to a solution of an yttrium salt. Since the ferricyanides of erbium, thulium and ytterbium are still less soluble than the yttrium compound, this process can be employed for the purification of yttrium material. The fractionation is very rapid. This was proved in a very simple manner. Yttrium oxide containing erbium was dissolved in hydrochloric acid, the solution was made neutral and brought to a boil. No special type of apparatus was used, the solution being heated in a beaker and precipitated by adding a solution of the ferricyanide. The precipitate was treated with sodium hydroxide, filtered, washed, dissolved in hydrochloric acid and precipitated with oxalic acid. The oxalate was ignited, dissolved in hydrochloric acid and reprecipitated as the oxalate. The equivalent was then determined in the usual manner.

The filtrate from Fraction 1 was again treated with more potassium ferricyanide and the precipitate removed and treated similarly to Fraction 1. In all five fractions were obtained in this manner.

No. of fraction.	Atomic weight.
1	104.90
2	99.99
3	96.65
4	94.80
5	93.00

In conclusion, the writers would like to point out that the yttrium earth ferricyanides are much less soluble than heretofore believed. This method for the purification is perhaps the most rapid known, for the above fractionation was not carried out under very favorable conditions. This work is being continued.

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THE ARSENATES OF LEAD.

[THIRD PAPER.]

BASIC ARSENATES.

BY C. C. McDONNELL AND C. M. SMITH.

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There is very little published work concerning the basic arsenates of lead. It was observed by Graham as early as 1833[1] that when trisodium arsenate was added in excess to a solution of acetate of lead the resulting precipitate contained an excess of base. He apparently did not recognize this as a basic arsenate and did not investigate the reaction further. It is only comparatively recently that any definite knowledge has been gained in this direction. Two basic arsenates have been previously recorded and these, together with a third produced by us, are here described.

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[1] *Phil. Trans. Roy. Soc.*, 133, 266 (1833).

Octo-Lead Arsenate, $8PbO.As_2O_5.{}^1/_2H_2O$.—A compound approximating this formula was first reported by Strömholm.[1] He shook together freshly precipitated lead hydroxide and a small amount of 0.05 *N* disodium arsenate ($Na_2HAsO_4.7H_2O$) solution, and found that the arsenic was absorbed, leaving free sodium hydroxide in solution. Subsequent additions of the sodium arsenate left the solution with the same alkalinity up to a certain point, beyond which it decreased. The residue at this transition point was a voluminous mass of small crystals. Two lots of crystals so prepared were analyzed after drying and found to contain 88.37% and 87.91% PbO, respectively. He considered the remainder to be As_2O_5 and suggested the formula $15PbO.2As_2O_5$ though he stated that this was uncertain.

We repeated Strömholm's experiment as follows: A portion of freshly prepared lead hydroxide paste in an Erlenmeyer flask was treated with successive 25 cc. portions of approximately 0.05 *N* $Na_2HAsO_4.7H_2O$ (15 g. per liter), and shaken vigorously after each addition. At first the As_2O_5 was rapidly and completely withdrawn from the solution. The addition of the sodium arsenate was continued until a small amount remained in excess after prolonged shaking. The residue was then filtered from the alkaline solution, washed carefully with hot water, dried between filter paper and finally over H_2SO_4. It was a white fluffy powder, which, under the microscope, showed irregular particles, some of which were crystalline. Analysis showed the product to contain:

Lead oxide, PbO	88.35%
Arsenic oxide, As_2O_5	11.14%
	99.49%

Molecular ratio, PbO/As_2O_5 = 8.17

In the reaction just described sodium hydroxide is liberated, which suggested that the addition of lead nitrate solution to sodium arsenate containing a large excess of sodium hydroxide might result in the formation of the same basic arsenate. 50 g. each of trisodium arsenate ($Na_3AsO_4.12H_2O$) and sodium hydroxide were dissolved and made to 600 cc., giving a solution with the molecular ratio, Na_2O/As_2O_5, of 15. To this mixture were added six successive 100 cc. portions of lead nitrate solution (250 g./L.), the precipitate being filtered off after each addition and the filtrate used for the next precipitation. The precipitates were washed, heated on the steam bath until dry enough to powder readily, and then analyzed.

