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OF NEODYMIUM IN LASER GLASSES**

G. R. Haugen
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September 19, 1974

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SPECTROPHOTOMETRIC DETERMINATION OF NEODYMIUM IN LASER GLASSES

Abstract

A procedure has been developed to determine the neodymium in laser glasses. The method is based on the ionic absorption of Nd (III) in perchloric acid at 795.5 nm. Samples containing 0.3 to 6 wt% neodymium may be analyzed with a relative accuracy and precision of 1.12%. The method is applicable to a variety of glass formulations. Among the few interferences are Dy (III), Er (III),

and Tm (III), which are not commonly present in laser glasses. The use of internal standards and reiterative regression analysis to obtain the extinction coefficient of Nd (III) in solutions of glasses improves the accuracy and precision of the method. Statistical analysis of the results of 22 glass samples representing several glass formulations are presented.

Introduction

The Laser Fusion Research Program at this Laboratory requires the analysis of several types of laser glasses for neodymium in the 0.3 to 6% concentration range, with a relative accuracy of $\pm 3\%$. The major constituents of the silicate glasses are SiO_2 , Al_2O_3 , CaO , La_2O_3 , Nd_2O_3 , and various alkali and alkaline metal oxides. The minor constituents are Fe_2O_3 , CeO_2 , and various doping or fining agents such as molybdenum and antimony. The major constituents of the phosphate glasses are P_2O_5 , alkali and alkaline metal oxides or fluorides, Nd_2O_3 , and various other metal oxides (ZnO , Al_2O_3 , La_2O_3). Evaluating methods for determining neodymium in this type of matrix showed nondestructive methods such as x-ray fluorescence and photoluminescence to be unsuitable on several counts: it is difficult to prepare stand-

ards and reproduce surfaces, cerium and other heavy elements tend to interfere, and changes in the matrix usually require a new set of standards.

Chelometric titration methods are suitable for determining rare earths at the levels and accuracy required.¹ However, the methods are nonspecific, determining total rare earths in the +3 oxidation state. As an example, Ce (III) would be titrated along with Nd (III), while Ce (IV) would interfere by oxidizing the indicator and require quantitative conversion of all cerium to Ce (III). A correction would then have to be made based upon an independent determination of cerium. In addition, other metals interfere in the titration, requiring both acidic and basic separation steps to isolate the rare earth elements, i.e., calcium, and aluminum.²

Several spectrophotometric methods have been developed for determining rare earth elements. Some of these methods use an organic reagent to form an intense color with rare earths and hence increase the sensitivity so that microgram quantities can be determined. These methods are nonspecific because the reagents usually react with all of the rare earths, which exhibit overlapping spectra. The ionic absorption spectra of Nd (III) in perchloric acid solution, however, appeared to offer suitable accuracy and

specificity to determine neodymium in the presence of other metal ions. The only interferences at the 795.5-nm absorption band of neodymium are reported to be dysprosium, erbium, and thulium,³ which were not constituents in the laser glasses under investigation. Therefore, studies were conducted to develop sample pretreatment and measurement techniques for the assay of neodymium based upon the ionic absorption of Nd (III) at 795.5 nm.

Experimental

APPARATUS AND EQUIPMENT

A Cary Model 14³ dual beam recording spectrophotometer was used with a strip chart recorder in all spectral studies. The recorder was equipped with two slide wires, to give full-scale deflection from 0 to 0.2 and 0 to 2 absorbance units. The 0-to-0.2 slide wire was used for all solutions having absorbance ≤ 0.2 units.

A matched pair of 2- or 5-cm path length sample cells with quartz windows was used in all measurements; calibrated pipettes were used for measuring sample and standard neodymium solutions.

REAGENTS

Reagent grade chemicals and deionized

water were used to prepare mockup and standard solutions.

