Since the above article was published in separate form as a thesis, Dr. W. A. Noyes has called attention to the fact that the work is really a determination of the ratios between sodium and chlorine and sodium and bromine. The accepted value for the atomic weight of sodium, 23.00, is based on oxygen through either silver or chlorine or bromine and hence, as a piece of atomic weight work, the value of sodium is to be calculated. This was accordingly done and with the results given in the last column of the table. The value of chlorine was taken as 35.458, of bromine 79.920.[1]

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THE FRACTIONATION OF THE YTTRIUM EARTHS BY MEANS OF THE SUCCINATES.

BY R. C. BENNER.

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During the past decade material contributions have been made to the study of the yttrium group of the rare earths. Among these it has been shown by Lenher that, through the agency of the succinates, considerable rapidity can be arrived at in the process of separating various mixtures of these earths. The succinates of the yttrium group are finely divided crystalline precipitates, which are best formed by the addition of a solution of neutral ammonium or sodium succinate to a neutral nitrate solution of the yttrium earths. This precipitate is of especial interest because the time of formation is so greatly delayed that it is possible for equilibrium to become more readily established. Under these conditions the separation is more sharply performed than if precipitation took place instantaneously.

In order to test the applicability of the succinates as reagents in the yttrium group, the yttrium earths were extracted from a number of rare earth minerals of widely differing character and the separation studied in some detail.

Samarskite.—The yttrium earths were extracted from samarskite and studied in considerable more detail than previously reported.[2] The atomic weight determinations and the study of the absorption spectra were used as a continual control on the process of fractionation. The atomic weight determinations were carried out with sufficient accuracy by means of the oxalate method. The absorption spectra studies were made by means of a Steinheil grating spectroscope, similar to the one described by Dennis.[3] The earths having the highest atomic weights were precipitated first, showing that the succinates of the earths having

[1] F. W. Clarke, *Loc. cit.*

[2] THIS JOURNAL, 30, 575.

[3] *Ibid.*, 24, 415.

lower atomic weights were the more soluble. In all cases the color of the oxides and the strength of the absorption spectra varied in the same ratio as did the atomic weights, all of which demonstrated that erbium and the other heavy earths concentrated in the first fractions, while yttrium concentrated in the last. Typical illustrations of this separation were given in the following series of atomic weights. A, 130, 116, 104; B, 123, 115, 98.5; C, 114, 108, 99.7; D, 104, 97.

Monazite.—In order that the influence of various factors in the succinate method might be verified by experiment, several hundred grams of the yttrium earths were separated from monazite, the solution being effected in nitric acid in such a manner that the solution formed was neutral to methyl orange.

A sodium succinate solution was made by adding sodium hydroxide to succinic acid until the solution was neutral to phenolphthalein, after which the strength was determined. An ammonium succinate solution of equal strength was prepared by the addition of ammonia to succinic acid until neutral to litmus. Sixty cc. of the yttrium earth nitrate solution, containing 7.84 grams of rare earth oxides, were diluted to one liter and fractioned in various ways, so that six fractions were obtained in each case.

Experiment 1.—The effect of fractionation in dilute was compared with the same operation in a strong solution, the strength of the succinate being varied as well as that of the earths.

Experiment 2.—The relative value of sodium succinate as a precipitating agent was compared with that of ammonium succinate.

Experiment 3.—The rapid addition of the succinates was compared with the addition of the same reagent drop by drop.

Experiment 4.—The effect of stirring during precipitation was studied.

Experiment 5.—The addition of various substances to the solution, such as sodium or ammonium acetate and nitrate, was studied.

The separation was most satisfactorily made when the precipitating reagent was added drop by drop. Sodium succinate appeared to be slightly superior to ammonium succinate as a precipitating reagent. The separation was apparently not aided by the presence of sodium acetate or nitrate, or by the corresponding ammonium salts.