Precipitates "A," "B" and "C" upon examination were found to consist of a mixture of two compounds, lead hydroxide and an arsenate of lead. The three remaining precipitates were practically identical in composition. It appears, therefore, that from sodium arsenate solution containing a

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[1] *Z. anorg. Chem.*, 38, 446 (1904).

large excess of sodium hydroxide, lead nitrate precipitates a mixture of lead hydroxide and a basic arsenate of lead until the alkalinity is reduced to a certain point, and from then on a definite basic arsenate.

	Loss at 105° (water).	PbO.	As_2O_5.	Molecular ratio.
A	1.02%	97.38%	1.06%	
B	1.32%	95.77%	2.32%	
C	0.30%	93.29%	5.20%	
D	0.26%	88.61%	10.76%	PbO/As_2O_5 = 8.4
E	0.21%	88.67%	10.91%	
F	0.18%	88.67%	10.94%	

Ten per cent. sodium hydroxide solution dissolves a considerable amount of dilead arsenate ($PbHAsO_4$), and if the latter is added beyond the saturation point, it will be found that the residue has been converted to this same basic arsenate. One such preparation showed on analysis a molecular ratio, PbO/As_2O_5, of 7.98.

When prepared by any of the processes just described, this compound is obtained as an amorphous powder, or containing only a few irregular crystalline particles. A well-crystallized product was obtained, however, by dissolving dilead arsenate in a 10% solution of sodium hydroxide to saturation (either hot or cold), filtering the solution, and pouring it into about five times its volume of boiling water. The precipitate forms almost immediately, its crystalline nature being frequently evident to the unaided eye by its glistening appearance. (The product here formed is influenced by the degree of dilution and the manner of mixing. It is sometimes accompanied by lead oxide and sometimes by another basic arsenate which is described later.) Several preparations made in this way showed, on analysis, considerable variation, the molecular ratios averaging 8.15. A more uniform product was obtained by using a 10% solution of *potassium* hydroxide in the cold and diluting by pouring rapidly into 5 to 8 volumes of boiling water. Six preparations were made by this method, varying the dilution uniformly between $5^1/_2$ and 8 volumes, and the resulting precipitates removed, dried at 110° to constant weight and analyzed.

	%.	%.	%.	%.	%.	%.	Av. %.	Theory for $8PbO.As_2O_5.\frac{1}{2}H_2O$. %.
Lead oxide, PbO	88.56	88.25	88.14	88.12	88.46	88.31	88.31	88.20
Arsenic oxide, As_2O_5	11.13	11.15	11.36	11.42	11.23	11.36	11.28	11.36
Water (loss on ignition)	0.14	0.58	0.34	0.39	0.33	0.28	0.34	0.44
	99.83	99.98	99.84	99.93	100.02	99.95	99.93	100.00
Molecular ratio PbO/As_2O_5.	8.20	8.15	8.01	7.94	8.11	8.03	8.07	8.00

This compound contains water equivalent to approximately one-half molecule which is not completely expelled at 200°. Since we are unable to say in what form this water exists we have given the formula its empirical form, $8PbO.As_2O_5.{}^1/_2H_2O$. Because of the ratio of lead oxide to arsenic oxide being 8 to 1 we have designated the compound "Octo-lead arsenate."

A phosphate of lead prepared by Kroll[1] is of similar composition except that it is anhydrous. He employed fusion, however, in its preparation.

Properties.[2]—The octo-lead arsenate crystals obtained were in very thin, usually square plates, though frequently the sides were somewhat rounded. They are apparently biaxial and positive. (Owing to the thinness of the crystals and to their low birefringence the interference figures obtained were not very distinct.) Extinction is sometimes parallel to the side of the square but generally to the diagonal; in the latter cases the plates are frequently made up of two right triangular crystals, apparently twins. These results would indicate that the crystals belong to the orthorhombic system. The lowest index of refraction is slightly above 2.22. (We were unable to prepare an immersion medium having an index higher than this.)

This compound has a specific gravity at 15/15, of 8.04. It fuses readily without decomposition, other than loss of water, and on cooling solidifies to a crystalline mass.

