.3	18.3	-
	-----	-----	-----	-----
Average	11.0	19.1	22.9	17.9
Average of Method		17.7		

TABLE V

Intensity Ratios for Various Concentration of Standards

Concentration of Standards ppm	Y 3242.28 ----- Tm 3128.11	Yb 2891.38 ----- Tm 3128.11	Er 3230.58 ----- Tm 3128.11	Lu 3359.56 ----- Tm 3128.11
80	1.3	0.54	0.24	0.72
130	1.68	0.66	0.28	0.91
230	2.25	0.97	0.48	1.37
530	4.12	1.76	1.04	2.59
1030	-	2.68	2.35	3.8

Intensity ratios are average of 11 values each

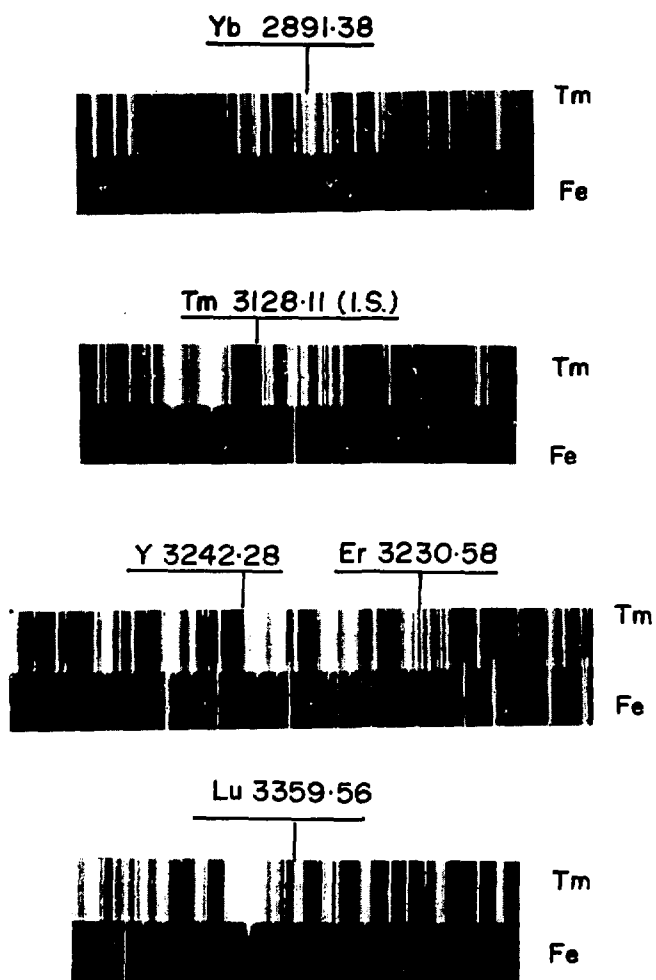


FIG. 1. IDENTIFICATION CHART FOR IMPURITIES IN THULIUM OXIDE

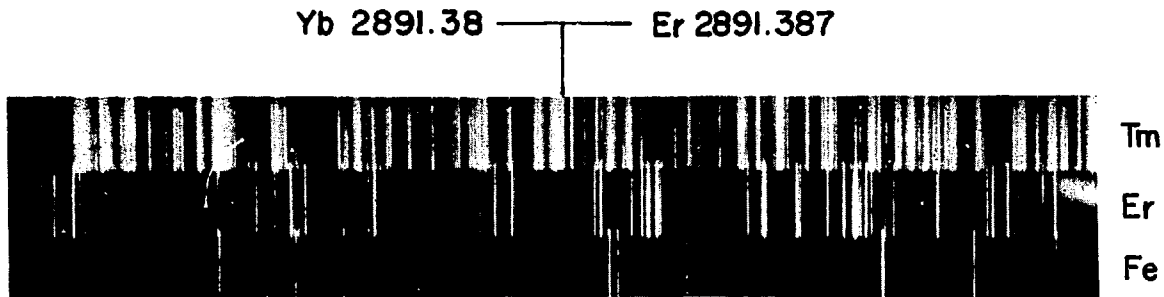


FIG.2. SPECTRUM SHOWING INTENSITY OF INTERFERING Er LINE IN PURE SALT AND INTENSITY OF 500 ppm Yb LINE IN Tm STANDARD.

