AMMONIOBORITE, A NEW MINERAL*

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SUMMARY

Ammonioborite, a new mineral, is a hydrous borate of ammonium, from Larderello, Italy. In chemical composition it is identical or very similar to the known borate, larderellite, but its optical properties are different. The exact formula of both minerals is uncertain; they seem to represent dimorphous forms of $(NH_4)_2O\cdot 5B_2O_3\cdot 5H_2O$.

Optically both minerals are positive, $2V$ about 60°, with a high birefringence of 0.07. The refractive indices of ammonioborite are: $\alpha=1.470$, $\beta=1.487$, $\gamma=1.540$; of larderellite, $\alpha=1.493$, $\beta=1.509$, $\gamma=1.561$; and of the artificial salt $(NH_4)_2O\cdot 5B_2O_3\cdot 8H_2O$, $\alpha=1.426$, $\beta=1.429$, $\gamma=1.486$.

INTRODUCTION

The specimen of ammonioborite first studied, was purchased by the U. S. National Museum, from Willy Hirsch, a mineral dealer in Germany, under the label "bechilite." The writer, in his studies of the natural borates, extending over many years, has never been able to find a specimen of true bechilite.

On seeing the specimen in the National Museum, labeled bechilite, the writer made several qualitative tests to see if it really was bechilite, but as it dissolved readily in hot water, the mineral evidently was not a calcium borate. Further tests showed the absence of calcium and the presence of only boric acid, ammonia, and water. Determination of the optical properties showed that it was different from larderellite and consequently a new ammonium borate, which is here named ammonioborite. The late Dr. G. P. Merrill was kind enough to permit the sacrifice of about half of the small specimen, which weighed only two grams, in order to determine its properties and composition.

Ammonioborite is very similar in composition to larderellite but sufficiently different in properties to show their separate distinctness. The interpretation of the analyses of ammonioborite presented considerable difficulty, as the new mineral was mixed with variable quantities of sassolite. As the available material was very limited in quantity, the analytical results obtained and here presented, are not as satisfactory as could be desired. Were it not for the difference in the refractive indices and the absence of the characteristic rhombic shape of the crystals of larderellite, the new mineral could not have been differentiated therefrom.

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Chemical analyses indicate that the new mineral has the formula $(NH_4)_2O \cdot 5B_2O_3 \cdot 5H_2O$. This is also the formula now accepted for larderellite,[1] the old formula $(NH_4)_2 O \cdot 4B_2O_3 \cdot 4H_2O$, based on a single analysis, being discredited.

In a more recent paper by d'Achiardi[2] the two new analyses of larderellite given support the formula $(NH_4)_2O \cdot 5B_2O_3 \cdot 5H_2O$. As however no quantitative optical data are given for any of the material analyzed by him it remains uncertain whether his material was larderellite or ammonioborite. The formula of larderellite must still be considered as somewhat uncertain.

The values of the indices of refraction of the two minerals are sufficiently different to show that there are two ammonium borates occurring at Larderello, Italy. X-ray patterns confirm this conclusion. If they have the same composition, they are dimorphous. All of the samples of both minerals, available for study, contain considerable sassolite. Larderellite apparently forms only very sharp straight-edged rhombic-shaped crystals; ammonioborite forms very fine-grained granular masses as well as crystals which rarely are bounded by straight lines, the edges usually being considerably rounded.

DESCRIPTION OF AMMONIOBORITE

The specimen first studied is a compact mass of white material, showing in the difference of luster, the presence of two minerals. The ammonioborite is granular, white, and lustrous, while the associated sassolite is duller, and more powdery. In general appearance and color, luster, and hardness, the new mineral closely resembles larderellite and can not be told therefrom by visual inspection.

Much of the ammonioborite is an aggregate of irregularly bounded masses, compacted together and intergrown with sassolite. Individual crystals also occur whose edges are characteristically somewhat rounded in striking contrast to the straight-edged rhombic-shaped crystals of larderellite. The outlines of some of the more typical crystals of ammonioborite are shown in Fig. 1, A.

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[1] d'Achiardi, G., Boric acid and borates of the boron solfotaras in Tuscany: *Annali d. Univ. Toscane,* (Sci. nat.), Pisa, vol. **23,** pp. 1–34, 1901, and Larderellite from the solfotaras of Tuscany: *Rendi R. Acad. Lincei,* Rome, vol. **9,** fasc. **11,** pp. 342–345, 1900. Abstr. in *Zeitsch. f. Krystall.,* vol. **35,** pp. 519–521, 1902.

