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PREPARATION OF NEODYMIUM ACETATE FOR USE IN NUCLEAR AREA AND NANOTECHNOLOGY

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ABSTRACT

Neodymium and its compounds are being increasingly applied in the manufacture of new materials. In nuclear area neodymium isotopes are used in a variety of scientific applications. Nd-142 has been used to produce short-lived Tm and Yb isotopes. Nd-146 has been suggested to produce Pm-147 and Nd-150 has been used to study double beta decay. Due to the several modern applications using nanomaterials, more and more highly rare earth compounds have been demanded. The researches at IPEN uses the experience gained in rare earth separation for the preparation of some pure acetates, purity > 99.9% for application in nanotechnology research. A simple and economical chemical process to obtaining neodymium acetate of high purity is studied. The raw material in the form of mixed rare earths carbonate comes from Brazilian monazite. It is used the technique of strong cationic exchange resin, proper to water treatment, to the neodymium's fractionation and it is achieved a purity of 99.9% in Nd_2O_3 and yield greater than or equal 80%, with the elution of rare earths by EDTA solution in pH controlled. The complex of EDTA-neodymium is transformed in neodymium oxide, subsequently the oxide is dissolved in acetic acid to obtain the neodymium acetate. The solid salt was characterized via molecular absorption spectrophotometry, mass spectrometry, thermal analysis, chemical analysis and X ray diffraction. In summary the analytical data collected allowed to conclude that the stoichiometric formula for the neodymium acetate prepared is $Nd(CH_3COOH)_3.1.5H_2O$.

1. INTRODUCTION

Monazite is a heavy mineral composed of phosphates of rare earths (cerium, lanthanum, neodymium, praseodymium, samarium and heavy rare earth), uranium, thorium and silicon crystallized in the monoclinic system, has a hardness of between 5 and 5.5 on the Mohr scale and density 5.1 $g.cm^{-3}$. In general, the monazite is yellowish, reddish-brown or red. Monazite occurs as accessory constituent of some granites, gneisses, pegmatites and the sands coming from the decomposition of these rocks [1]. The world's largest deposits are in Brazil and India. In Brazil, it is possible to find monazite in river beds of the states of Bahia, Minas Gerais, Goias and Mato Grosso and the beaches of the coast of Bahia, Espirito Santo and Rio de Janeiro that may contain from 25 to 30% of monazite. The other minerals are quartz, zircon, ilmenite, magnetite and rutile [2].

The story of the discovery of rare-earths points to the difficulty of separating the various elements through chemical processes. The procedure for the separation of neodymium to obtain pure acetate was carried out using the raw material from a process of separation of uranium, thorium and rare earths in monazite using fractional precipitation and ion exchange techniques to obtain high purity neodymium oxide and in the analytical control the determination of trace elements by the mass spectrometry technique, based on the separation of atoms because of their weight difference provides an effective means for determining the relative abundance of each of elements, even when present in extremely small quantities and molecular absorption spectrophotometry for the determination of neodymium content in each fraction. At IPEN - CNEN/SP, researchers explore the separation of rare-earths to meet domestic demand in areas of research and development [3-15].

2. EXPERIMENTAL

2.1. Starting Raw Materials

A representative sample of the low cerium carbonate (LCC) was used. Its chemical composition is shown in Table 1. Nitric acid, acetic acid, ammonium salt of ethylene diamine tetra acetic acid (EDTA) and other reagents were of analytical grade. The solutions of RE (rare earth) nitrates were prepared by the dissolution of LCC in nitric acid. The solutions of RE nitrates at 10-15 g RE_2O_3 L^{-1} were filtered to separate small amounts of residues.

Table 1: Composition of Low Cerium Carbonate (LCC) Concentrate

Constituent	%	Constituent	%
La_2O_3	42-47	Y_2O_3	1-3
CeO_2	3-7	Ca O	4-5
Pr_6O_{11}	5-6	SiO_2	0.3
Nd_2O_3	30-34	U_3O_8	n. d.
Sm_2O_3	4-5	ThO_2	n. d.
Gd_2O_3	2-4		

Analysis by X-Ray fluorescence. n. d. denotes not detected.

2.2. $Nd_2O_3 \geq 90\%$ Purity. Ion Exchange 1 – Stage 1

The strong cationic exchanger S-100, produced by Bayer Co. in 50–100 mesh was used in this investigation. This resin is commonly used for water purification and freely available in Brazil. The solutions of RE nitrates at 10-15 g (RE_2O_3) L^{-1} were passed continuously through a column system filled with the resin and subsequently rinsed with deionized water. The RE elements loaded in the resin were eluted with ammoniacal EDTA solution (0.005 M to 0.010 M) at pH 3.5-4.0. The eluate was collected in fractions, precipitated as oxalates and then converted to oxides, by calcining at 900°C (1-4h). The ion exchange system was built with three columns; 300cm in height and 12 cm in diameter connected in series. The system could handle 10 kg of rare earth oxides, in total. This set up produced an eluate from which it was possible to obtain neodymium oxide greater than 90-95% purity with an 80% yield.

