

azotization of difficultly diazotizable amines is ineffective in the case of picramide.

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The Preparation and Purification of Hydrous Lanthanum Hydroxide Sols

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Although hydrous lanthanum hydroxide sols have been prepared by several workers,¹⁻⁵ the methods used are laborious or yield unstable suspensions. While attempting to improve upon some of these methods, it was noted that lanthanum hydroxide freshly precipitated in the presence of lanthanum chloride is readily peptized by the latter when the temperature is raised to

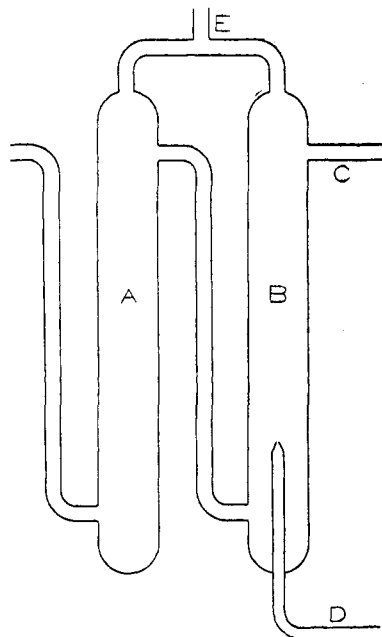


Fig. 1.—"Sweeping-out" apparatus.

50°. The following procedure based upon this fact has been found convenient: 3.5 g. of lanthanum chloride heptahydrate is dissolved in a small amount of carbon dioxide-free water and from three-tenths to nine-tenths of the equivalent amount of normal ammonium hydroxide added. This gives a slimy, gelatinous precipitate. Sufficient carbon dioxide-free water is added to make

- (1) Böhm and Niclassen, *Z. anorg. Chem.*, **132**, 1 (1923); cf. Müller, *ibid.*, **57**, 311 (1908).
- (2) Freundlich and Schalek, *Z. physik. Chem.*, **108**, 153 (1924).
- (3) Britton, *J. Chem. Soc.*, **127**, 2142 (1925).
- (4) Sadolin, *Z. anorg. Chem.*, **160**, 133 (1927).
- (5) McCutcheon and Smith, *THIS JOURNAL*, **29**, 1460 (1907).

a total volume of 400 cc., and the suspension is warmed to 50°. Peptization begins immediately, and within a few minutes the entire precipitate is dispersed to an homogeneous sol. The sol is cooled to room temperature, diluted to 500 cc., and dialyzed in collodion bags⁶ stoppered to exclude air.

In agreement with previous reports^{7,8} concerning the relatively high basicity of lanthanum hydroxide and the ease with which its aqueous suspensions absorb carbon dioxide, it was found that dialysis against distilled water containing carbon dioxide converted the dispersed hydroxide into crystalline lanthanum carbonate. Accordingly, an apparatus was designed in which a continuous supply of carbon dioxide-free water was prepared by heating the water to 95° and sweeping out the residual gas with a current of nitrogen. The procedure is as follows: distilled water is heated by passing it through thirty feet (9.2 meters) of 10-mm. glass tubing immersed in an oil-bath maintained at 95 ± 1°. The hot water then enters the "sweeping-out" apparatus, the details of which are shown in Fig. 1. The two columns A and B are each 5 cm. in diameter and 40.5 cm. in height. The water enters at C and flows down column B countercurrent to a stream of nitrogen introduced at D. The exit gases are led off at E where a slight suction is maintained to ensure ready removal. From B the water flows into column A which serves to remove any entrained bubbles of gas not taken out in B. The exit water from A, after being cooled to any desired temperature in a countercurrent cooling system, flows into the dialyzer. The columns are supported in the oil-bath, and the nitrogen, after being passed over soda-lime, is preheated in a fifteen foot (4.6-meter) length of 8-mm. glass tubing before being passed into B. Pyrex glass is used throughout.

Sols dialyzed against water freed of its carbon dioxide in this apparatus are practically free from lanthanum carbonate. However, they readily absorb carbon dioxide from the air unless protected. Data for some of the dialyzed sols are given in Table I. It will be noted that all sols contain small amounts of chloride. Since attempts to remove the chloride completely by prolonged dialysis always have resulted in complete coagulation, it would appear that some lanthanum

- (6) Madson and Krauskopf, *J. Phys. Chem.*, **35**, 3237 (1931).
- (7) Vesterberg, *Z. anorg. allgem. Chem.*, **94**, 371 (1916).
- (8) Euler and Nilsson, *Ber.*, **57**, 217 (1924).