[2] d'Achiardi, Giovanni, Nuovi dati e ricerche sulla larderellite: *Periodico di Mineralogia,* vol. **1,** No. 3, pp. 3–8, 1930.

These outlines are distinctly different from those shown by larderellite, the most typical of which are shown in B. A more complete presentation of the outlines of the various modifications of crystals of larderellite is given by d'Achiardi.[3] The different shapes illustrated by him are due to the development of the basal cleavage, as shown by Larsen.[4]

Much of the ammonioborite is very fine grained. Many of the grains are irregular in shape and are composed of a mosaic of minute individuals, heterogeneously aggregated, so that the grains show no extinction but retain the bright interference colors in all positions. A few of the mosaic-like grains approximate in outline to forms of larderellite, suggesting that if the two minerals have a different chemical composition, the ammonioborite is pseudomorphous after larderellite. If the two minerals have the same composition, and a paramorphic change has taken place, the direction of change is likewise that of ammonioborite after larderellite.

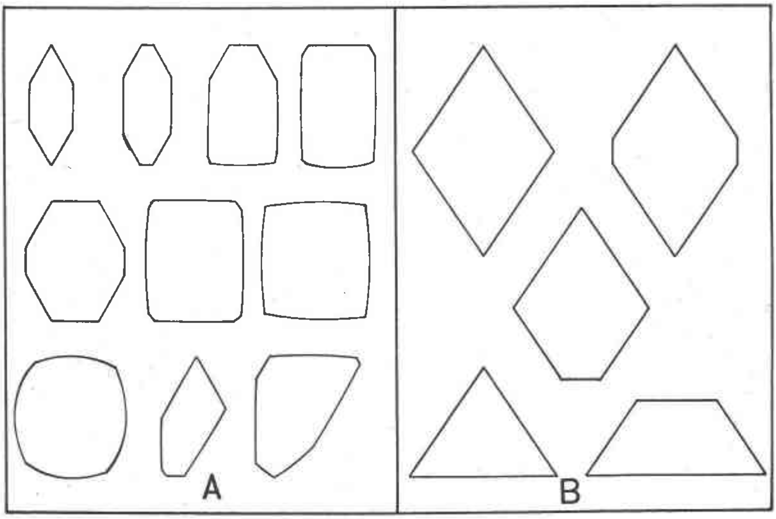

Fig. 1. A, Outlines of individual crystals of ammonioborite; B, Outlines of crystals of larderellite.

The most perfect crystals of ammonioborite were observed on

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[3] d'Achiardi, G., Boric acid and borates of the boron solfotaras in Tuscany: *Annali d. Univ. Toscane,* (Sci. nat.) Pisa, vol. **23,** pp. 12–13, 1901.

[4] Larsen, E. S., The microscopic determination of the nonopaque minerals: *U. S. Geol. Survey, Bull.* No. **679,** p. 98, 1921.

one corner of a specimen in the U. S. National Museum (U. S. Nat. Mus. Catalog No. 93756), labelled larderellite. These crystals are similar in shape and size to those observed on the specimen of supposed "bechilite" but in some of them the edges are much straighter though characteristically most of the edges are more or less rounded.

The best measurements gave an average value of about 57° for the upper acute angle of the crystals. This is not far from the angle of 68° measured for crystals of larderellite by d'Achiardi.

Another characteristic distinction between the two minerals is the absence in the better formed individual crystals of ammonioborite of a well developed cleavage, normal to the plates, which in larderellite often truncates the acute corners of the rhombs, as shown in Fig. 1, B. The crystals of ammonioborite are platy, many of them grouped together in parallel position, and can be observed on edge imbedded in the sassolite. The crystals reach an observed maximum length of about 0.08 millimeter, averaging from 0.015 to 0.03 millimeter, and are from a half to a third as wide.

Ammonioborite is either monoclinic or triclinic. Several of the crystals suggest triclinic, others seem more monoclinic in their symmetry.

The density of ammonioborite was not determined.

It was readily observed that when the coarsely crushed mixture of ammonioborite and sassolite was treated with cold water, part of the mixture readily dissolved, leaving a sandy residue of much less ready solubility. The sassolite readily dissolves in cold water, leaving most of the ammonioborite behind in a sandy powder, the sassolite having acted as a cement for the whole specimen.

