14. By the action of sodium telluride upon ammonium molybdate and upon sodium tungstate we have indications of the existence of telluro salts.

The author desires in closing to make grateful acknowledgment to Professor Victor Lenher, under whose guidance and inspiration this work has been carried out.

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THE BROMATES OF THE RARE EARTHS. PART II. THE BROMATES OF THE CERIUM GROUP AND YTTRIUM.

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In THIS JOURNAL, **30**, 182, a new method for the separation of the yttrium earths was described, which involved the fractional crystallization of the bromates. As this method gave—and is still giving—excellent results, it was decided to investigate the pure bromates of all of the rare earths. This paper describes the preparation and properties of the bromates of lanthanum, cerium, praseodymium, neodymium, samarium and yttrium, each prepared from material of the highest purity. Though some of these compounds have been prepared by the early investigators, it is doubtful if their material was very pure.

The bromates are usually prepared either by dissolving the oxide of the element in bromic acid, or by the metathesis of the sulphate of the metal with barium bromate. In the former case there is nearly always an excess of bromic acid, which causes trouble during the subsequent evaporation. The latter method is preferable, since barium bromate is soluble in about 130 parts of cold water and its solubility decreases enormously in the presence of the very soluble bromates. Thus we can employ an excess of barium bromate and very readily obtain pure bromates by crystallization. Because the rare earth sulphate solutions deposit crystals upon heating, it is best to cover the barium bromate with water, heat upon the water bath and add gradually, with plenty of stirring, the sulphate of the desired element. Under these conditions one encounters no difficulties and the barium sulphate filters well.

Lanthanum Bromate, $La_2(BrO_3)_6.18H_2O$.—This salt was prepared by the double decomposition of lanthanum sulphate solution with barium bromate. The product of the reaction was filtered, the filtrate boiled down and allowed to stand, when any remaining barium bromate separated. The refiltered liquid was further concentrated and the lanthanum bromate crystallized out. The crystals were then drained upon a Hirsch funnel at the filter pump and lastly dried in the air upon filter paper. When found necessary, this material was recrystallized.

Lanthanum bromate forms colorless hexagonal prisms. However, it usually separates out in small crystals about the size of granulated sugar. When the dried salt is ground up, it apparently tends to give up a small part of its water of crystallization, which causes the resulting powder to cake together. If alcohol is added to a saturated solution of this compound, two layers are formed, the lower of which crystallizes with difficulty upon continued stirring. The essential characteristic of this bromate is its great solubility in water as compared with the other bromates of the cerium group. One hundred parts of water dissolve 416 parts of the salt at 25°. This does not agree with the results obtained by Marignac, who, according to Urbain[1] and other authors, gives the solubility as one in three and a half parts of water at 15°. The solubility does not differ anything like that extent between these two temperatures. Lanthanum bromate differs from the most soluble yttrium earths with regard to the respective solubilities in alcohol, as "ytterbium" bromate is soluble while lanthanum bromate is insoluble. The bromate of lanthanum has a very great tendency to form supersaturated solutions. The melting point of this substance in its own water of crystallization is about 37.5°, which is very low when compared with the other members of the group.

Calculated: Br_2O_5, 52.53; La_2O_3, 23.80; H_2O (diff.), 23.67.
Found: Br_2O_5, 52.83; La_2O_3, 23.95; H_2O (diff.), 23.22.

When $La_2(BrO_3)_6.18H_2O$ is heated for some time at 100° it loses water, forming a lower hydrate corresponding to the formula $La_2(BrO_3)_6.4H_2O$. Loss: calculated, 18.41; found, 18.57.

The anhydrous salt was obtained by heating the lower hydrate to 150°. On heating to a high temperature it decomposes, giving out light and heat.

Cerous Bromate, $Ce_2(BrO_3)_6.18H_2O$.—The preparation of this compound presents greater difficulties, owing to the fact that the salt decomposes readily when heated in aqueous solution. Finally the evaporation was carried out in a vacuum at about 35°. The concentrated solution obtained in this manner was allowed to crystallize. These crystals were dried entirely by suction, because the mother liquor contains another compound, more highly oxidized, which causes filter paper to ignite explosively.

Cerous bromate forms colorless hexagonal crystals. After keeping, the crystals become slightly colored and an odor of bromine develops. Its most important property is its tendency to decompose, forming an insoluble basic compound, while some cerium is left in solution, probably in the state of ceric bromate. Cerous bromate melts at 49° and decomposes just above this temperature. It is very soluble in water, coming between lanthanum and praseodymium bromates, but the rapidity of its decomposition prevented its accurate determination.

Calculated: Br_2O_5, 52.43; Ce_2O_3, 23.95; H_2O (diff.), 23.62.
Found: Br_2O_5, 52.68; Ce_2O_3, 23.93; H_2O (diff.), 23.39.