This basic arsenate, when made from pure dilead arsenate, is white and permanent in sunlight, but when made from commercial lead salts, it frequently possesses the property of being sensitive to light to a high degree, turning dark brown or purple in a few minutes. This may be due to silver which is often present in small amounts in lead compounds, although the phenomenon has never been noted in any of the other lead arsenates made from the same lead salts.

4,1,3,1-Lead-hydroxy Arsenate[3] **(Hydroxy Mimetite),** $Pb_4(PbOH)(AsO_4)_3.H_2O$.—Berzelius[4] stated that trilead arsenate results from the action of ammonia on dilead arsenate. Volck[5] observed that the product resulting from the action of excess ammonia on dilead arsenate contained more lead and less arsenic than the theoretical amount for trilead arsenate, but he considered this to be due to the retention of other lead compounds. Tartar and Robinson[6] showed that (when using excess ammonia) the reaction is practically constant and suggested that the compound formed was a true

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[1] *Z. anorg. Chem.*, **78**, 105 (1912).

[2] We wish to acknowledge our indebtedness to Mr. Wm. H. Fry, Laboratory of Physical and Chemical Investigations, Bureau of Soils, for assistance in the determinations of the optical properties of these basic arsenates.

[3] In order to avoid the use of long, cumbersome names we have adopted for the designation of the lead-hydroxy arsenates, the method of expressing numerically the relative number of molecules of Pb, (PbOH), AsO_4 and H_2O in the order given.

[4] *Ann. chim. phys.*, [2] **11**, 229 (1819).

[5] *Science*, **33**, 870 (1911).

[6] THIS JOURNAL, **36**, 1848 (1914).

basic arsenate to which they ascribed the formula $21Pb_3(AsO_4)_2.2Pb(OH)_2.10H_2O$. (It is evident that an error was made in their calculations for their analytical results lead to the formula $7Pb_3(AsO_4)_2.2Pb(OH)_2.5H_2O$.)

We found[1] that ammonia converts dilead arsenate to trilead arsenate under limited conditions, but when employed in excess a basic arsenate is formed. When ammonia was distilled into water containing pure crystallized dilead arsenate the latter was changed to a fine amorphous powder. On analyzing the solution it was found that 40% of the arsenic had been dissolved, leaving the lead and arsenic in the residue in the proportion of 10 mols. PbO to $3As_2O_5$, in accordance with the following equation:

$$10PbHAsO_4 + xNH_3 + aq. = 10PbO.3As_2O_5.yH_2O + 4(NH_4)_3AsO_4 + (x - 12)NH_3 + aq.$$

G. Ennis Smith,[2] in a paper published at the same time, noted the formation of this basic arsenate and suggested the same formula.

The preparation of this compound in crystallized form was accomplished by using the following method: To a boiling 70% ammonium acetate solution, to which had been added about $^1/_4$ of its volume of concentrated ammonia water, was added dilead arsenate, which dissolved to a slight extent. This solution, after filtration, was poured into 5 to 10 times its volume of boiling water, when a voluminous white precipitate separated. Two lots of the material were prepared in this way, filtered, washed with boiling distilled water and dried to constant weight at 105°. When examined under the microscope, they were seen to consist of small, slender, prismatic crystals, the larger ones resembling hexagonal prisms. Analyses of these crystals gave the following results, which are compared with the theoretical values for the two suggested formulas:

	Found.		Theory for $Pb_4(PbOH)(AsO_4)_3.H_2O$.	Theory for $7Pb_3(AsO_4)_2.2Pb(OH)_2.5H_2O$.
Lead oxide, PbO	74.92%	74.70%	75.00%	74.72%
Arsenic oxide, As_2O_5	23.54%	23.54%	23.20%	23.43%
Water of const. & cryst. (diff.)	1.54%	1.76%	1.80%	1.85%
	100.00%	100.00%	100.00%	100.00%
Molecular ratio, PbO/As_2O_5	3.30	3.27	3.33	3.28

It is seen that the results are in closer agreement with the second formula, which is likewise true of the analyses given by Tartar and Robinson,[1] and G. Ennis Smith.[3] However, analytical methods are hardly of sufficient accuracy to differentiate between them.