Optical examination showed that the sandy residue of ammonioborite was not changed to a different salt by the action of the cold water. A portion of it remained undissolved for a considerable time. Comparative tests showed that for material of about the same grain size (diameter of particles about 0.1 m.m.), 0.2 gram of artificial sassolite (boric acid) dissolved completely in 75 cc. cold water in about 15 minutes and in less time if constantly stirred, whereas ammonioborite did not completely dissolve, under the same conditions in less than 2 hours, even if stirred. Advantage was taken of this difference in solubility to prepare a small sample of ammonioborite free from sassolite for analysis and for X-ray study.

OPTICAL PROPERTIES

The better developed crystals of ammonioborite show a small inclined extinction against their elongation. Measurements ranged from 7 to 13°, mostly closer to the lower figure. The direction of elongation corresponds closely to *Z*, the crystals becoming almost invisible in an immersion liquid of index 1.54. The mineral is positive and the obtuse bisectrix *X*, emerges from the large flat face of the crystals, which, if ammonioborite is monoclinic, would be the clinopinacoid $b\{010\}$ with the axial plane normal thereto. The axial angle $2V$ is medium, about 60° ±, dispersion, $r<v$.

The refractive indices of ammonioborite determined in the sample with admixed sassolite are given below under 1, and the indices determined on the same material washed free from sassolite under 2. These values are essentially identical with those of the unknown mineral from Larderello described twice by Larsen,[5] once on page 45, under Bechilite No. 2 (specimen from the American Museum of Natural History, New York), and again on page 50, under Boussingaultite No. 2 (collection of Col. Roebling, now in the U. S. National Museum). This last specimen was examined through the courtesy of Dr. W. F. Foshag and found to be an ammonium borate, mixed with sassolite, but free from magnesium and sulphate and therefore cannot be boussingaultite. The optical properties show that it is ammonioborite. The indices of refraction of these two minerals, as given by Larsen, are reproduced under 3 and 4.

Of the three specimens labeled larderellite in the U. S. National Museum, only one (U. S. Nat. Mus. Catalog No. 85174, described by Larsen[6]), is larderellite, the other two being ammonioborite. Of the latter two, one (U. S. Nat. Mus. Catalog No. 93756) is largely yellowish sassolite with small white masses of ammonioborite (indices given under 5 in Table 1), and the other (U. S. Nat. Mus. Catalog No. 94172) is a loose powder of ammonioborite (indices given under 6 in Table 1). Ammonioborite, therefore, seems to be a relatively common mineral at Larderello, Italy, and in fact may be more abundant there than larderellite.

The average of these six sets of determinations of indices of refraction of ammonioborite is given under 7 in Table 1.

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[5] Larsen, E. S., *loc. cit.*

[6] Larsen, E. S., *loc. cit.*, p. 98.

TABLE 1. OPTICAL PROPERTIES OF AMMONIOBORITE

	1	2	3	4	5	6	7
	Mixed with sassolite	Washed free from sassolite	Larsen, Bechilite No. 2	Larsen, Boussingaultite No. 2	U.S. Nat. Mus. 93756	U.S. Nat. Mus. 94172	Average
α	1.467	1.469	1.470	1.473	1.471	1.474	1.470
β	1.487	1.488	1.488	1.486	.....	.....	1.487
γ	1.541	1.539	1.542	1.539	1.539	1.541	1.540
$\gamma-\alpha$	.074	.070	.072	.066	.....	.....	.070
Sign	+	+	+	+	.....	.....	+
2V	Medium	.....	62°±5°	55°±5°	Medium	.....	60°±
Dispersion	.....	r<v	Slight	.....	.....	.....	r<v

The refractive indices of larderellite have been measured by the writer and Dr. C. S. Ross has also redetermined them. The results are shown below in Table 2 and for comparison, the average values for ammonioborite are given in the last column.

TABLE 2. OPTICAL PROPERTIES OF LARDERELLITE

	Larsen	Schaller	Ross[c]	Average[d]	Ammonioborite
α	1.509[a]	1.493	1.493	1.493	1.470
β	1.52[b]	1.512	1.509	1.509	1.487
γ	1.561	1.561	1.561	1.561	1.540
$\gamma-\alpha$	.052	.068	.068	.068	.070
Sign	+	+	+	+	+
2V	60°±	60°±	58°	58°	60°±
Dispersion	.....	.....	r<v	r<v	r<v
Orientation	X=*b*	X=*b*	X=*b*	X=*b*	.....
[e]	$Z\wedge c=24°$	$Z\wedge c=$small	$Z\wedge c=15°$	$Z\wedge c=$small	.....

