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X-RAY FLUORESCENCE ANALYSIS OF THULIUM OXIDE/OXALATE
FOR RARE EARTH IMPURITIES

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Descriptors

THULIUM OXIDES

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X-RAY FLUORESCENCE ANALYSIS

QUANTITATIVE CHEMICAL ANALYSIS

BORIC ACID

ACCURACY

SENSITIVITY

A B S T R A C T

An X-ray fluorescence spectrometric method for the analysis of thulium oxide is described. For the analysis, the sample in oxalate form is mixed with boric acid binding material and pressed into a pellet over a supporting pellet of boric acid. A wavelength dispersive Philips PW 1220 X-ray fluorescence spectrometer is used for the experiments; the minimum determination limits are 0.002% for Ho, Lu and Y, 0.005% for Dy and Er and 0.01% for Yb. Calculations for theoretical minimum detection limits and percent standard deviation at each concentration of the standard are carried out.

**X-RAY FLUORESCENCE ANALYSIS OF THULIUM OXIDE/OXALATE
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I. INTRODUCTION

Pure thulium (Tm) is likely to contain Dy, Ho, Er, Yb, Lu and Y as impurities in it. There are no earlier reports concerning X-ray fluorescence (XRF) analysis of Tm. However, there is one optical emission spectrographic (OES) method developed by Knisely et al⁽¹⁾ for the analysis of thulium oxide to determine Ho, Er, Yb, Lu and Y in the concentration range 0.02-1%. We have a continuing programme of developing sensitive XRF methods⁽²⁻¹⁵⁾ for the analysis of high purity rare earths (REs). In continuation of this programme an XRF method has been developed for the analysis of thulium oxide. The method being reported is more sensitive than the earlier reported OES method. The minimum determination limit (MDL) of the method being reported is 0.002% for Ho, Lu and Y; 0.005% for Dy and Er and 0.01% for Yb. Determination of Dy in this matrix was not tried by earlier OES workers and it is being reported here for the first time. Apart from better sensitivity in the present case, the XRF method has an advantage over OES method that it dispenses with the costly consumables like photographic plates, high purity electrodes etc.

II. EXPERIMENTAL

II.1 Method

The thulium oxide sample is converted to thulium oxalate by dissolution in nitric acid and precipitation with oxalic acid. 450 mg of dry oxalate powder is mixed well with 150 mg of boric acid powder binding material. The mixture is pressed to form a $\frac{1}{4}$ inch diameter double layer pellet over about 4 gm of boric acid backing pellet. The sample surface is irradiated with high intensity X-rays from a tungsten target X-ray tube and the fluorescent X-rays are analysed by a LiF(200) crystal. The intensities of characteristic L_{α_1} X-rays of Dy, Ho, Er, Yb and Lu are measured by a flow proportional counter while that of K X-ray of Y is measured by a scintillation counter. Standards are prepared synthetically by adding known amounts of RE oxide solution to thulium oxide solution and precipitating them as oxalates. The background intensities are measured on a pure thulium oxide pellet at the 2θ angles of impurity element X-rays and these are subtracted from the total counts to arrive at the net counts. The net counts for standards are plotted against their concentration to obtain the working curves for different elements. The concentration of the impurity in a sample is obtained by reading the value of net counts from the appropriate working curve.

II.2 Preparation of Standards and Samples

Rare earth oxides of Dy, Ho, Er, Yb, Lu and Y obtained from Rare Earth Products Ltd., Gresham, England, are dissolved in nitric

acid (G.R., Merck) and three standard solutions containing 500 γ /ml, 50 γ /ml and 5 γ /ml of each rare earth oxide are prepared. Appropriate amounts of Tm_2O_3 are weighed out separately and dissolved in nitric acid to which the individual rare earth solutions are added. The standards prepared contained blank (no impurities added), 20,50,100, 200, 500, 1000, 5000 and 10,000 ppm by weight of each rare earth oxide in Tm_2O_3 . These standard solutions are then precipitated as oxalates by a saturated solution of oxalic acid. The precipitates are filtered and dried. 450 mg of dry oxalate is mixed with 150 mg of boric acid binding material and ground in an agate mortar. This mixture is pressed at a pressure of 20 tonnes to obtain a double layer pellet.