Standard neodymium solutions were prepared from laboratory purified commercial Nd_2O_3 (American Potash and Chemical Corp. Code 629.9), containing less than 0.1% other rare earths, as follows: 1 to 2 g of Nd_2O_3 was dissolved in 10 to 20 ml of 6 M HCl, diluted to about 150 ml with deionized water, and precipitated with about 25 ml of 10% solution of oxalic acid. The resultant neodymium oxalate precipitate was collected on ashless filter paper (Whatman No. 40) and washed with a 1% oxalic acid solution. The precipitate was transferred to a tared platinum crucible, heated slowly to 900°C, and maintained at 900°C until it remained at a constant weight. The resultant Nd_2O_3 was dissolved in 20 ml of 11.6 M HClO_4 and quantitatively transferred to a 250-ml volumetric flask with water to yield an approximately 1-M- HClO_4 solution. The neodymium concentration was calculated using

³Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Atomic Energy Commission to the exclusion of others that may be suitable.

0.8574 as the gravimetric factor for Nd/Nd₂O₃.

The concentration of the standard neodymium solution was further verified by titrating aliquots with a standard solution of ethylene-diamine-tetra acetic acid (EDTA).¹ Aliquots of the neodymium solution were pipetted into a flask containing about 40 ml of water, 3 to 5 drops of pyridine added, and the solution adjusted to, and maintained at, pH 5.5 to 6.5 with NH₄OH and HCl. Two drops of 0.5% arsenazo indicator were added and the solution titrated with EDTA to the end point, indicated by a sharp color change from purple to orange. The concentration of neodymium obtained by the titration agreed with the gravimetric calculation to within ±0.2% in several trials. Aliquots of the standard solutions were taken to mockup glass solutions for spectral curves and for preparing calibration curves.

RECOMMENDED PROCEDURE FOR SAMPLE DISSOLUTION AND PRETREATMENT

Slice the glass into thin wafers (~2- to 3-mm thick) and score with a diamond-point marker to facilitate fracturing into small fragments. Clean first with water, then with absolute methanol. Place about 2 to 5 g (depending upon the nominal neodymium content) in a mortar and pound into a coarse powder with a pestle; to minimize the introduction of impurities from the mortar and pestle, do not grind. Weigh five portions of the powdered sample, each containing 10 to 25 mg of neodymium. Add aliquots of standard Nd (III) solution containing about 3, 6,

and 9 mg of neodymium to three of the sample replicates for internal calibration. Add 5 to 10 ml of concentrated HClO₄ and 4 to 5 drops of 48% HF solution; heat on a moderately warm hot plate. Continue to add 4 to 5 drops of HF every 3 to 5 min until the glass dissolves. Add 1 ml of HF, 1 ml of concentrated HNO₃, and continue heating until the HF is evaporated and strong fumes are given off; repeat this step at least three times. Finally, heat until the excess HClO₄ is evaporated (final volume of ~2 ml). Cool and transfer to a 25-ml volumetric flask with 1 M HClO₄. Transfer about 25 ml of each replicate to 25-ml screw cap centrifuge tubes and centrifuge for 15 min at 2700 rpm. Prepare a set of standard Nd (III) solutions with a neodymium concentration ranging from 0.1 to 1.8 mg/ml in 1 M HClO₄.

ABSORBANCE MEASUREMENT

Measure the absorbance of the standard solutions against a 1-M-HClO₄ blank at 795.5 nm in optical cells with 2- or 5-cm path lengths. Measure the absorbance of the samples against a reagent blank solution processed in the same manner as the standards. A first approximation of the neodymium content of the samples may be obtained by directly comparing the absorbance of the samples to that of the standards. However, the extinction coefficient of Nd (III) in the glass sample matrix is about 2 to 6% lower than in the standard solutions, and varies with variation in the glass composition; therefore, for highest accuracy, the data should be treated by regression analysis.

Results and Discussion

EVALUATION OF THE PROCEDURE

Standard solutions of Nd (III) in 1 M HClO_4 conform to Beer's law over the range of 0.1 to 1.8 mg of neodymium per milliliter. Spectral curves of a trial ED-2 glass and a laboratory prepared mockup glass solution both exhibited a wavelength-independent light scattering that slowly decreased with time. This is apparently owing to traces of silicates, even though the HF-HClO_4 dissolution procedure was expected to remove all silicates by volatilization. Centrifuging the solutions before measuring the absorbance eliminates the light scattering, and then the absorbance of the solutions remains constant indefinitely.