2.3. Neodymium Purification – Ion Exchange 2- Stage 2

The neodymium oxide obtained using the procedure described Fig. 1, was refined further by using the same strong cationic resin in an ion exchange system comprised of five columns; 100 cm in height and 5 cm in diameter, connected in series.

The feed neodymium nitrate solution for this stage was prepared by dissolving of 90-95% pure neodymium oxide produced in the previous stage in nitric acid 50°C. The required dilution was made to obtain neodymium nitrates of 10-15 g (Nd_2O_3) L^{-1}. The resin was loaded with approximately 200 g RE_2O_3 (the maximum loading capacity of the system was 500 g R_2O_3). As in the previous stage, the loaded resin was eluted with EDTA 0.01 mol. L^{-1} at pH 3.5 - 4.0. A final neodymium oxide with purity higher than 99.9% was obtained.

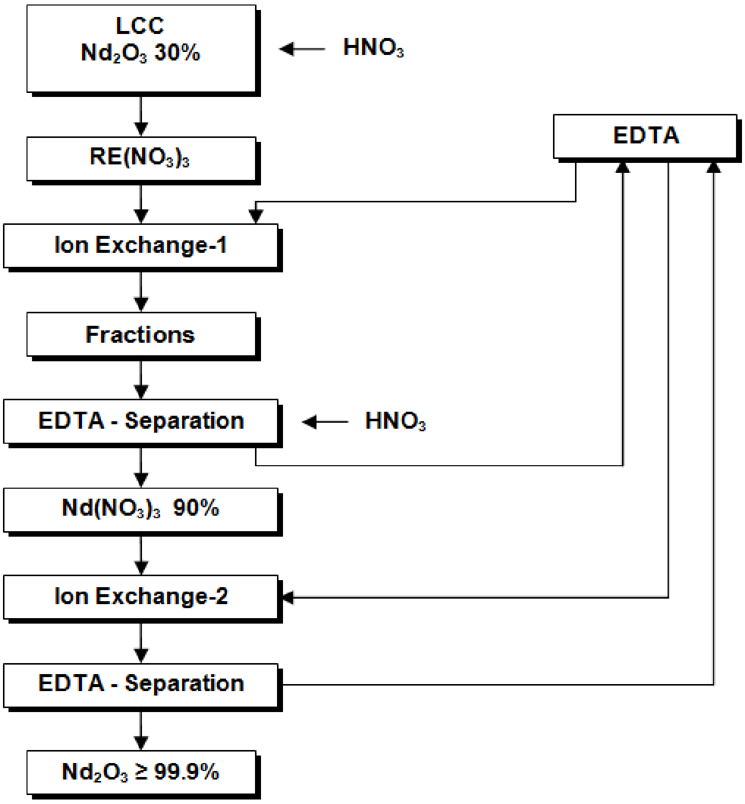

Figure 1: Procedure for the preparation of pure neodymium oxides

2.4. Obtaining neodymium acetates of high purity - Stage 3

For the preparation of neodymium acetates of high purity, the neodymium oxide with higher than 99.9% purity prepared here was used. The experimental procedure was such that the neodymium oxide was added over the acetic acid. The mixture was stirred continuously until complete dissolution was achieved. After concentration of the solution by evaporation the crystals of neodymium acetates were obtained.

3. RESULTS AND DISCUSSION

3.1. Analytical control of the process – stage 1 and stage 2

Molecular absorption spectrophotometry and sector field inductively coupled plasma mass spectrometry (SF ICP-MS), Element, from Finnigan MAT (Bremen, Germany), was used to insure the quality of the neodymium oxide obtained [13,14].

3.1.1. Characterization of the high pure neodymium acetate prepared

Table 2 shows values of REE found as impurities in the neodymium acetates. Table 3 shows values of metals impurities.

Table 2: Impurities of others rare earths found in neodymium acetates.