The oxide sample is converted to oxalate and treated similar to the standards to obtain a $1\frac{1}{4}$ inch dia. pellet.

II.3 Sample to Binding Material Ratio and Saturation Thickness

Experiments

To conserve the amount of sample needed for the analysis, the double layer technique is adopted. In order that the sample does not peel off from the backing pellet of boric acid, the sample is mixed with boric acid in the weight ratio 3:1. This ratio of sample to binder was found to be useful in our earlier works^(13,14) and therefore retained for this analysis also.

(4)

Experiments were done to find out the minimum weight of sample-binder mixture (3:1) which will give saturation thickness when converted to a $1\frac{1}{2}$ inch diameter double layer pellet. Double layer pellets over 4 g boric acid were prepared with 50,100,200,400,600, 1000 and 1500 mg sample-binder mixture of a 800 ppm standard. Intensities of RE elements contained in the standard were measured for 40 s (for Y-100 s). The results of these studies are plotted in Fig.1. From these studies it was concluded that a 400 mg mixture gives saturation thickness for the impurity X-rays. However, taking a safety factor, the minimum weight of the mixture was fixed at 600 mg.

A fixed amount (4g) of boric acid as backing material is used in the preparation of double layer pellets since the quantity of backing material contributes to the scattered X-rays for hard K_{α} line of Y.

II.4 Instrument and Operating Conditions

A semiautomatic X-ray fluorescence spectrometer Philips model PW 1220 is used for the analysis; out of the three crystals it can hold at a time, the LiF(200) was found to be suitable. The instrument has a choice of two collimators (480 μ m and 160 μ m) and two detectors (flow proportional and scintillation). The instrument has 4 portholes for samples each of which can hold a tablet of $1\frac{1}{2}$ inch diameter. The sample can be kept rotated or stationary and the X-ray path can be

evacuated if needed. The conditions selected for the analysis are given in Table-I. The wavelengths of selected analytical lines are given in Table II. It was possible to use L_{α_1} lines for Dy, Ho, Er, Yb and Lu, whereas for Y, the K_{α} line was used. A strip chart record of 1% standard is given in Fig.2 where the impurity lines of analyte elements are marked.

III. RESULTS

III.1 Working Curves

The working curves relating the concentration of analyte element oxide with net intensity ($N_p - N_b$) are shown in Figs. 3 and 4. The net intensity is obtained by subtracting the counts obtained from a blank (N_b) from total counts (N_p) at 2θ angle of each analyte. A blank reading is taken after every three readings so that any variation in intensity with time is corrected for in the observations. The average net counts for different analyte elements in each standard are given in Table III.

III.2 Precision

The precision of the method was calculated in terms of percent standard deviation (SD%). Initially the net counts ($N_p - N_b$) are obtained for 11 sets of reading. From these σ_{net} is calculated by

(6)

using the formula $(\sum d^2/n-1)^{\frac{1}{2}}$ where d is individual difference of net count from the average of n readings. Finally SD% is obtained which is equal to $(\sigma_{net}) \times 100 / (N_p - N_b)$. The precision so calculated for each analyte element at each concentration of the standard is given in Table IV.

III.3 Theoretical Minimum Detection Limits

A concentration which gives a signal equal to three times the standard deviation of background is taken as theoretical minimum detection limit (TMDL). This is calculated using the formula.

$TMDL = 3 (N_b)^{\frac{1}{2}} \times \text{concentration} / (N_p - N_b)$. The calculated TMDL values are listed in Table V.