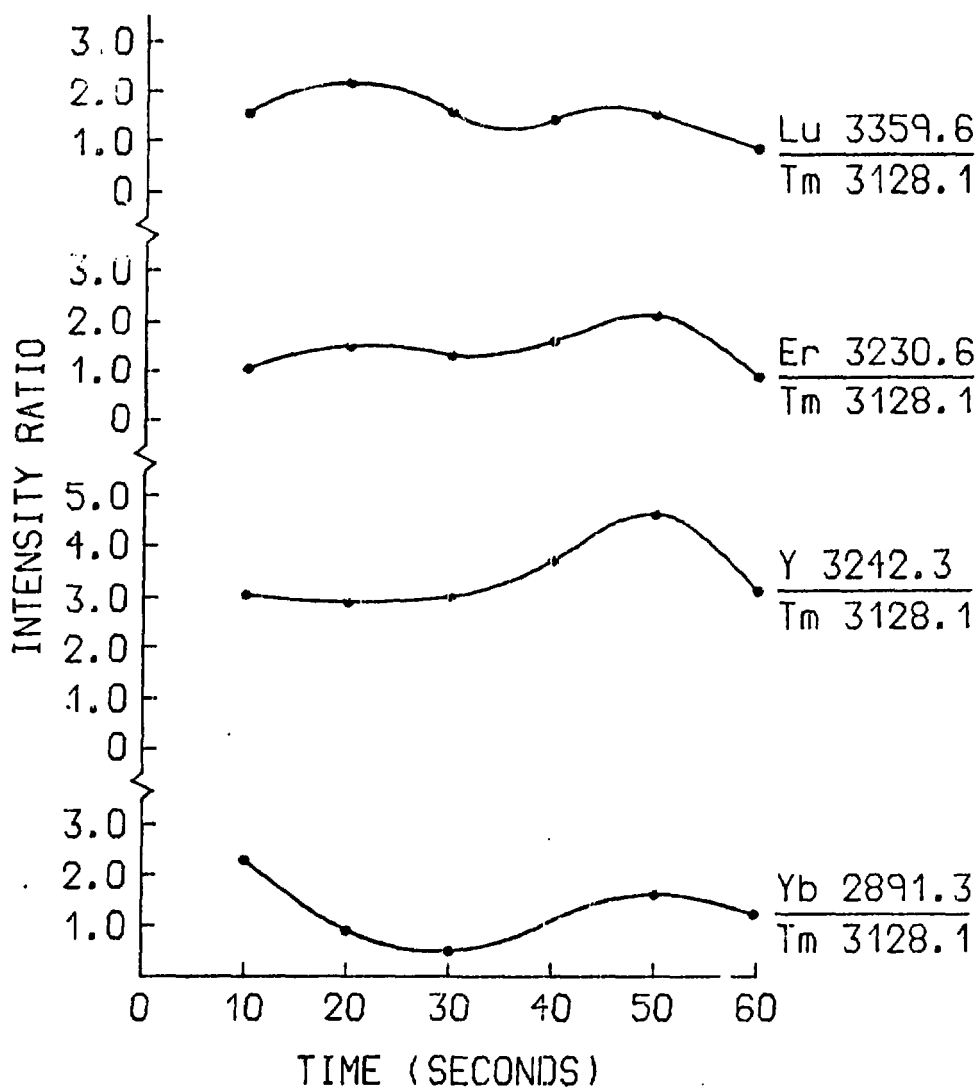


FIG.3. VOLATILISATION CHARACTERISTICS OF IMPURITIES IN THULIUM OXIDE

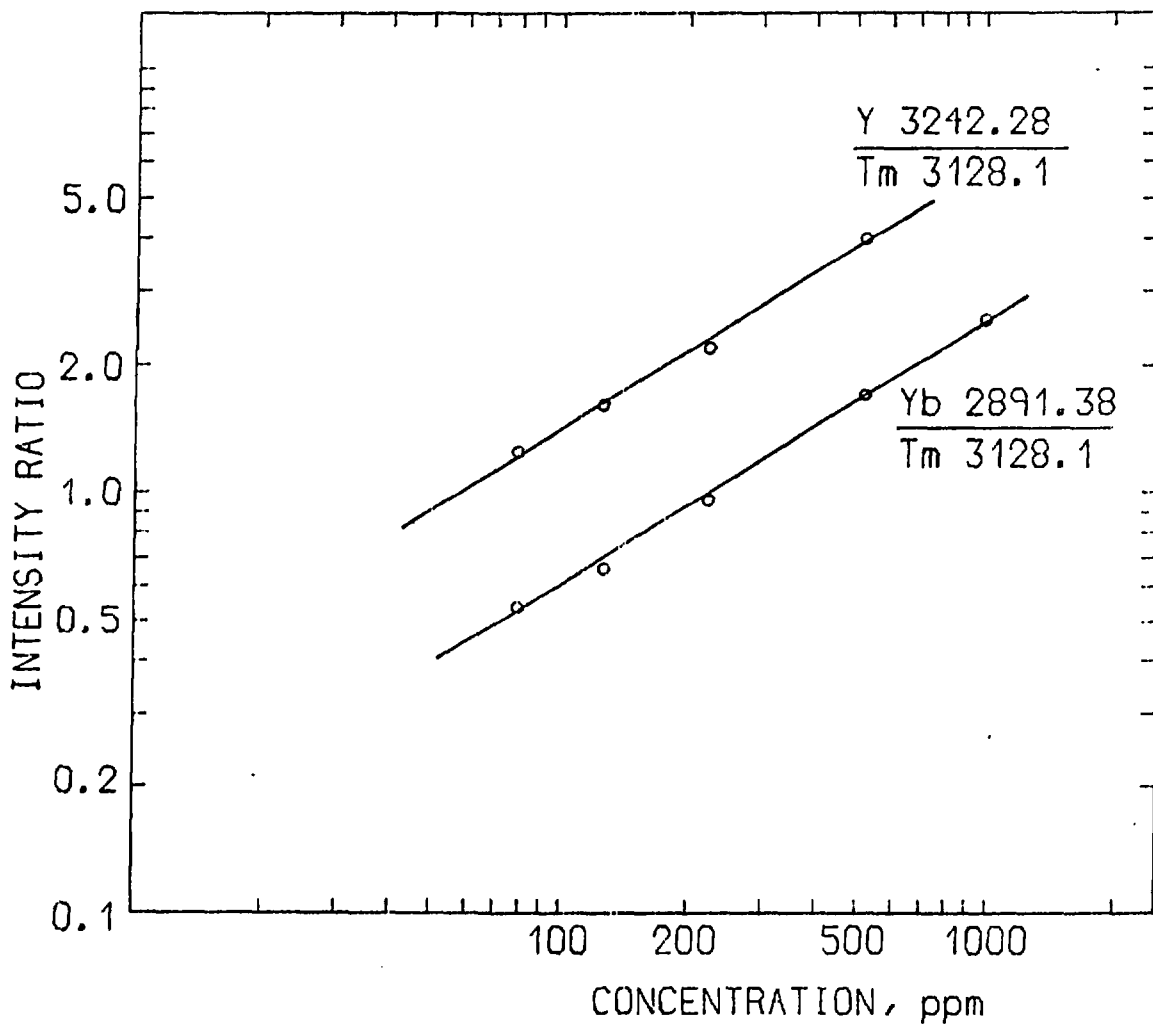