Behavior of Sodium Succinate towards Mixtures of the Cerium and Yttrium Groups.—The material chosen for this experiment was a mixture of the monazite earths containing a large portion of the earths of the cerium group. The oxalates of this mixture were ignited to the oxide, dissolved in nitric acid, and evaporated to a sirup. The cerium was reduced to the cerous form by hydrogen peroxide and the excess destroyed by boiling the solution. The solution containing sixty-one grams of these oxides, in form of the neutral nitrates, was diluted to one liter and fractionally precipitated by means of a ten per cent. sodium succinate solution, 100 cc. of the solution being added at one time. The fractions, after being ignited to the oxide, were of a similar dark brown color, except the last two, which were of a lighter shade. Their atomic weights were as follows: 149.5, 147.0, 147, 150.0, 149.0, 146.0, 143.0, 143.0, 143.0. It was evident that there was very little separation of the elements of lower atomic weight from those of higher. The absorption spectra of these fractions failed to show any difference except in case of the last, in which the didymium lines were fainter and the oxide had a slightly paler color than that of the previous fractions.

Xenotime.—Ninety-five grams of the finely powdered mineral were thrown, in small amounts at a time, into fused hydrogen ammonium sulfate. The greenish mass was extracted with water containing a little hydrochloric acid, and the extraction continued until ammonia no longer gave a precipitate. This was then treated with an excess of potassium sulfate and the soluble double sulfates precipitated with oxalic acid and converted to the oxides by ignition. These oxides were converted to the neutral nitrates and a solution of 6.83 grams per liter was fractioned with a 2 per cent. sodium succinate solution. In th s instance the sodium succinate solution was added drop by drop, the solution being kept at a boiling temperature and constantly stirred with a mechanical stirrer. Each fraction was filtered after the addition of 12.5 cc. of the sodium succinate solution, and the treatment repeated on the filtrate, the volume being kept at one liter during the experiment. The following different fractions were obtained: 112.5, 109.4, 105.7, 101.6, 98.5. By comparison of the different fractions as to color of the ignited oxides and the absorption spectra, it was noted that elements of higher atomic weight concentrated in the first fractions, while yttrium accumulated in the mother liquor. This followed in all respects the yttrium earths from samarskite.

Gadolinite, from Langesundfiord, Norway.—Ninety-five grams of the finely powdered mineral were treated with aqua regia until the residue was colorless, the solution evaporated to dehydrate the silica, the residue extracted with water, and to the clear solution ammonium oxalate added as long as a precipitate formed. These oxalates were converted to the oxides, dissolved in the least possible amount of hydrochloric acid, treated with an excess of potassium sulfate in the cold and the soluble double sulfates precipitated by means of oxalic acid. Twenty-five grams of the oxides were converted to the neutral nitrates, diluted to one liter and fractioned by successive additions of 40 cc. of a 14 per cent. solution of sodium succinate. The atomic weights of the fractions obtained were: 113.8, 109.9, 108.0, 107.3, 105.6, 103.2, 98.1, 95.1.

The yttrium earths from this specimen of gadolinite were in all respects similar to those from xenotime, as far as the behavior toward sodium succinate was concerned. The color of the oxides and the absorption spectra were found to be similar to the earths from xenotime, except for the more gradual change in atomic weights, which latter would be expected on account of the greater number of fractions.

Fergusonite, from Gaalenerne, Norway.—One hundred and five grams of the finely powdered mineral were fused with 400 grams of potassium acid sulfate. The fused mass was pulverized, extracted with ice water, and washed with cold water until the washings failed to give a precipitate with ammonia. The solution was treated with ammonia and the precipitate obtained dissolved in nitric acid and heated for several days, water being added to replace that lost by evaporation. The precipitated metallic oxides were filtered off, the filtrate neutralized, and the earths precipitated by means of oxalic acid. To the hydrochloric acid solution of the earths potassium sulfate was added and the soluble double sulfates, when free from didymiums, were precipitated with oxalic acid and converted to the oxides. Ten and eighty-five hundredths grams of the oxides were changed to the nitrates, the solution made neutral to methyl orange, and diluted to one liter. This solution was fractioned by the addition of 25 cc. portions of a 5 per cent. sodium succinate solution, the solution being constantly stirred and the volume kept constant. Atomic weight and spectroscopic observations were made on the various fractions. The atomic weights were: 115.4, 112.4, 110.5, 102.5.

This series was of more interest than any of the preceding, as the spectroscopic observations showed the mixture to be of a more complex character. The separation, however, appeared to be somewhat sharper in the more rapid disappearance of the number of lines. The oxides were found more varied in color than was the case with the other minerals.