TABLE I
DATA FOR LANTHANUM HYDROXIDE SOLS

Sol	NH ₄ OH, % of equiv. dialyzed ^a	Hours dialyzed ^a	La ₂ O ₃ , mg. per l.	Cl, mg. per l.	pH
6c	33.3	40	250	22.9	6.9
6d	33.3	45	500	17.2	7.0
6e	33.3	48	829	34.4	7.4
6f	33.3	51	755	37.0	
6g		84	438	10.5	7.3
6z	33.3	120	553	15.0	7.0
6h(1)	50.0	67	1158	103	7.8
6h(2)	67.0	67	1984	60.7	8.3
6h(3)	89.0	67	2312	48.7	7.9

^a All sols dialyzed at 20 to 25°.

chloride is necessary for stability. When protected from carbon dioxide, the more dilute sols are reasonably stable, but slow sedimentation takes place in the more concentrated ones. The sols are bluish-white by both reflected and transmitted light, but on strong illumination, the light transmitted is rich in the orange, a qualitative verification of the Rayleigh equation. The particles are positively charged.

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Preparation of Pellets of Radioactive Lead

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In the lead mirror method of detecting free radicals,² the lead used must be as pure as possible; the presence of oxide is distinctly objectionable. In experiments in which the lead transported is measured by the use of a radioactive isotope (Ra D) it is found necessary to prepare lead pellets of minimum size and maximum purity so as to ensure maximum sensitivity of the method. Various methods of preparation, which might be expected to work but generally have proved unsatisfactory, are described in the literature. We have found that the one described below, based upon a reaction used by Stas,³ gave pellets of desirable form and character.

Several hundred crushed radon tubes were triturated in a Pyrex mortar with concentrated aqua regia for a prolonged period of time, and the extract filtered, through paper, into a quartz beaker. The treatment with concentrated acids was re-

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(2) Cf. Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

(3) Stas, *Bull. Acad. Belg.*, [2] 10, 295 (1860); *Chem. News*, 4, 307 (1861).

peated on the siliceous residue, and the two filtrates combined, giving a total volume of 60-70 cc. At this point a definite weight of pure lead nitrate was added, the quantity depending on the size of pellet and the degree of radioactivity desired; in the following procedure the amounts stated are for the preparation of a 0.1-g. pellet of lead.

The next step was the removal of nitric acid by repeated evaporation to dryness with hydrochloric acid, on a hot plate. The residue was then dissolved in 33 cc. of 5 *N* hydrochloric acid, and treated with hydrogen sulfide to precipitate the mercury (contained in the radon tubes as a result of the method of filling the latter), the mercuric sulfide being filtered off on paper and washed with hot dilute hydrochloric acid. The filtrate so obtained was again evaporated to dryness, repeatedly, this time with water, to remove hydrochloric acid, and the residue of lead chloride crystals was dissolved by warming in 30 cc. of water. The removal of the hydrochloric acid is necessary in order to precipitate the lead as oxalate from a neutral solution without too high a concentration of ammonium salts resulting from the neutralization of acid. To the cold aqueous solution, then, was added 4 cc. of saturated ammonium oxalate solution and 2-3 drops of dilute ammonium hydroxide. After stirring and thorough cooling the mixture was allowed to stand overnight. The precipitate was then filtered on a Neubauer porcelain microcrucible, with suction, washed with cold water, and dried partially with air. This was followed by thorough drying (and partial decomposition to oxide) at 250°.

For the reduction to the metallic state, the dry residue of oxalate + oxide was transferred into an ordinary porcelain crucible, and covered with 1-2 g. of dry potassium cyanide. The inclined, open crucible was heated slowly and carefully on a Bunsen flame, and finally heated very strongly for about ten minutes. On cooling, the potassium cyanide was washed away with water, and the lead pellet picked out and dried. If the lead thus finally obtained should prove to be powdery, or finely divided rather than in the form of one or a few pellets, the potassium cyanide treatment is repeated on the dry lead, until the metal is obtained in a satisfactory pellet or two.

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