INTERNAL STANDARDS

The apparent extinction coefficients of samples and prepared standards may differ slightly because of differences in matrix and instrumental conditions. Optimum conditions for instrumental non-truncation of the peak height requires the bandwidth of the instrument to be equal to or less than one-tenth of the natural bandwidth of the absorbing species.⁴ However, in the red region of the spectrum, the instrumental bandwidth increases for a fixed signal-to-noise ratio as a consequence of reduced detector sensitivity. Peak-height truncation is most pronounced with slight slit-width changes in this region. Variations in the apparent extinction coefficient due to instrumental effects or to differences in the solution matrix, where there is no interfering

absorbing species, can be compensated for by the standard addition technique.

DATA PROCESSING

Reiterative linear regression analysis of absorbance vs concentration was used to determine the best fit least-squares equations for calculating the neodymium concentration in the glass samples.⁵ First, the extinction coefficient was determined in standard solutions and used to find the first approximation of the extinction coefficient for neodymium in the sample solutions. The regression coefficient between the standard and sample coefficients was determined; then new extinction coefficients were calculated until the regression coefficient approached 1.0, using internal standards to reveal differences between the standard solution and samples.

Equation (1) was used to calculate the coefficient of standard solutions.

$$\text{OD}_u = \text{OD}_B - \beta_0 + \beta_1 \frac{\epsilon \ell}{V_D} C_s V_s \quad (1)$$

where

OD_u = optical density of the neodymium solution

OD_B = optical density of the blank

β_0 = absorbance at zero concentration, regression coefficient representing the intercept

β_1 = regression coefficient, set to = 1 for the standards

ϵ = extinction coefficient of the neodymium standard solution

C_s = amount of neodymium in the standard solution in milligrams

V_s = volume of the standard solution in milliliters

l = path length of cell in centimeters

V_D = final volume of the sample solution in milliliters

Four mockup solutions were analyzed and yielded the following results,

intercept: -1.2×10^{-4}

extinction coefficient: $0.05073 \pm 1.6 \times 10^{-4}$

correlation coefficient: 0.99984

standard deviation: $\pm 3\%$ relative

A plot of this data is shown in Fig. 1.

Fig. 1. Composite calibration curve for Nd (III) in four mockup glass samples in 1 M HClO_4 . The slope, equal to the extinction coefficient, is $0.05073 \pm 1.6 \times 10^{-4}$ ml/mg cm. The circle encompasses four mockup standards.

Equation (1) was rewritten to show the relationship between the optical densities of internal standards and glass samples, as shown in Eq. (2).

$$\text{OD}_u - \text{OD}(W_G = 0) = \frac{\epsilon l}{V_D} W_G \beta_0 + \frac{\epsilon l}{V_D} C_s V_s \beta_1, \quad (2)$$

where

OD_u = optical density of the sample

$\text{OD}(W_G = 0)$ = optical density of the blank

ϵ = extinction coefficient of the neodymium standard solutions

l = path length of the cell in centimeters

V_D = final volume of the sample solution in milliliters

C_G = milligrams of neodymium per gram of glass sample

W_G = weight of glass in grams

V_s = volume of neodymium standard added in milliliters

β_0 = regression coefficient representing the amount of neodymium in the glass sample, C_G

β_1 = regression coefficient (would = 1 if no change in ϵ between standards and samples).

The coefficients found for a typical glass sample were:

$$\beta_0 = 25.82090 \pm 0.03755 \text{ with a correlation coefficient of } 0.93571$$

Fig. 2. Optical density per gram of laser glass vs the extinction coefficient. (a) Estimated from standard calibration curve. (b) Calculated from internal standards.

$\beta_1 = 0.96388 \pm 0.00257$ with a correlation coefficient of 0.76289.

