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DETERMINATION OF RARE EARTH IMPURITIES IN PRASEODYMIUM OXIDE AND OXALATE BY X-RAY FLUORESCENCE TECHNIQUE

PURE praseodymium contains neighbouring elements lanthanum, cerium, neodymium and samarium in trace levels as impurities. Fassel *et al.*¹ have developed an optical emission spectrographic (OES) method for the determination of first three impurities. Radwan² and Murty³ have extended the OES analysis to all the four elements. In OES technique, even after the use of high resolving power spectrographs, the line overlaps between impurity lines and matrix lines are frequent because of the richness of the spectrum lines. On the other hand, in the X-ray fluorescence (XRF) technique, the analysis is simple since the number of lines in X-ray region is small and line overlaps are few. Using XRF, Lytle and Heady⁴ have reported a method for the determination of four rare earth impurities named above. They presented the oxide powder sample to the helium purged spectrometer and using fixed count method obtained a minimum determination limit (MDL) of 0.01%. To obtain this MDL they had to use long counting times of upto 600 seconds.

We have developed an XRF method for the determination of these impurities employing a vacuum path spectrometer and fixed time counting. The sample in our method is taken as an oxalate and presented to the X-ray instrument in the form of a 1¼" diameter double layer pellet. The double layer form of sample presentation has the advantage that the sample requirement is minimised while retaining the advantages of pelletising, *viz.*, presenting a reproducible surface of uniform density and similar geometry to the primary X-rays. Because of the improved form of sample presentation the required MDL was attained even with a small counting time of 100 seconds.

A Philips ultrastable generator PW 1140 is used to supply power to a Philips 3 kW tungsten target tube, operated at 60 kV and 35 mA, which supplies the

primary X-rays to irradiate the sample. The secondary X-rays generated in the sample are dispersed by a LiF (200) crystal in a Philips semi-automatic X-ray spectrometer PW 1220. Fine collimator (160 µm) is used for X-rays and the path is evacuated to a vacuum of 0.5 torr. The intensities of L_α lines of lanthanum, cerium and neodymium and L_{β1} line of samarium are counted for 100 seconds each by a flow proportional counter. The analysis lines used are found to be free from the interference of matrix lines of praseodymium. Under these conditions, the impurities can be determined in the range 0.01-1%.

Standards are prepared synthetically by adding impurity rare earth nitrate solutions to praseodymium nitrate solution. Five standards containing 0.01, 0.025, 0.1, 0.5 and 1% of each impurity in praseodymium oxide are prepared. These solution standards are precipitated by a saturated solution of oxalic acid. The precipitate is taken on a filter-paper and dried. 400 mg of dry oxalate is mixed with 400 mg of boric acid binding material. The mixture is ground in an agate mortar and pressed to form a 1¼" diameter pellet over a boric acid backing pellet.

The sample, if in oxide form, is converted to oxalate through its nitrate solution. The sample is then handled similar to standards.

The precision is calculated by evaluation of percent standard deviation (SD%) using the formula

$$SD\% = 100 (\sigma N_p^2 + \sigma N_b^2)^{1/2} / (N_p - N_b)$$

where

$$\sigma N_p^2 = \Sigma d_p^2 / n - 1$$

and

$$\sigma N_b^2 = \Sigma d_b^2 / n - 1.$$

In this formula Σd_p^2 and Σd_b^2 represent the sum of the squares of differences of individual peak counts from mean of replicate measurement of peak counts (N_p) and individual background counts from mean of replicate measurement of background counts (N_b) respectively. 'n' represents the total number of values taken for calculations which was 15 in our case. From our calculations it is found that standard deviation is concentration dependent; precision being better at higher concentrations. The SD% values for each element and various concentrations are given in Table I.

The theoretical minimum detection limit (TMDL) defined as the concentration discernible above the background radiation N_b is calculated on three sigma basis using the formula

$$TMDL = 3 \sqrt{N_b} \times \text{concentration/net counts.}$$

The TMDL calculations and their values are given in Table II.

TABLE I
Precision

Sl. No.	Standard %	Per cent		Standard Deviation	
		La	Ce	Nd	Sm
1	1.0	0.98	0.35	0.51	0.16
2	0.5	1.03	0.69	0.74	1.7
3	0.1	3.4	7.7	2.5	7.8
4	0.025	17.1	7.0	9.1	7.7
5	0.01	42.0	37.4	21.1	25.7

TABLE II
Theoretical minimum detection limits (TMDL)

Sl. No.	Element	Back-ground counts N_b	$\sigma = \sqrt{N_b}$	3σ	*Net counts for 100 sec.	TMDL ppm
1	La	9,430	97	291	2,239	32.5
2	Ce	19,419	139	417	3,575	29.2
3	Nd	32,052	179	537	6,148	21.8
4	Sm	25,652	160	480	3,375	35.6

* Net counts are for 250 ppm standard.

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MESOMORPHIC BEHAVIOUR OF SOME NAPHTHALENE SCHIFF BASES: 4-*n*-ALKOXY-1-NAPHTHYLIDENE-*p*-*n*-BUTOXYANILINES

MESOMORPHISM is exhibited mainly by compounds with relatively rigid, polar, rod-shaped molecules that tend to be oriented with their long axes parallel because of the intermolecular attractive forces. It is generally found that nematic compounds have high melting points, because, the molecular characteristics that are necessary for nematic mesomorphism, also produce stable crystalline lattices. For practical applications

nematic mesophases which exist near room temperature are desirable. Pure low melting mesomorphic compounds can be prepared by the introduction of dissymmetry in the molecule or by the introduction of lateral substitutions in the molecule.

The introduction of a naphthalene nucleus into a potentially mesomorphic compound should affect its mesomorphic behaviour considerably. Dave *et al.* have observed that the introduction of a 1, 4-substituted naphthalene nucleus considerably reduces the mesomorphic properties of the compounds.^{1,2} To further investigate this phenomenon, the following Schiff base compounds of the series 4-*n*-alkoxy-1-naphthylidene-*p*-*n*-butoxyanilines have been synthesized by condensing various 4-*n*-alkoxy-1-naphthaldehydes¹ with *p*-*n*-butoxyaniline³. The mesomorphic properties of these compounds have been investigated under a Leitz Ortholux Polarizing Microscope, equipped with Leitz heating stage. The melting points and transition temperatures of these compounds are given in Table I. The combustion analysis for C, H and N for these compounds agree well with their calculated values.

TABLE I

Compound	Alkyl Group	Solid-nematic	Nematic-Isotropic or Solid-Isotropic	
1	CH ₃	..	91.0	
2	C ₂ H ₅	(70.5)	88.0 ^a	84.0 ^b
3	C ₂ H ₇	(56.5)	80.0	
4	C ₄ H ₉	(70.5)	87.5	
5	C ₅ H ₁₁	(61.5)	80.0 ^a	74.0 ^b

Figures in parenthesis indicate monotropy.
a, stable modification.
b, metastable modification.

The compound No. 1 is non-mesomorphic; the rest are monotropic nematic in nature. Compounds No. 2 and 5 exhibit two solid modifications. The metastable solid modification C_{II} is obtained by a sudden cooling of the isotropic liquid. Both the solid forms on heating give the isotropic liquid. The metastable solid modification melts at a lower temperature than the stable solid modification C_I. In both the cases the isotropic liquid cools to give a monotropic nematic phase. These can be represented as follows in Fig. 1.

The non-mesomorphism of compound No. 1 can be attributed to its relatively high melting point. It is observed that the melting points and transition temperatures of these compounds are higher than the corresponding members of the series 4-*n*-alkoxy-1-