[a] Larsen's value for α is too high.

[b] Approximate. Given as 1.52±0.01.

[c] Very carefully made. Error about ±0.001.

[d] The value of β determined by Ross is taken.

[e] As observed on the flat lying crystals, the extinction is parallel to the diagonals of the rhomb-shaped crystals.

Some of the optical properties of the two minerals are very similar, thus both are positive, the optic angle $2V$ is almost the same, and the birefringence (0.07) is practically identical.

On the other hand there are some marked differences, as the following tabulation shows.

TABLE 3. DIFFERENCES IN OPTICAL PROPERTIES OF AMMONIOBORITE AND OF LARDERELLITE

	Ammonioborite	Larderellite
Shape	Irregular, crystals with rounded outlines	Straight-edged rhombs
Cleavage	Not observed	Perfect {001}
Extinction on platy crystals	Inclined, 7°+	Parallel
Emerges on plates	X	Y
α	1.470	1.493
β	1.487	1.509
γ	1.540	1.561

The two minerals can readily be differentiated optically by immersing them in oils of known index. In an oil of index of 1.49–1.50, larderellite disappears when the shorter diagonal of the rhombs is parallel with the vertical cross-hair of the microscope, whereas ammonioborite stands out in relief in all positions, one direction of extinction being much lower and the other much higher, in index value, than the oil. In an oil with index of 1.56, larderellite disappears when the longer diagonal of the rhombs is parallel with the vertical cross-hair, whereas ammonioborite stands out clearly defined, all indices being lower than 1.56.

CHEMICAL COMPOSITION

Qualitative tests showed the presence of only ammonia, boric acid, and water. The admixed sassolite (boric acid) presented difficulty in the analysis as at first no way was found to remove it. Finally, it was found that it could be dissolved in cold water. In this way a very small sample (0.09 gram) of pure ammonioborite was obtained, which was seen on microscopic examination to be free from sassolite. Sassolite can readily be recognized microscopically as it is nearly isotropic, $2V$ being only 7°, so that the plates normal to the acute bisectrix show a very low birefringence, with a nearly uniaxial figure. The birefringence of ammonioborite is high, yielding brilliant interference colors.

Attempts were made to prepare ammonioborite artifically so that the composition of this compound could be determined on ample material before the natural mineral was analyzed. All such attempts resulted in failure. Larderellite likewise has not been been made artificially. The well known compound $(NH_4)_2O \cdot 5B_2O_3 \cdot 8H_2O$ was the only salt obtained, boric acid crystallizing out with it if an excess was present.

A solution of the 1:5:8 compound, when boiled, loses ammonia, even when boric acid is added. It is possible, though, that with the proper quantity of boric acid added, an equilibrium can be reached, so that a solution of the 1:5:8 compound can be boiled without losing ammonia. Out of such a boiling solution, it is possible that the lower hydrate, namely the 1:5:5 compound, might crystallize. Time was not available for studying such possibilities.

In the analysis of ammonioborite, the sample was dissolved in cold water, solution being complete on standing over night. The cold water solution was titrated with $\frac{N}{10}$ HCl for the ammonia, using methyl red as indicator, an excess of $\frac{N}{10}$ NaOH solution then added, and the solution boiled for 20 minutes with a return condenser, open at the top. The boiling was continued for 5 minutes after the escaping steam no longer turned red litmus paper blue, due to the escaping ammonia. The excess alkali was then titrated to neutrality with methyl red as indicator and the freed boric acid then titrated with $\frac{N}{10}$ NaOH, using phenolphthalein and mannite.

A check on the titration method for alkali and for boric acid was made on recrystallized borax crystals, without the boiling with caustic soda. The analytical results obtained were in good agreement with the calculated values.

TABLE 4. TITRATION METHOD CHECKED BY ANALYSIS OF BORAX CRYSTALS

	Found		Calculated
Na_2O	16.10	16.07	16.26
B_2O_3	36.58	36.71	36.52
H_2O (by diff.)	47.32	47.22	47.22
	100.00	100.00	100.00

As all the sassolite could be completely dissolved out of the mixture of sassolite and ammonioborite with cold water in ten minutes or so, a small quantity of pure ammonioborite for analysis was secured in this way. Only ninety-three milligrams of the pure mineral were so obtained and the following analysis (Table 5) made on this small quantity. For the analysis of the mixtures of the two minerals (Table 6) and for the other analyses given in this paper, 0.2 gram samples were used. The values obtained are given to two decimals simply for the sake of uniformity, though it is well realized that even the first decimal has little claim to accuracy.