A plot of this data is shown in Fig. 2a. Note that the coefficient β_1 would be 1.000 if the extinction coefficient for the sample were the same as for standard solutions. Differences arise because a lower coefficient is obtained from the standard solutions; an estimate of the new coefficient, ϵ_1 , is then obtained. Replacing ϵ with ϵ_1 in Eq. (2) and recalculating, we obtain:

$\beta_0 = 26.78850 \pm 0.03896$ with a correlation coefficient of 0.93571

$\beta_1 = 1.0000 \pm 0.00267$ with a correlation coefficient of 0.76239 and a multiple correlation coefficient between the standards and the glass samples of 0.99991.

A plot of the recalculated data is shown in Fig. 2b. The multiple correlation coefficient shows that it is a good fit.

The variance for the slope and intercept of a linear least-squares model are given by

$$\frac{\sigma^2}{\left[\sum_{i=1}^m (X_2 - \bar{X})^2 \right]}$$

and

$$\left(\frac{\sigma^2 \sum_{i=1}^m X_2^2}{\left[\sum_{i=1}^m (X_2 - \bar{X})^2 \right]} \right),$$

respectively. The symbol X_2 represents the independent variable and σ^2 the variance of the random error associated with the dependent variable. To minimize the variance in the slope of a linear model, the independent variable should have the maximum range physically permissible.

Yet, minimizing the variance in the intercept of a linear model requires using the largest possible number of values of the independent variable and selecting these values so that their mean is as near zero as possible. These conditions are not compatible with the requirements for minimum variance of the slope. However, by rearranging Eq. (2) to remove the contribution of the second term, we can eliminate the conflict:

$$\begin{aligned} OD_u - OD(W_G = 0) &= (\epsilon_i \pm V_G C_S) / V_D \\ &= \frac{\epsilon_i \pm W_G}{V_D} \beta_0 \end{aligned} \quad (3)$$

A plot of this data is shown in Fig. 3.

The value for β_0 is 26.78847 ± 0.03398 with a correlation coefficient of 0.99983.

Fig. 3. Optical density per gram of laser glass minus the optical density contributed by internal standards vs the optical density contributed by glass.

RESULTS OF SAMPLE ANALYSIS

The precision of the method was established by analyzing 12 wafers of one ED-2,3 glass sample. Replicates of each wafer were taken and the absorbance measurement treated by the regression analysis described above. The relative standard deviation and 95% confidence limit were 1.12% and 2.47%, respectively. The results are shown in Table 1.

Table 1. Analysis of a typical ED-2,3 laser glass for neodymium confidence limits calculated by using the student t-distribution.

Sample	Wt% Nd ₂ O ₃ glass	Standard deviation	No. of points	95% confidence
1	3.090	±0.013	10	±0.029
2	3.117	±0.008	10	±0.018
3	3.138	±0.008	10	±0.018
4	3.146	±0.011	10	±0.025
5	3.152	±0.009	15	±0.019
6	3.025	±0.014	2	±0.178
7	3.123	±0.013	10	±0.029
8	3.087	±0.013	8	±0.031
9	3.135	±0.008	10	±0.018
10	3.122	±0.012	10	±0.027
11	3.137	±0.010	10	±0.023
12	3.297	±0.006	18	±0.013
Mean	3.115	±0.035	12	±0.077

Twenty-two glass samples representing various types of laser glass were then analyzed. A reiterative linear regression analysis of the data was used to determine the regression coefficients for Eqs. (2) and (3) (see Table 2). The mean relative standard deviation and 95% confidence limit for determining the neodymium content of these glasses were 0.36% and 0.83% respectively. These results are shown in Table 3.

Table 2. Linear regression coefficients.

