

2. A modified form of electrolytic cell utilizing a mercury cathode for the direct electrolysis of chloride solutions is described.

3. The percentage of cadmium in anhydrous cadmium chloride is found to be 61.319, while Quinn and Hulett found only 61.298%. The former percentage corresponds to an atomic weight of cadmium of 112.417 ( $Cl = 35.457$ ), a value which is in perfect agreement with the earlier one found by Baxter, Hines and Frevert, 112.418. If chlorine is taken at 35.458, the atomic weight of cadmium becomes 112.421.

The analysis of cadmium bromide by a similar method is now under way in this laboratory, and the results closely confirm the higher value for the atomic weight of cadmium. The method will also be applied to the analysis of other metallic halides.

We are greatly indebted to both the Carnegie Institution of Washington and the Elizabeth Thompson Science Fund for very generous assistance which has enabled us to obtain apparatus best suited for the work.

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## THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS.

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### Historical.

But little attention appears to have been paid to the possibility of separating the rare earths by electrolysis of aqueous solutions of their salts. Edgar F. Smith<sup>1</sup> stated that "didymium is not precipitated, either as nitrate or acetate, although a partial precipitation takes place at the positive pole." Brauner<sup>2</sup> electrolyzed a solution of didymium acetate using platinum electrodes. There formed on the negative pole a pale red crystalline crust which contained didymium and acetic acid. Solutions of the nitrate and of the sulfate of didymium gave similar products. Brauner's object in these experiments was to ascertain whether a superoxide would appear on the positive pole. No such formation was noted, and he did not pursue the subject further. In a brief article entitled "Electrolysis of Solutions of the Rare Earths,"<sup>3</sup> Krüss makes the following statement: "A solution of a chloride of a rare earth behaves upon electrolysis like a solution of an hydroxide in dilute hydrochloric acid; chlorine and hydrogen are set free at the electrodes, the solution loses more and more hydrochloric acid, and as the amount of the solvent diminishes, the hydroxide of the earth is precipitated in increasing amount. In this manner the rare earths can be removed from chloride solutions of mixtures of the earths, the amounts thus precipitated depending upon the

<sup>1</sup> *Ber.*, 13, 751 (1880).

<sup>2</sup> *Monatsh.*, 3, 1 (1882).

<sup>3</sup> *Z. anorg. Chem.*, 3, 60 (1893).

strength of the current and the duration of the electrolysis. It is to be expected that those bases which are the weakest toward hydrochloric acid will first be precipitated as hydroxides as soon as a part of the hydrochloric acid is decomposed by the electrolysis. The stronger bases will remain in solution as the more stable chlorides. In order to remove the hydrochloric acid uniformly from all parts of the solution of the chlorides of the rare earths, electrodes of large surface were employed." Krüss electrolyzed the solution for ten minutes, and then removed the heavy, dense deposit of hydroxide by filtration. The solution was then again electrolyzed for ten minutes, and in this manner small fractions of less than one gram each were obtained. Two electrolyses of solutions of impure yttria were carried out, and determinations of the atomic weights of the earths in the several fractions showed that the method gave quite rapid separation of the different earths. Krüss states at the close of this brief article that electrolysis of solutions of the rare earths might prove suitable for the separation of these elements. It does not appear, however, that he followed the matter further.

Considerable work has been done upon the anodic oxidation of cerium through electrolysis of solutions of cerium salts with platinum electrodes, but inasmuch as this does not concern the direct separation of the earth from solution upon electrolysis, the researches upon this subject will not here be reviewed.

### Experimental.

**Material.**—The material that was employed in the experiments described below consisted of the earths of both the didymium and yttrium groups from which cerium and thorium had been removed. The earths of the didymium group were extracted from the crude double sulfates of potassium and the didymium group, a large amount of this material having kindly been presented to the writers by Dr. H. S. Miner of the Welsbach Light Company. The lanthanum and praseodymium nitrates were prepared from quite pure samples of these two salts that we owe also to the kindness of Dr. Miner. The earths of the yttrium group were obtained from the crude rare earth oxalates from xenotime: the mixture that was used in the experiments showed strong absorption bands of erbium, and rather faint bands of europium, samarium, and holmium. The didymium bands were very faint.