TABLE 5. ANALYSIS OF PURE AMMONIOBORITE, FREE FROM SASSOLITE

Analysis		Ratios	
$(NH_4)_2O$........	9.78	0.188 or 1.00	0.96 or 1×0.96 or 1
B_2O_3............	74.18	1.066 or 5.67	5.47 or 5×1.09 or 5
H_2O (by diff.)....	16.04	0.891 or 4.74	4.57 or 5×0.91 or 5
	100.00		

The water in this sample was necessarily determined by difference and consequently any error in the B_2O_3 determination will affect that of H_2O. The ratio of $(NH_4)_2O:B_2O_3:H_2O$, taking ammonia as unity, is, 1:00:5.67:4.74. If the B_2O_3 determination is a little high, as seems probable from the ratios, then that of water would be correspondingly low, so that the correct ratio would seem to be 1:5:5, giving the formula of amonioborite as $(NH_4)_2O \cdot 5B_2O_3 \cdot 5H_2O$.

Before the above analysis of ammonioborite free from sassolite was made, the natural mixture of the two minerals had been analyzed. In these analyses, the boric acid was titrated directly after the ammonia had been titrated with HCl, without realizing that the ammonia present (as ammonium chloride) would consume some NaOH, due to the reaction $(NH_4)Cl + NaOH = NaCl + (NH_4)OH$.

Some comparative tests were therefore made on the 1:5:8 artificial salt, of which abundant material was available, to see how far the presence of the ammonium salt would influence the determination of B_2O_3. The percentage of B_2O_3 determined in the 1:5:8 salt, without removing ammonium, is 66.49 (Av. of 66.88, 66.82, 66.00, 66.27). The percentage of B_2O_3, first removing ammonium by boiling with NaOH solution, was determined to be 64.48 (Av. of 64.33, 64.63). The B_2O_3 determination, without removing ammonium, is therefore about two percent too high. If the corresponding correction be applied to the determination of B_2O_3 in the ammonioborite-sassolite mixture, its analysis is as follows:

TABLE 6. ANALYSIS OF AMMONIOBORITE-SASSOLITE MIXTURE

	Analysis	Average	Ratio
$(NH_4)_2O$.........	5.71– 6.00	5.86.	0.1127 or 1.00
B_2O_3.............	64.10–64.31	64.21	0.9226 or 8.19
H_2O (by diff.).....	....	29.93	1.6628 or 14.75
		100.00	

In interpreting these ratios, that for $(NH_4)_2O$ is reduced to unity and the proper proportion of B_2O_3 and H_2O (1:3) deducted, to allow for the admixed sassolite.

TABLE 7. RATIOS OF ANALYSIS OF AMMONIOBORITE-SASSOLITE MIXTURE, DEDUCTING SASSOLITE

		Sassolite deducted	Ratios of pure Ammonioborite
$(NH_4)_2O$	1.00	....	1.00
B_2O_3	8.19	3.19	5.00
H_2O	14.75	9.57	5.18

By arbitrarily deducting enough B_2O_3 from the ratios of the mixture to yield a 5:1 ratio of $B_2O_3:(NH_4)_2O$, the ratio of the remaining water to $(NH_4)_2O$ is also 5:1, yielding the same ratio for the pure mineral as previously obtained, namely $(NH_4)_2O\cdot 5B_2O_3\cdot 5H_2O$. According to these ratios, the mixture analyzed consisted of 57 per cent of ammonioborite. As ammonioborite theoretically contains 10.61 per cent $(NH_4)_2O$, the determination of 5.86 per cent $(NH_4)_2O$ shows that 55 percent of ammonioborite was present in the mixture—a close agreement.

X-RAY EXAMINATION

On the assumption that a study of the structures of these minerals by X-ray methods might contribute further evidence as to the difference between larderellite and ammonioborite, Dr. E. Posnjak of the Geophysical Laboratory kindly took photographs of the X-ray spectra of both these minerals, which are reproduced in Fig. 2. They show a distinct difference in the structure of the two minerals.

The sassolite present in the samples was dissolved out with cold water, and microscopic examination of the remaining powder showed that both were pure. The larderellite (L in Fig. 2) was furnished by Prof. E. S. Larsen from the Harvard Collection. The ammonioborite (A in Fig. 2) is from the sample wrongly labelled boussingaultite in the Roebling Collection (now in U. S. Nat. Mus. Cat. No. R6167), whose optical properties were described by Larsen under Boussingaultite No. 2 and reproduced in column 4 of Table 1.