Ceric Bromate, $Ce(BrO_3)_4$.—This compound is probably the powerful oxidizing substance left in solution through the partial decomposition of cerous bromate. An attempt to prepare this ceric compound was made by dissolving hydrated cerium dioxide in bromic acid and evaporating in a vacuum at 35°. A reddish brown liquid was obtained, which required very careful handling, as it causes explosive combustion of organic material. Unfortunately, owing to an accident, the solution was lost before it could be definitely proved whether or not it was possible to isolate the salt in crystalline form. This subject will be taken up again at the earliest opportunity.

Praseodymium Bromate, $Pr_2(BrO_3)_6.18H_2O$.—This bromate, obtained in a similar manner to the lanthanum compound, forms green hexagonal prisms isomorphous with the other rare earths. Its melting point is about 56.5°. One hundred parts of water dissolve 190 parts of the solid at 25°.

Analysis.—The Pr_2O_3 was estimated by titrating the oxalate with potassium permanganate.

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[1] Moissan, "Traité de Chimie Minerale," Vol. 3, page 842.

Calculated: Br_2O_5, 52.42; Pr_2O_3, 23.97; H_2O (diff.), 23.61.
Found: Br_2O_5, 52.55; Pr_2O_3, 24.00; H_2O (diff.), 23.45.

On heating the normal hydrated bromate for some time to 100° it lost water, forming $Pr_2(BrO_3)_6.4H_2O$. Loss calculated, 18.35; found, 18.29.

The anhydrous salt was decomposed with evolution of heat and light by heating to 150° while it can exist at 130°.

Neodymium Bromate, $Nd_2(BrO_3)_6.18H_2O$. — This salt crystallizes in hexagonal prisms possessing the color characteristic of neodymium compounds. It melts about 66.7°. With regard to its solubility it lies between praseodymium and samarium bromates. One hundred parts of water dissolve 146 parts $Nd_2(BrO_3)_6.18H_2O$ at 25°. Like the corresponding salts of lanthanum and praseodymium, it does not dissolve in alcohol.

Calculated: Br_2O_5, 52.12; Nd_2O_3, 24.39; H_2O (diff.), 23.49.
Found: Br_2O_5, 52.19; Nd_2O_3, 24.34; H_2O (diff.), 23.47.

When heated to 100° the normal salt loses water readily, forming $Nd_2(BrO_3)_6.4H_2O$. Loss: calculated, 18.27; found, 18.29.

The anhydrous salt was obtained by heating to 150° and decomposes with evolution of light and heat on heating to a higher temperature, but less violently than any of the preceding.

Samarium Bromate, $Sm_2(BrO_3)_6.18H_2O$. — This compound, prepared according to the method already described under lanthanum, forms yellow-colored crystals of the same system as those previously mentioned. It melts at 75° and is the least soluble of the cerium group bromates, for one hundred parts of water dissolve only 114 parts of the salt at 25°. This substance is very slightly soluble in alcohol.

Calculated: Br_2O_5, 51.69; Sm_2O_3, 25.04; H_2O (diff.), 23.28.
Found: Br_2O_5, 51.66; Sm_2O_3, 24.97; H_2O (diff.), 23.37.

When the salt containing 18 molecules of water of crystallization is heated to 100° it becomes constant after a long time. The resulting hydrate corresponds to four molecules of water similar to the other members of the group. Loss: calculated, 18.12; found, 18.34.

All water of crystallization is lost at 150° while the salt decomposes at a higher temperature.

Efforts were made to utilize the fact that cerium bromate readily undergoes decomposition in aqueous solution to purify this element and as a means for its gravimetric estimation. Experiments along the latter direction, in which many mixtures were tried, showed that a complete separation was impossible. The mixed bromates were dissolved in water, evaporated to dryness, placed in a steam oven for an hour and the residue taken up with water. Upon filtering off the insoluble portion, washing and igniting, it was found that only 90 per cent. of the cerium had been separated. The filtrate was again boiled down to dryness and treated as in the first case. About 7 per cent. more was obtained by this second operation. The third operation gave usually about 1½ per cent. On the other hand, this principle can be employed for the purification of cerium. By heating a mixture of cerium bromate with an excess of "didymium" bromate, cerium material was obtained in the first operation, which did not show any absorption bands even when observed through a thick layer of the concentrated solution. The second precipitate above mentioned is found to contain some didymium when the spectroscope is brought to bear upon the solution.