**Apparatus.**—The first electrolysis was performed in a small crystallizing dish and stationary electrodes of sheet platinum were used. On electrolyzing a slightly acid solution of the nitrates of the didymium group, no precipitate appeared until the free nitric acid had been broken down by the current. As soon as this had been effected, however, a separation of the hydroxides of the earths appeared at the cathode, and the internal resistance of the cell rapidly increased. Upon interrupting the current

and examining the contents of the cell it was found that a portion of the hydroxides had separated in flocculent form resembling aluminum hydroxide, and also that that part of the cathode which was immersed in the solution was heavily covered with a dense, granular precipitate of the hydroxides. It was this coating of the cathode surface that interfered with the passage of the current and caused marked fluctuations in the voltage.

It was thus evident that no definite voltage could be maintained for any considerable length of time unless the cathode surface could be kept free from deposit of the hydroxides. To attain this end, a rotating cathode of copper in the form of a wheel 15 cm. in diameter and 2.5 cm. in thickness was next employed. This was mounted on a horizontal shaft of the same material and was set in such position that the wheel dipped into the solution of the nitrates of the earth to a depth of three centimeters. An anode of platinum was used. A copper scraper was fastened in such position that it rested against the edge of the cathode wheel, and it was hoped that by means of this arrangement the deposit of hydroxides upon the cathode might rapidly be removed, and the voltage in this manner be kept sufficiently constant to permit of fractional decomposition of the different nitrates in solution. The apparatus did not give satisfactory results, and after thorough trial it was abandoned, and a mercury cathode was employed. The mercury was placed in a glass cell about 12 cm. in diameter and 13 cm. high, the layer of mercury being about three centimeters deep. The surface of this mercury cathode was kept clean by violently agitating it by jets of air, the air being conducted into the mercury through a glass tube with three outlets. The anode consisted of a piece of platinum wire 0.76 mm. in diameter. The source of current was a set of eight storage cells, an ammeter and variable resistance were placed in series with the cell, and a voltmeter was connected in shunt with the cell. The aqueous solution of the rare earths that was to be subjected to electrolysis was placed in the cell upon the surface of the mercury.

#### I. Separation of Lanthanum from the Other Earths of the Didymium Group.

A neutral solution of the nitrates of the rare earths neodymium, praseodymium, lanthanum and samarium, that contained 50 g. of the oxides of the earths in one liter of the solution, was placed upon the mercury cathode in the cell, the mercury was set in agitation by a blast of air, the current was turned on, and the voltage was gradually stepped up to a point where fairly rapid precipitation of the hydroxides took place. The voltage was maintained constant at this value, 9 volts, throughout the series of fractionations, and this voltage was used in the three fractional electrolyses described below. The first fractional electrolysis was of six hours' duration. The current was then turned off, the hydroxides were

allowed to settle, the clear supernatant liquid was siphoned off, and the remaining solution was separated from the precipitate by filtration through a Büchner funnel. The filtrate was then returned to the cell and was again electrolyzed. In this manner eleven fractions were obtained. The hydroxides of each fraction were first thoroughly washed with hot water, were then dissolved in hydrochloric acid, and the small amount of mercury that they were found to contain was removed by double treatment with hydrogen sulfide. The rare earths in the solution were then precipitated from a slightly acid solution with oxalic acid, were thoroughly washed, and were then ignited to the oxides. The atomic weights of the rare earth elements were determined by igniting one portion of the oxalate to oxide and determining the oxalic acid in another portion by titration with potassium permanganate. The details of this run are shown in Table I.