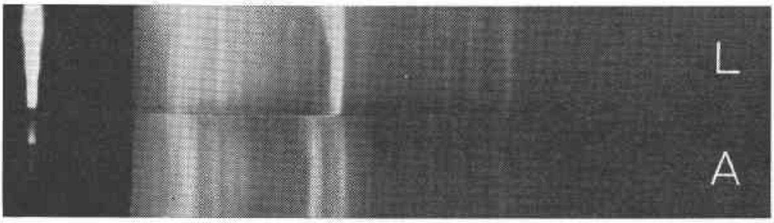

FIG. 2. *X*-ray spectra of larderellite (L) and ammonioborite (A). Taken by Dr. E. Posnjak of the Carnegie Geophysical Laboratory.

THE 1:5:8 ARTIFICIAL SALT

The well known salt $(NH_4)_2O \cdot 5B_2O_3 \cdot 8H_2O$, readily crystallizes out of a cold water solution in orthorhombic crystals, commonly forming twins and trillings. A quantity of this salt was prepared in order to have abundant material of an ammonium borate available for testing the chemical methods of analysis. It was found experimentally that a mixture of 40 grams boric acid, 35 c.c. strong ammonia, and 800 c.c. water, left to crystallize at room temperature, yielded a crop of crystals of the 1:5:8 compound, with very little free boric acid. Smaller quantities of ammonia always yielded an abundance of crystals of boric acid as well as the 1:5:8 salt.

The optical properties of the 1:5:8 salt are as follows, the data of the first two columns being taken from the literature. The results given by d'Achiardi are only approximate, the determination of β being considerably in error.

TABLE 8. OPTICAL PROPERTIES OF THE ARTIFICIAL SALT, $(NH_4)_2O \cdot 5B_2O_3 \cdot 8H_2O$

	Bolland[a]	d'Achiardi[b]	Schaller	Ross
α	1.44 approx.	<1.471	1.425	1.426
β	.....	1.471	1.430	1.429
γ	1.485 approx.	1.498	1.488	1.486
Sign	+	.....	+	+
2V	46½° (red)	.....	.....	35°
Dispersion	.....	.....	.....	$r<v$

[a] Taken from Winchell, A. N., The optic and microscopic characters of artificial minerals: *Univ. Wisconsin Studies*, No. **4**, 1927, p. 56.

[b] Taken from Abstract (*Mineral. Abstracts*, vol. 5, p. 146, 1932) of d'Achiardi, G., Considerazioni e ricerche sulla larderellite, etc. *Periodico di Mineralogia*, vol. 3, (No. 1), pp. 1–9, 1932.

The analysis of the 1:5:8 salt yielded the following values (Table 9), the solution of the salt being boiled with an excess of NaOH solution to remove ammonia, before titration of the boric acid.

TABLE 9. ANALYSIS OF 1:5:8 SALT

	1	2	3	4	Average	Ratios
$(NH_4)_2O$	8.79	8.60	8.69	8.60	8.67	0.1667 or 0.90 or 1
B_2O_3[a]	64.33	64.63	....	....	64.48	0.9264 or 5.02 or 5
H_2O by diff.	.....	.....	....	....	26.85	1.4917 or 8.08 or 8
					100.00	

[a] Determination of B_2O_3 immediately after the ammonia titration with HCl, without boiling with NaOH solution to remove the ammonia, gave higher results, namely, 66.88, 66.82, 66.00, 66.27.

The ratios obtained are: 0.90:5.02:8.08; close to 1:5:8.

Determinations of loss upon ignition leaving only B_2O_3 behind, both the ammonia and the water escaping, show that a little B_2O_3 also escapes under these conditions (Table 10). For the ammonium borates, the residue after simple ignition does not yield accurate values for B_2O_3. Ignition with lime would probably retain all the B_2O_3.

TABLE 10. DETERMINATION OF B_2O_3 AS RESIDUE ON IGNITION, IN AMMONIUM BORATES, SHOWING TOO LOW A RESULT

	B_2O_3, as residue on ignition	B_2O_3, by titration
Mixture of ammonioborite and sassolite	62.30	64.10, 64.31
1:5:8 salt	62.72, 62.94	64.48
Boric acid	53.65	55.64, 55.83