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TABLE-I

APPARATUS AND OPERATING CONDITIONS FOR THE ANALYSIS OF
THULIUM OXIDE

1. Spectrometer	Philips semiautomatic X-ray fluorescence Spectrometer PW 1220.
2. Generator	Philips ultrastable generator PW 1140 Voltage and current regulated to 0.01%
3. X-ray tube	Philips 3 kW tungsten target tube operated at 60 kV and 35 mA.
4. Collimator	Fine (160 μ m) for Dy, Ho, Er, Yb and Lu Coarse (480 μ m) for Y.
5. X-ray path	Vacuum 0.5 torr
6. Detector	Flow proportional operating on 90% Ar + 10% CH ₄ gas for elements Dy, Ho, Er, Yb and Lu; Scintillation NaI (Tl) type for Y.
7. Pulse Height selection	For FPC; Base 300, Window 350 For S.C.; Base 200, Window 450.
8. Counting time	40s for Dy, Ho, Er, Yb and Lu 100s for Y.
9. Analysing Crystal	LiF(200). All elements in 1 order
10. Sample spinner	On

TABLE-II

ANALYTICAL LINES AND DETERMINATION RANGE FOR THE ANALYSIS
OF THULIUM OXIDE

Element	Line	2 θ angles degrees (LiF-200)	Wavelengths λ	Energy keV	Determination Range %
Dy	L_{α_1}	56.85	1.90881	5.494	0.005 - 1.0
Ho	L_{α_1}	54.67	1.84500	6.719	0.002 - 1.0
Er	L_{α_1}	52.7	1.78425	6.947	0.005 - 1.0
Yb	L_{α_1}	49.28	1.67189	7.414	0.01 - 1.0
Lu	L_{α_1}	47.57	1.61951	7.654	0.002 - 1.0
Y	K_{α}	23.82	0.83024	14.931	0.002 - 1.0

TABLE-III

MEAN NET COUNTS FOR STANDARDS

Standard %	Mean net counts					
	Dy	Ho	Er	Tb	Lu	Y
1.0	122,955	200,919	203,869	92,066	165,312	319,882
0.5	62,355	102,456	104,535	46,557	84,166	161,605
0.1	15,822	36,683	35,784	15,009	28,147	59,786
0.05	9,550	16,507	17,940	7,549	14,324	29,135
0.02	4,139	9,751	9,043	5,211	7,101	15,235
0.01	2,046	4,731	4,374	1,987	3,652	8,027
0.005	869	2,348	1,988	-	2,099	4,211
0.002	-	1,003	-	-	1,141	2,215

TABLE-IV

PERCENT STANDARD DEVIATION

<u>Standard</u> <u>%</u>	<u>Dy</u>	<u>Ho</u>	<u>Er</u>	<u>Yb</u>	<u>Lu</u>	<u>Y</u>
1.0	0.3	0.5	0.4	1.5	1.3	0.4
0.5	0.5	0.6	0.7	1.6	1.4	0.6
0.1	1.5	1.0	2.0	3.9	1.3	1.8
0.05	1.8	2.7	3.4	8.7	2.4	2.5
0.02	4.0	3.3	6.4	13.3	4.7	4.5
0.01	7.5	4.4	13.3	26.8	9.4	8.8
0.005	18.2	12.5	28.1	-	17.2	16.1
0.002	-	20.9	-	-	31.1	34.6

TABLE-V

THEORETICAL DETECTION LIMIT CALCULATIONS

Element	Net Counts* $N_p - N_b$	Blank counts N_b	$\frac{1}{N_p}$	$\frac{1}{N_b}$	TMDL ppm
Dy	9,550	17,647	132.8	398.4	20.9
Ho	16,507	18,826	137.2	411.6	12.5
Er	17,940	33,925	184.2	552.6	15.4
Tb	7,349	65,456	255.8	767.4	52.2
Lu	14,324	27,785	166.7	500.1	9.0
Y	29,135	23,961	154.8	464.4	8.0