TABLE I.—SEPARATION OF LANTHANUM FROM OTHER EARTHS OF THE DIDYMIUM GROUP.

Number of fraction.	Time in hours.	Color of oxides.	Atomic weights (original material, 140.6).
1.....	6	Light brown	140.9
2.....	5	Light brown	141.2
3.....	7	Light brown	141.5
4.....	6	Light brown	141.9
5.....	4	Color fading	141.7
6.....	5	Color fading	141.0
7.....	4	Color fading	140.4
8.....	5	Color faint	139.6
9.....	3	Color very faint	139.5
10.....	4	White	139.0
Residual solution.....	..	White	138.9

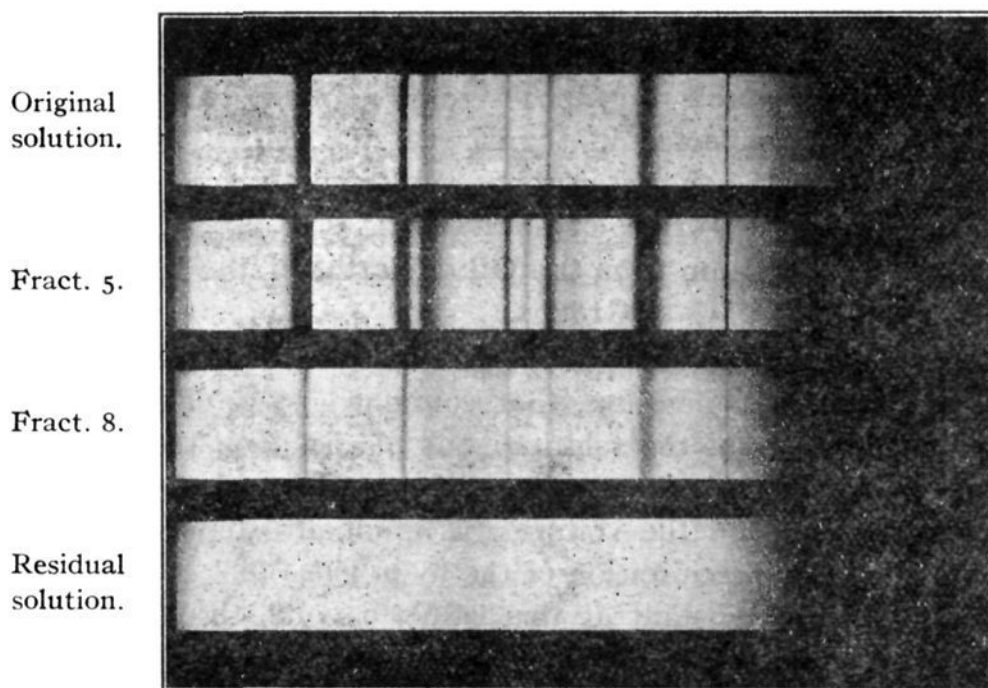


Plate I.

The absorption spectra of the original solution of Fractions 5 and 8, and of the residual solution were photographed with the aid of a Hilger wavelength spectrometer, Model 1912, with an oxyhydrogen zirconia lamp as the source of illumination. The different solutions used were of the same concentration in respect to the weight of the rare earth oxides contained in a unit volume. For photographs in black and white the Cramer trichromatic plate, which is especially sensitive to the red, was found to give quite satisfactory results (Plate I).

## II. Separation of Lanthanum from Praseodymium.

Nineteen and six-tenths grams of fairly pure praseodymium dioxide and 18.9 g. of lanthanum oxide were mixed, dissolved in nitric acid, the solution twice evaporated to dryness, redissolved in water, and diluted to 500 cc. Upon electrolysis of this solution the results shown in Table II were obtained.