Euxenite, from Arendal, Norway.—Three hundred grams of the mineral were treated in a lead dish with hydrofluoric acid until the action ceased. The insoluble fluorides were washed with hydrofluoric acid until most of the soluble matter was extracted and converted to the sulfates by heating with concentrated sulfuric acid, the excess of which was driven off. After this treatment the pulverized sulfates were dissolved in ice water. The solution was treated with potassium sulfate, the soluble double sulfates precipitated with oxalic acid, converted to the oxides and then to the nitrates. The yttrium earths were then fractioned with sodium succinate, and in all respects appeared to be quite similar to those obtained from fergusonite. The atomic weights of the fractions were: 115.5, 112.7, 110.0, 108.2, 104.5, 102.5.

Gadolinite, from Texas.—Three hundred grams were treated with hydrofluoric acid, the insoluble fluorides converted to sulfates, the cerium didymium group removed by potassium sulfate, as usual. Twenty-seven grams of the oxides obtained were converted to the neutral nitrates and dissolved in one liter of water. This solution was fractionally precipitated with a 5 per cent. solution of sodium succinate. The atomic weights of the various fractions were: 122.0, 117.0, 112.0, 112.0, 108.5, 103.0, 102.5. The absorption spectra showed that the earths varied in the same manner as did the atomic weights.

Keilhauite, from Tvedestrand, Norway.—Fifteen hundred grams of the mineral were treated with hydrofluoric acid. The insoluble fluorides were converted to the sulfates, and the sulfate solution submitted to treatment with potassium sulfate in order to remove the cerium-didymium group. Seventeen grams of the oxides thus obtained were converted to the neutral nitrates and diluted to one liter. This solution was fractioned with a 5 per cent. solution of sodium succinate. The fractions showed atomic weights of 116.5, 116.5, 108.0, 104.0, 104.0. In general, the atomic weights were somewhat higher than the earths from fergusonite, but in all other respects were found to be identical.

Deportment of the Succinates of the Erbium Earths.—The study of these minerals indicated that sodium succinate showed the same general behavior towards different mixtures of the earths having low atomic weight. The separation seemed to be more marked as the average atomic weight of the mixture increased. In order to experimentally investigate this in more detail, erbium earths were extracted from monazite and samarskite. The erbium earths from monazite were separated from other members of the yttrium group by the chromate method. From a neutral nitrate solution containing 10 grams of these oxides per liter, fractions were obtained by means of a 5 per cent. sodium succinate solution. The atomic weights were: 152.5, 154, 148.5, 139, 124. A fraction of the samarskite earths, showing an atomic weight of 122.5 obtained by the succinate method, was converted to the neutral nitrates and again fractioned by the sodium succinate method. The atomic weights of these fractions were as follows: 133.0, 134.0, 131, 127.0, 122.5, 112.5, 103.0, while the color of the oxides varied from nearly white to brown. It was apparent, therefore, that the succinate method gave a more rapid separation with earths having comparatively high atomic weight.

Composition of Yttrium Succinate.—A few succinates have been made and analyzed. Czudnowicz and Cleve[1] (analysis given) report the succinate of lanthanum as $La_2(C_4H_4O_4)_3.5H_2O$. Cleve reports the succinate of samarium[2] (without analysis) as $Sm_2(C_4H_4O_4)_3.5H_2O$, also the succinate of yttrium[3] (with analysis) as $Yt_2(C_4H_4O_4)_3.4H_2O$, (with analysis) the succinate of erbium as $Er_2(C_4H_4O_4)_3,9H_2O$.[4] Czudnowicz[5] tells how to

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[1] *Bull. soc. chim.*, **21**, 202.

[2] *Ibid.*, **43**, 172.

[3] *Ibid.*, **18**, 296.

[4] *Ibid.*, **43**, 172.

[5] *Jahresb.*, 1861, 189

make the succinate of cerium and gives some of its properties. It is reported as $Ce(C_4H_4O_4).1.5H_2O$. Recently Sir Wm. Crookes made the succinate of scandium, to which he gave the formula $Sc_2(C_4H_4O_4)OH.H_2O$.