* 500 ppm standard

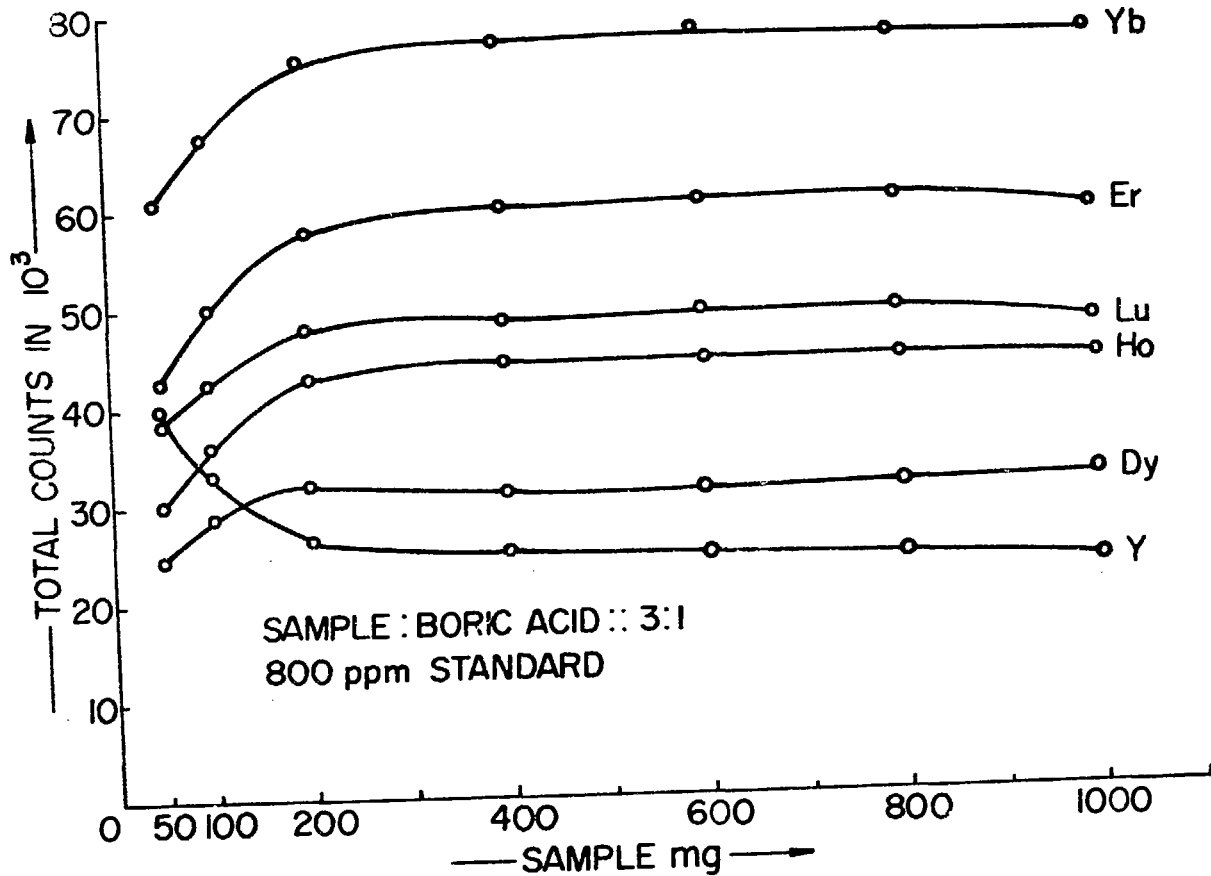


FIG. I. SATURATION THICKNESS STUDIES ON DOUBLE LAYER
 PELLETT OVER BORIC ACID