The atomic weights of the rare earth elements in these fractions were determined by the method mentioned under I. Inasmuch as praseodymium was present, the active oxygen in the ignited oxide was determined by the Bunsen method and this was deducted from the weight of the oxide

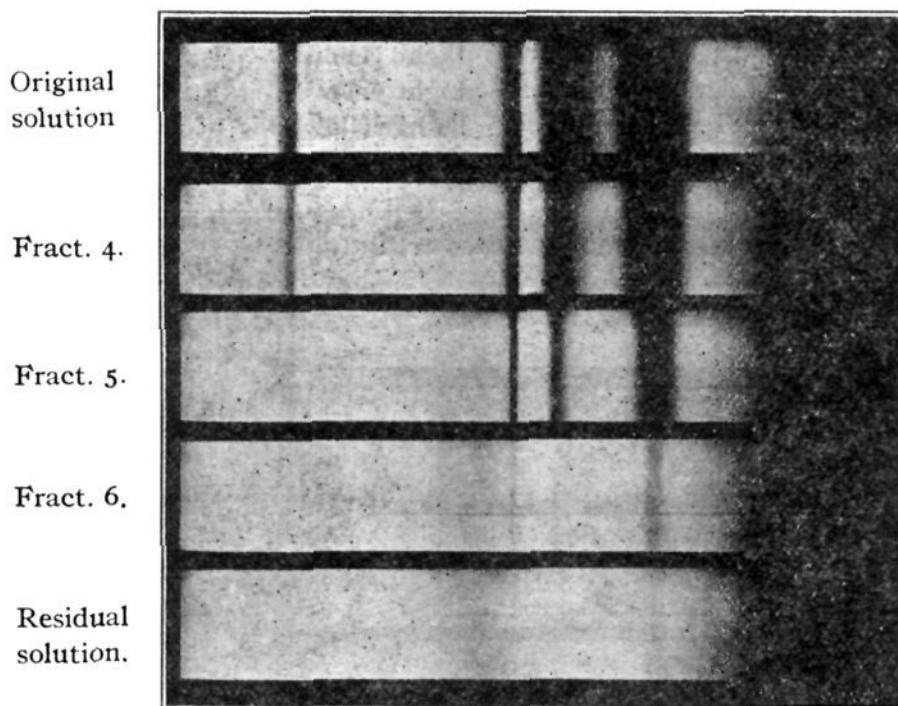


Plate II.

in order to arrive at the amount of  $\text{Pr}_2\text{O}_3$  that was present. That the atomic weights of the earths in Fractions 1 to 4 inclusive were higher than that of praseodymium is due to the fact that small amounts of other earths of this group were present.

TABLE II.

Number of fraction.	Time in hours.	Color of oxides.	Atomic weights, (original material 141.2).
1.....	9	Black	142.1
2.....	7	Black	141.9
3.....	8	Dark brown	142.0
4.....	9	Brown color fading	141.7
5.....	8	Brown color faint	140.3
6.....	7	Brown color very faint	139.5
Residual solution.....	..	White	138.8

Photographs of the original solution, of Fractions 4, 5 and 6, and of the residual solution are reproduced in Plate II. It will be noted that lanthanum is freed from praseodymium by a very small number of fractional electrolyses.

### III. Fractional Electrolysis of the Earths from Xenotime. Separation of Erbium from Yttrium.

Six fractional electrolyses were made with the results as set forth in Table III.

TABLE III.

Number of fraction.	Time in hours.	Color of oxides.	Atomic weights (original material, 103.85).
1.....	10	Light yellow	104.89
2.....	8	Light yellow	111.00
3.....	9	Light yellow	109.23
4.....	7	Light yellow	99.73
5.....	8	Faint yellow	93.50
Residual solution.....	..	Very faint yellow	92.08