The fact that neodymium bromate is less soluble than praseodymium bromate is well worthy of being especially emphasized, as it gives a method in which the former is obtained in the least soluble portion. This separation proved to be much better than one would suspect after testing the solubilities. After three series of crystallizations of didymium, free from lanthanum and samarium, the end fractions showed different colors. After six series the most soluble took on a greenish tint. By the time the tenth series was reached the most soluble was green, although it still showed faint neodymium bands. The least soluble showed the raspberry tint due to neodymium. By spontaneous evaporation we can obtain pinkish crystals while the mother liquor dries up around them, forming a deep green crust. As lanthanum bromate is very soluble and tends to form supersaturated solutions readily, one would expect to find this a very good method for its purification. This was not tried, as the conversion to the bromate takes some time when working with large quantities of material. Also it is doubtful if it could compete with the simple method of the double ammonium nitrates. The bromates of Nd and Pr crystallize nicely even when small portions are worked.

Yttrium Bromate, $Y_2(BrO_3)_6.18H_2O$.—The material used in the preparation of this compound was purified by a modification of the Muthmann and Böhm chromate process, the essential difference being that in the modified method the oxides are dissolved in nitric acid after which potassium dichromate is added and the whole fractionated by means of a solution of potassium chromate according to the original method. This method is much more economical and appears to give results which are just about as good.

The bromate was prepared by the double decomposition between yttrium sulphate and barium bromate.

It forms colorless hexagonal prisms isomorphous with the other bromates. One hundred parts of water dissolve 168 parts of the solid. This brings the solubility between the bromates of praseodymium and neodymium. It is slightly soluble in alcohol.

Yttrium bromate melts at 74°. If it is heated still further, some of the lower hydrate separates out. It was thought that this might be used for separating yttrium from erbium. It was found, however, that when a mixture of yttrium and erbium bromates was treated in this way and filtered, keeping the temperature constant, yttrium carried erbium along with it.

Calculated: Br_2O_5, 56.74; Y_2O_3, 17.80; H_2O (diff.), 25.54.
Found: Br_2O_5, 56.74; Y_2O_3, 17.85; H_2O (diff.), 25.41.

The normal hydrate was then heated for some time at 100°, when it lost water being converted into a hydrate containing six molecules of water of crystallization $Y_2(BrO_3)_6H_2O$; hence we find a difference from the cerium group, as they contain four molecules of water in the lower state of hydration.

Loss: Calculated, 17.02; found, 17.26.

SUMMARY OF THE BROMATES OF THE CERIUM GROUP.

	La.	Ce.	Pr.	Nd.	Sm.
Melting points of hydrates ($18H_2O$)	37.5°	49°	56.5°	66.7°	75°
190 parts H_2O dissolve	416	...	190	146	114

The lower hydrates, containing four molecules of water of crystallization, are obtained by heating the normal hydrates to 100°.

The anhydrous salts are obtained by heating to 150° with the exception of praseodymium, which should not be heated above 130°.

The property possessed by cerium bromate to decompose can be used for purifying this element.

Because the praseodymium salt is more soluble than that of neodymium, the latter can be obtained in the least soluble portion and in this respect differs from nearly all the other methods for its separation.

In conclusion, it may be as well to mention that the third part of this paper will appear shortly. We also acknowledge our indebtedness to the Welsbach Company for material supplied for future investigation through the courtesy of Dr. H. S. Miner.

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THE QUANTITATIVE SEPARATION OF CALCIUM FROM MAGNESIUM.

BY WALTER C. BLASDALE.

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Although methods for the separation of these elements, which depend upon the relative solubilities of their carbonates, chromates and sulphates, respectively, have found advocates, none of these possess decided advantages over the more generally used oxalate process. The theory of the last-mentioned method has been discussed by Richards, McCaffrey and Bisbee,[1] who also determined the magnitude of the error resulting from the occlusion of magnesium by the precipitated calcium under a series of varying conditions. These experiments showed that this error could be greatly reduced by precipitating with oxalic acid from a slightly acid solution and subsequent neutralization, rather than by precipitating with ammonium oxalate from an alkaline solution according to the usual method. A somewhat extended use of the newer method has in general given excellent results, but as the experiments referred to were practically limited to cases in which approximately equivalent amounts of calcium and magnesium were present, and as the method seemed to be, for many practical purposes at least, unduly elaborate, it seemed desirable to secure further experimental data with regard to its more general application.

Limitation of the Problem.—In taking up the further study of the method its practical application to the conditions usually met with in analytical work was constantly kept in mind. In order to render the problem a definite one it was assumed that the substance to be analyzed might vary continuously in composition from pure calcite to pure magnesite, and that the amount used for the analysis was 0.6 gram. It was further assumed that chlorine was the only negative ion present in the solution, that the latter in every case contained 3.5 grams of ammonium chloride and was heated to boiling and diluted to 300 cc. before the precipitant was added. These limitations were adopted partly as the result of practical considerations and partly as the result of previous experience with the method. There are three main sources of error to be considered.

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[1] *Proc. Am. Acad. Arts Sci.*, **36**, 375 (1901).