Glass type	ϵ_i^a	σ_i^a	$E_{q,(2)}^b$			$E_{q,(3)}^b$		
	(ml/cm)	(ml/cm)	β_0	σ_0	γ_0	β_0	σ_0	γ_0
ED-H	0,05049	0,00037	27,82455	0,03823	0,98279	27,82479	0,03464	0,99999
AO-36C9	0,04925	0,00070	42,28157	0,19813	0,96519	42,28176	0,16891	0,99994
S-33	0,04945	0,00067	37,66153	0,18596	0,95556	37,66181	0,16236	0,99993
LSG-91H	0,04739	0,00096	25,61036	0,22584	0,93903	25,61012	0,19973	0,99976
AO-2828	0,04771	0,00061	25,69907	0,09551	0,96456	25,69889	0,08675	0,99995
LSG-91	0,04657	0,00100	26,49440	0,18985	0,96526	26,51310	0,16285	0,99959
ED-2,6	0,05050	0,00071	49,60713	0,12669	0,98757	49,60213	0,11348	0,99988
ED-2,3	0,04889	0,00029	26,55444	0,05344	0,95458	26,55598	0,04772	0,99995
ED-2,2	0,04803	0,00030	17,24723	0,05002	0,93517	17,24725	0,04273	0,99989
ED-2,1	0,04920	0,00059	8,71578	0,08332	0,89736	8,71553	0,08191	0,99884
ED-2,3	0,04890	0,00021	26,78850	0,03896	0,93571	26,78849	0,03398	0,99983
EK-2460	0,04655	0,00051	18,98982	0,07071	0,95872	18,99023	0,06175	0,99996
VY10R NBS1	0,04845	0,00034	7,25806	0,17656	0,52378	7,25810	0,15990	0,99758
VY10R NBS2	0,04947	0,00021	3,32229	0,07205	0,42230	3,32227	0,06809	0,99541
KIGRE B-1	0,04922	0,00036	38,18951	0,06624	0,97767	38,18951	0,06230	0,99997
CaF ₂	0,04896	0,00022	26,92969	0,05002	0,94933	26,92969	0,04500	0,99998
EK-2182	0,04711	0,00013	9,84181	0,01805	0,86661	10,59709	0,01540	0,99997
EK-2172	0,04824	0,00021	2,70139	0,03605	0,59022	2,84083	0,03485	0,99745
EK-2499	0,04782	0,00026	16,63935	0,04639	0,90524	17,63091	0,04915	0,99990
P-100	0,04889	0,00024	20,11719	0,04322	0,93978	20,87624	0,04149	0,99996
P-107	0,04883	0,00018	19,70473	0,05516	0,86478	20,46987	0,05308	0,99594
M-679	0,05036	0,00047	27,94162	0,06308	0,97375	28,14483	0,06143	0,99995

^a ϵ_i and σ_i are the internal extinction coefficient and its standard deviation, respectively.

^b β , σ , and γ represent the regression coefficient, standard deviation of the coefficient, and correlated coefficient, respectively.

Table 3. Total Nd_2O_3 concentration in glass.

Glass type	No. of points	Weight % ^a	Standard deviation	95% confidence region ^b
ED-2-H	6	3.245	± 0.004	± 0.010
AO-3669	5	4.932	± 0.020	± 0.056
S-33	5	4.393	± 0.019	± 0.053
LSG-91H	5	2.987	± 0.023	± 0.064
AO-2828	5	2.997	± 0.010	± 0.028
LSG-91	12	3.092	± 0.019	± 0.042
ED-2.6	23	5.786	± 0.013	± 0.027
ED-2.3	18	3.097	± 0.006	± 0.013
ED-2.2	19	2.912	± 0.005	± 0.011
ED-2.1	17	1.026	± 0.005	± 0.011
ED-2.3	103	3.125	± 0.004	$\pm 0.008^c$
EK-2460	5	2.215	± 0.007	± 0.019
VY10R NBS1	6	0.847	± 0.019	± 0.048
VY10R NBS2	12	0.388	± 0.008	± 0.017
KIGRE B-1	14	4.454	± 0.007	± 0.016
CaF_2	8	3.757	± 0.006	± 0.0148
EK-2182	5	1.236	± 0.002	± 0.0049
EK-2172	5	0.331	± 0.004	± 0.0096
EK-2499	5	2.056	± 0.006	± 0.0134
P-100	5	2.435	± 0.005	± 0.0113
P-107	5	2.388	± 0.006	± 0.0146
M-679	5	3.283	± 0.007	± 0.0169

^aWt% of Nd_2O_3 , except for CaF_2 where it is reported as wt% NdF_3 .^bCalculated from t-distribution, except as noted.^cCalculated from normal distribution.

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