Element	Samples [(a)]
Y	0.9 +/- 0.2
Sc	5.1 +/- 0.2
La	1.0 +/- 0.8
Ce	6.1 +/- 0.7
Pr	34.40 +/- 0.80
Nd	------------------
Sm	12.80 +/- 0.80
Eu	1.10 +/- 0.90
Gd	15.40 +/- 0.40
Tb	29.30 +/- 0.50
Dy	5.20 +/- 0.50
Ho	7.40 +/- 0.10
Er	14.6 +/- 0.7
Tm	0.3 +/- 0.1
Yb	2.5 +/- 0.6
Lu	1.0 +/- 0.5

[(a)] (μg g^{-1}) +/- σ (standard deviation calculated for n=5)

Table 3: Metallic impurities (µg/g) in the high pure neodymium acetate

Element	Samples [(a)]	Element	Samples [(a)]
B	0.96+/- 0.2	Mo	1.70+/- 0.5
Tl	0.80+/- 0.1	Pd	2.60+/- 0.5
V	0.96+/- 0.2	Sn	2.80+/- 0.4
Cr	1.40+/- 0.1	Cd	3.90+/- 0.2
Mn	2.84+/- 0.2	Sb	2.80+/- 0.2
Fe	52.80 ± 0.50	Pb	2.80+/- 0.2
Co	2.90+/- 0.41	Bi	3.00+/- 0.9
Ni	8.30+/- 0.55	Th	2.20+/- 0.4
Cu	4.50+/- 0.12	U	3.00+/- 0.4
Zn	5.90+/- 0.2		
Sr	1.80+/- 0.2		
Nb	7.40 +/- 0.10		

(a) (μg.g^{-1}) +/- σ (standard deviation calculated for n=5)

3.1.2- Elemental analysis

The carbon and hydrogen content in the acetate samples was determined by an element analyzer (CHN) using the equipment Elemental Analyzer-2400, Perkin Elmer, Table 4 shows values [14].

Table 4: Elemental analyses of C, H and Nd for Neodymium acetate prepared.

Compound	Calculated (%)			Experimental (%)		
	C	H	Nd	C	H	Nd
$Nd(CH_3COO)_3.1.5H_2O$	20.68	3.47	41.40	20.50	3.40	41.00

The percent calculated and experimentally obtained for the neodymium acetate hydrate prepared here from the TG and DTG analyzes are shown in Table 5[14].

Table 5: Elemental and water assay for the neodymium compound.

Compound	$Nd(CH_3COO)_3.xH_2O$	H_2O		Atmosphere
$Nd(CH_3COO)_3.xH_2O$	x	calc.(%)	exp.(%)	N_2
	1.5	7.75	7.80	

calc.(%): calculated (%), exp.(%) :experimental(%)

3.1.3. Thermal characterization (TG/DTG) of neodymium acetate

Samples of highly pure neodymium acetate were submitted to thermal analysis for their characterization. The equipment used it was a Shimadzu TGA-50H equipment consisting of a microbalance with continues recording, an oven and a device for gas work. The samples were analyzed under dynamic atmosphere of synthetic air with a flow of 50 $mL.min^{-1}$ and heating rate of 10 $^0C.min^{-1}$ and the temperature program rate from 25 ^0C to 900 ^0C. The data collected using representative neodymium acetate prepared is depicted in Fig. 2[14].

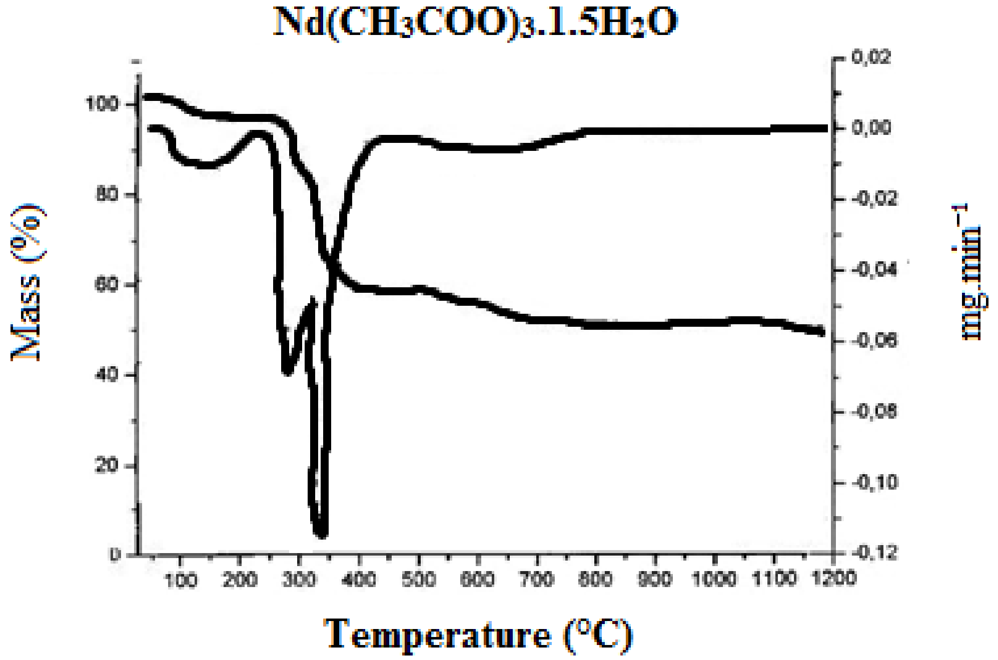

Figure 2: TG/DTG of the neodymium acetate prepared $Nd(CH_3COO)_3.1.5H_2O$

3.1.4- X-ray analyze of the neodymium acetate prepared.