FIG.4. WORKING CURVE FOR Y AND Yb IN THULIUM OXIDE

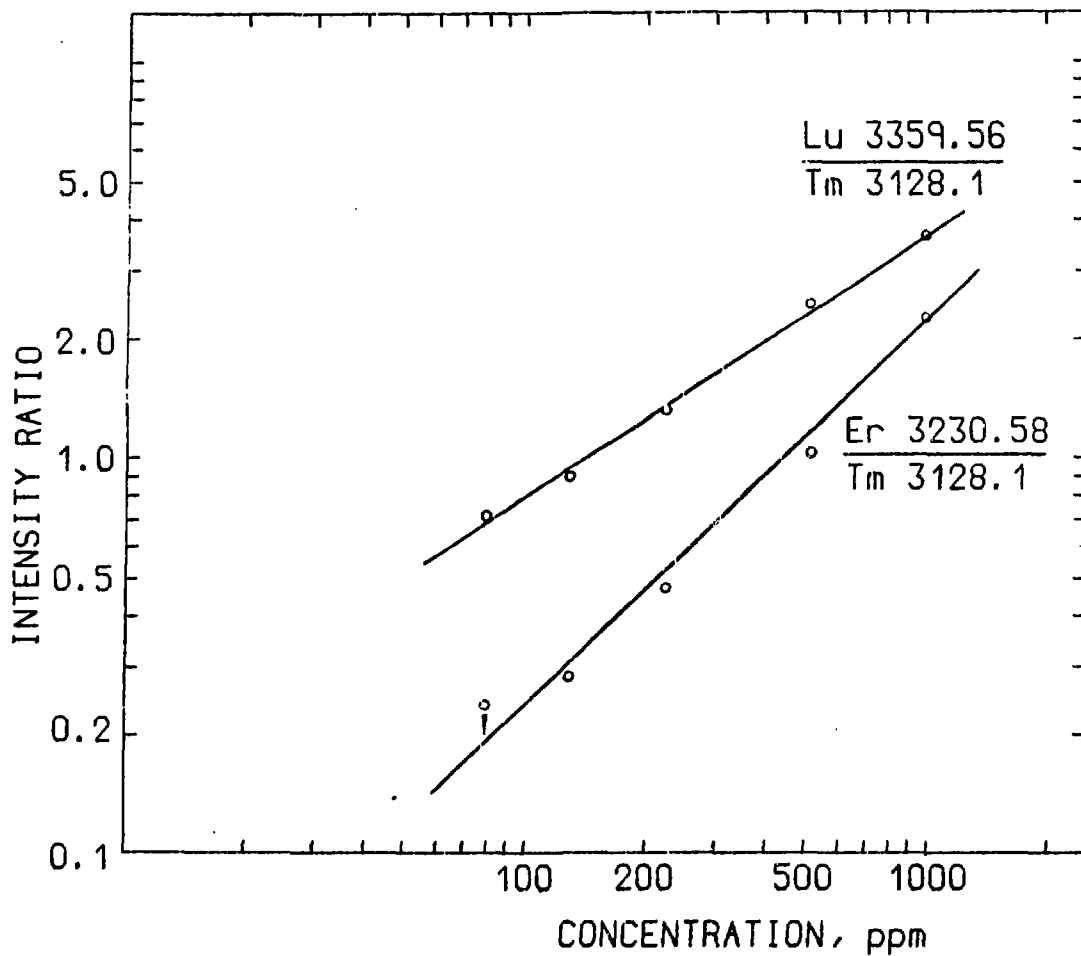


FIG.5. WORKING CURVE FOR Lu AND Er IN THULIUM OXIDE