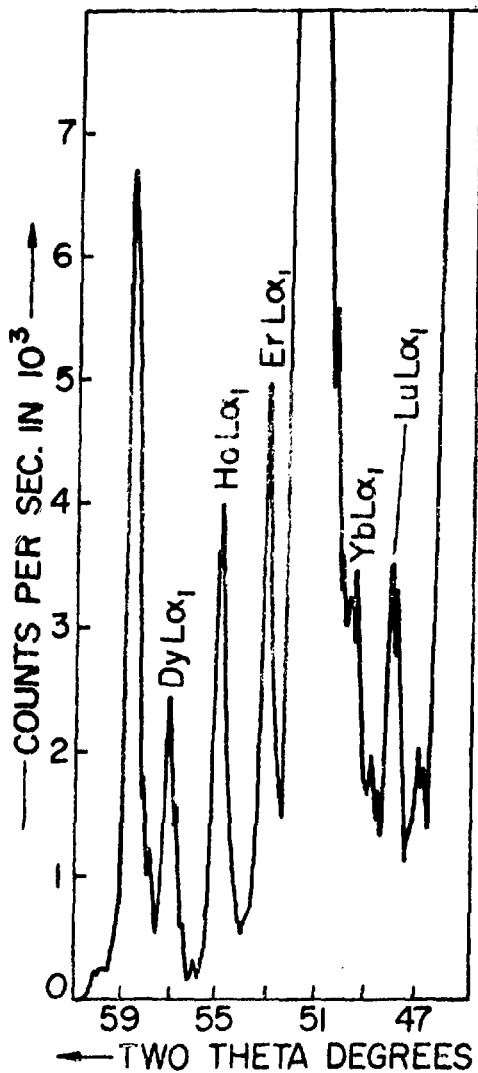


FIG. 2. STRIP CHART RECORD OF 1% IMPURITIES IN THULIUM OXIDE

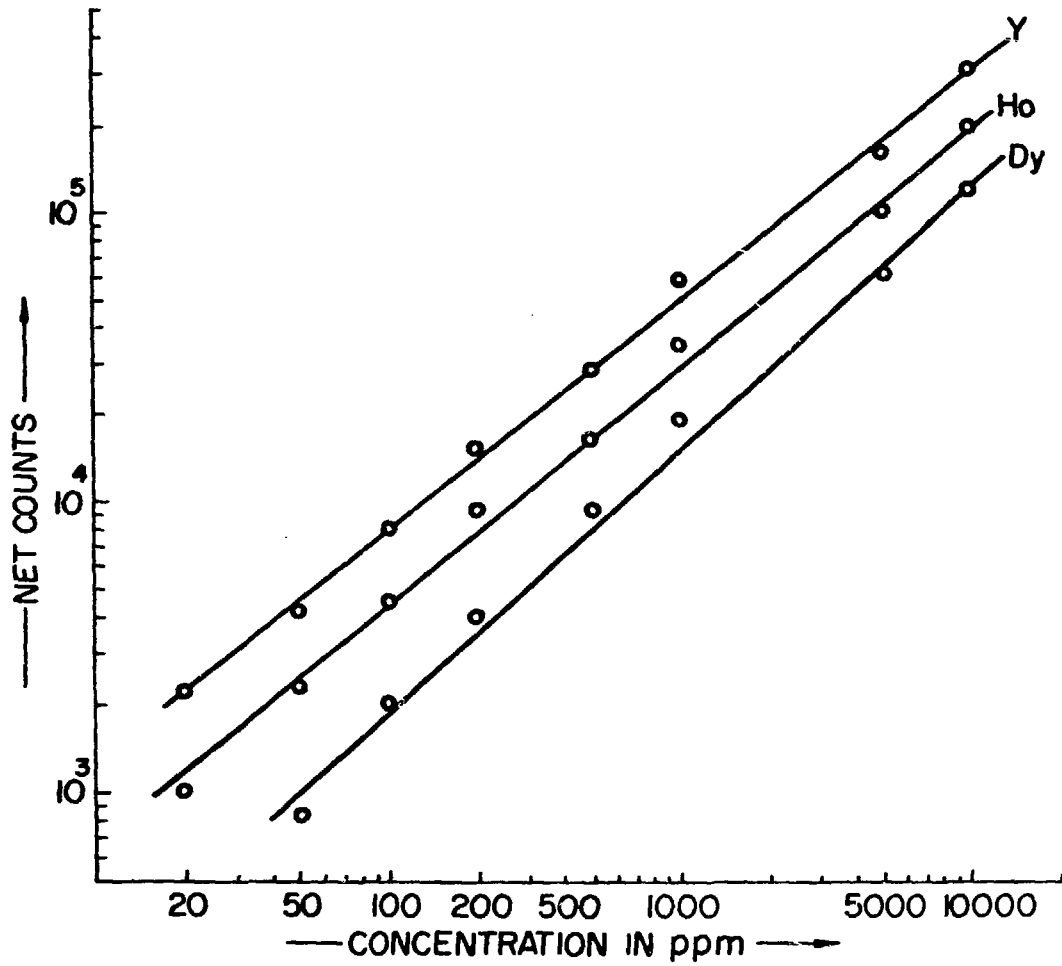