The interpretation of the results was made using the standard pattern of the JCPDS data bank. The graphic obtained are show in Fig. 3[14].

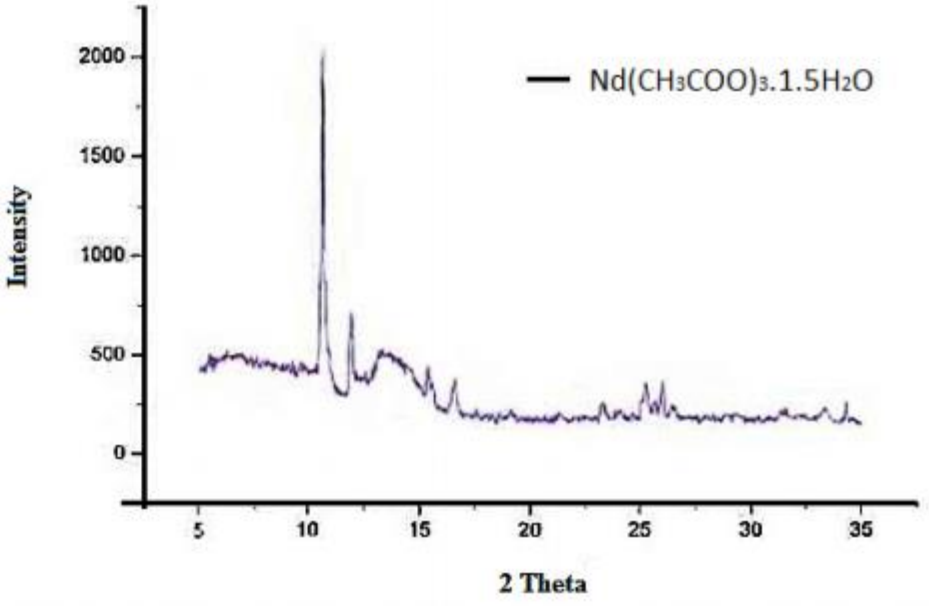

Figure 3: X ray powder diffractograms of the neodymium acetate prepared

4. CONCLUSIONS

A simple and economical procedure based on ion exchange, using common cationic ion exchange resins and avoiding the barrier ion, it was possible to prepare high pure neodymium oxide and in sequence high pure neodymium acetate.

The analytical date collected here for the crystallized neodymium acetate led to the conclusion that the neodymium acetate obtained exhibited the analogous chemical composition published by the technical literature [14].

The neodymium acetate has the stoichiometric composition of **$Nd(CH_3COO)_3.1.5H_2O$.** Considering the results of the thermal analyses the following steps were identified, reaction 1 to 4:

$Nd(CH_3COO)_3.1.5H_2O(s) \rightarrow Nd(CH_3COO)_3.H_2O\ (s) + 0.5\ H_2O(g)$ (1)
$Nd(CH_3\ COO)_3.H_2O\ (s) \rightarrow Nd(CH_3\ COO)_3\ (s) + H_2O\ (g)$ (2)
$Nd(CH_3\ COO)_3\ (s) \rightarrow Nd_2O_2CO_3\ (s) + 3\ CH_3COCH_3\ (g) + 2\ CO_2$ (3)
$Nd(CH_3\ COO)_3\ (s) \rightarrow Nd_2O_3\ (s) + CO_2\ (g)$ (4)

We also conclude that the results obtained by x-ray diffraction are compatible with the formula $Nd(CH_3COO)_3.1.5H_2O$. Neodymium acetate of high purity and quality achieved was applied, replacing the imported product in the research and development of automotive catalysts with the purpose of increasing its useful life with the formation of neodymium oxid e nanoparticles in the catalyst structure [14].

The typical neodymium acetate prepared contain the followings contaminants in micrograms per gram: Y (0.9), Sc (5.1), La (1.0), Pr (3.4), Sm (12.8), Eu (1.1), Gd (15.4), Tb (2.9), Dy (5.3), Ho (7.4) Er (1.5), Tm (0.3), Yb (2.5), Lu (1.0).

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