Yttrium was prepared in a fairly pure condition from mixed residues by the chromate method. The material selected gave only the slightest trace of absorption spectra when observed in a saturated solution 20 cm. thick. A neutral solution of this yttrium as nitrate was precipitated in a dilute solution at a boiling temperature by the addition of sodium succinate, drop by drop, with constant stirring. The precipitate was filtered, washed with boiling water and dried over sulfuric acid until the weight was constant. The crystallin compound prepared in this manner was pure white. Analysis showed it to be a normal succinate.

THEORETICAL FOR $Yt_2(C_4H_4O_4)_3.2\frac{1}{2}H_2O$ YT = 90.1.

	Theoretical.	Found.	
Yt	31.40	31.89	31.79
C	25.12	25.83	25.45
H	3.00	3.28	3.30

Solubility of Yttrium Succinate.—The salt was introduced into a flask with distilled water, connected with a reflex condenser, boiled for seven hours and filtered hot. One liter, when evaporated to dryness in a platinum dish, gave 0.054 gram of oxide, equivalent to 0.135 gram of yttrium succinate. The same experiment was repeated, the boiling being continued in this instance for twenty-one hours, and showed a solubility of 0.152 gram of the succinate. These determinations showed that the normal succinate was only sparingly soluble in water. Qualitative observations seemed to indicate that the solubility was greatly affected by the presence of an excess of either yttrium nitrate or sodium succinate.

Conclusion.

As a precipitation method the use of the succinates can be highly recommended. The precipitates are readily handled, and by ignition converted to the oxides. Should it be desirable to conduct this separation on a scale in which the question of economy is to be considered, the succinates can easily be converted to the hydroxides by means of sodium hydroxide.

The best separation can be performed by precipitating a nearly neutral boiling solution of the nitrates with sodium succinate, added drop by drop. It makes very little difference whether the solution is stirred or not. As long as the concentration of the yttrium earths does not exceed 2 to 3 per cent. the separation is satisfactory.

Yttrium succinate is a normal salt having the formula $Yt_2(C_4H_4O_4)_3.2.5H_2O$. This is a white salt, slightly hygroscopic and very nearly insoluble in water, 0.0574 gram of the oxide, equivalent to 0.1435 gram of the succinate, being soluble in one liter of boiling water.

The author wishes at this time to express his thanks to Professor Victor Lenher for valuable suggestions in this work, and to H. S. Miner, of the Welsbach Light Company, for a large part of the material.

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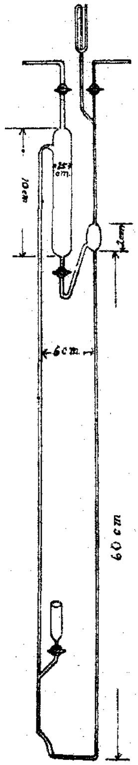
NOTE.

A Modified Boltwood Pump.—The modification of the Boltwood pump, which is represented by the accompanying diagram, may be of interest to those engaged in work which requires a high vacuum.



The original pump as stipulated by Boltwood[1] consists of a large bulb, 6 cm. diameter, which acts as the reservoir for the mercury and a smaller bulb of two to three centimeters diameter. The whole apparatus is about 120 cm. long, and 30 cm. wide, using from 700 to 1000 grams of mercury. The apparatus shown in the diagram is at present in use in this laboratory, and gives just as efficient service as the larger forms — sparks being obtained in Pflücker tubes after three minutes' operation, and within a quarter of an hour the pressure cannot be measured on an ordinary manometer—occupies only one-third the space, and requires 100 g. Hg for successful operation.

It might be added in this connection, that there is considerable deviation from the prescribed internal diameter of the dropping tube (2.5 mm.) in the manufactured forms; and it has been observed by the author, that a slightly larger tube refuses to give low vacuums—obviously while a tube smaller than 2 mm. works so slowly as to be comparable to the older hand-lift varieties.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

SOME DERIVATIVES OF PARA-AMINOBENZOHYDROL.[2]

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This paper is a report of the beginning of the work in an extensive research on derivatives of para-aminobenzophenone which is being con-

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[1] *Am. Chem. J.*, 19, 76 (1897).

[2] This research was suggested by the late Professor Henry A. Torrey and most of the experimental work was done under his direction, but the writing of the paper was deprived of the benefit of his supervision by his too early death.—C. L. JACKSON.