FIG.3. WORKING CURVES FOR Dy, Ho AND Y

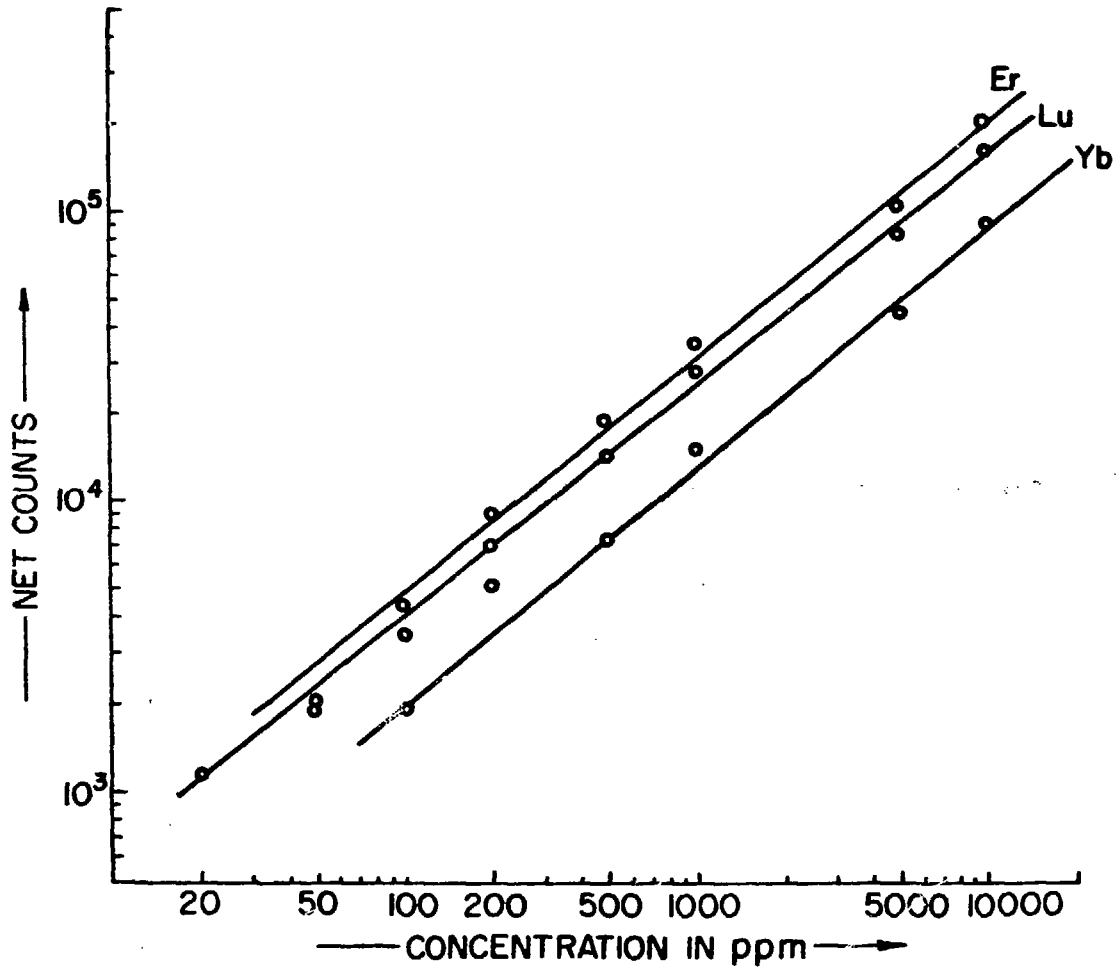


FIG. 4. WORKING CURVES FOR Er, Yb AND Lu