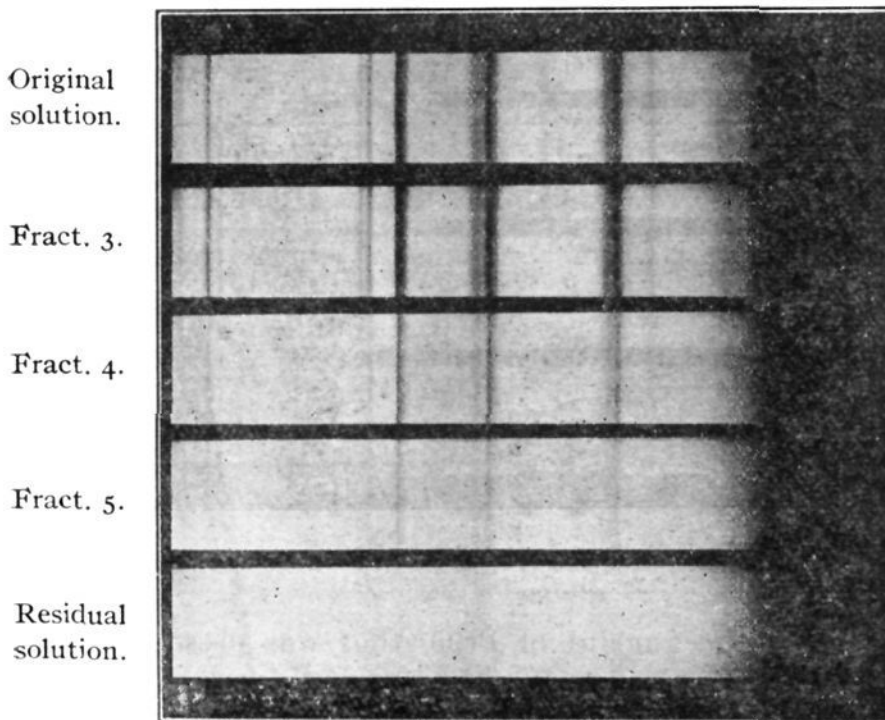


Plate III.

Photographs of the original solution, of Fractions 3, 4 and 5, and of the residual solution are reproduced in Plate III. It will be noted that erbium concentrated chiefly in the first three fractions and that in the succeeding fractions its amount rapidly decreased. The atomic weight of the rare earths in the final fraction, No. 6, was 92, which demonstrates the rapidity of the concentration of yttrium by this method.

The results of the experiments here described upon the fractional electrolysis of different mixtures of the rare earths appear to warrant the statement that the method yields quite rapid separations of some of the rare earths, and that these separations can be effected with far less expenditure of time and labor than by the customary methods of fractional crystallization or fractional precipitation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

### VACUUM AND PRESSURE STOPCOCKS.<sup>1</sup>

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The first essential of any stopcock of either hard or soft glass, no matter what its design, is that the glass be perfectly homogeneous and thoroughly annealed, as strains in either the key or frame will in time cause the stopcock either to jam or to leak. Unsymmetrical construction, whether due to poor design or poor workmanship, will, in general, have the same effect. Especially unfortunate is a lack of uniformity in the thickness of the walls of the frame.

Stopcocks of large taper in the key are easier to grind and polish than those of small taper, but are less satisfactory for the reasons that the key must necessarily be shorter, and that the lubricant has a greater tendency to float the key from the seat, especially when the stopcock is used under pressures slightly greater than that of the atmosphere. Careful grinding and very careful polishing are naturally essential.<sup>2</sup>

Probably the most serious defect of the ordinary straight-bore stopcock is the tendency of the bore to track bubbles and to scrape off the lubricant in its plane and thus allow leakage around the barrel.<sup>3</sup> The diagonal-bore stopcock does not allow direct leakage in this way and is, in a measure, self-sealing. It should be pointed out that the key of diagonal-bore stopcocks should be longer than that of straight-bore stopcocks of the

<sup>1</sup> This paper is written in response to several requests for the specifications of the stopcocks in use in this laboratory.

<sup>2</sup> Morley, Smithsonian Contributions No. 980, p. 89 (1895).

<sup>3</sup> This scraping and tracking can be partially prevented by proper construction of the apertures of the cross bore and frame.