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[1] THIS JOURNAL, **38**, 2034, 2366 (1916).

[2] *Ibid.*, **38**, 2016 (1916).

[3] *Loc. cit.*

Much larger crystals were obtained by a modification of the preceding process. The strongly ammoniacal ammonium acetate solution was saturated as before with pure dilead arsenate and an excess of the latter was then added. The flask containing this mixture was lightly stoppered to hinder the escape of the ammonia and placed upon the steam bath. It was necessary to add a little more ammonia from time to time to replace that lost by evaporation. In a few days crystals began to form around the flask near the level of the liquid and in the course of several months some of the individual crystals had become large enough to be visible with a small hand glass. The flask was then broken and the layer of crystals scraped off, washed and dried to constant weight at 105°. They were found to contain 74.51% PbO and 23.30% As_2O_5, molecular ratio = 3.30.

These crystals were examined optically and the following characteristics noted: They consisted principally of the hexagonal prism terminated by the basal pinacoid, frequently with the corners truncated by the second order pyramid. They have parallel extinction and are uniaxial with rather low negative birefringence; the average index of refraction is about 2.09. These results parallel those obtained on artificial mimetite prepared by us,[1] which, taken in connection with the analyses, we think sufficient justification for considering the compound to be hydroxy mimetite, as was noted in a previous article[2] and the excess water to be water of crystallization.

The specific gravity of the crystals, using water as the liquid, was found to be 6.86 at 15/15.

5,2,4-Lead-hydroxy Arsenate, $Pb_5(PbOH)_2(AsO_4)_4$.—In the description of the preparation of crystallized octo-lead arsenate it was noted that the degree of dilution played an important part in the purity of the product. It was observed that if the sodium or potassium hydroxide solutions, saturated with dilead arsenate, were poured into more than about 10 times their volume of boiling water, the precipitate was found to contain very small prismatic crystals, often crossed at an acute angle and sometimes occurring in bundles having the appearance of sheaves of wheat. When a dilution of twenty or more volumes is used the precipitate consists entirely of this material. Three lots were prepared in this way, the alkaline solutions at room temperature being poured into boiling water. The precipitates were washed, and dried to constant weight at 105°. The analytical results and the theoretical figures for the proposed formula are given in the following table.

We have considered the water in this compound to be water of constitution since only a very small amount of it is expelled below 200°

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[1] *Am. J. Sci.*, **42**, 139 (1916).

[2] THIS JOURNAL, **38**, 2034 (1916).

and the further fact that we have prepared a lead-chloroarsenate corresponding to this formula.[1]

Alkaline solution used.	10% NaOH.	10% KOH.	10% KOH.	$Pb_5(PbOH)_2(AsO_4)_4$.
Degree of dilution	1 : 25	1 : 25	1 : 50	....
PbO in product	76.65%	76.90%	76.57%	76.58%
As_2O_5 in product	22.38%	22.43%	22.63%	22.54%
Water of const. (loss on ignition)	0.74%	0.74%	0.74%	0.88%
	99.77%	100.07%	99.94%	100.00%
Molecular ration, PbO/As_2O_5	3.53	3.49	3.52	3.50

Properties.—Its specific gravity at 15/15, is 7.08.

The crystals are doubly refractive, with parallel extinction, negative elongation and index of refraction about 2.07.[2] Crystals were not obtained sufficiently large for more complete optical examination.

Summary.

1. The basic arsenate of lead first prepared by Strömholm has been more fully investigated and new methods of preparation have been described, some of which give a crystallized material. The empirical formula of this compound has been found to be $8PbO.As_2O_5.{}^1/_2H_2O$, and we have designated it octo-lead arsenate.

2. The basic arsenate prepared by the action of ammonia on dilead arsenate has been obtained in crystalline form. Its crystallographic and optical properties are similar to those of mimetite, which, together with the analytical data, show it to be hydroxy mimetite containing one molecule of water of crystallization, $Pb_4(PbOH)(AsO_4)_3.H_2O$. It may be represented as 4,1,3,1-lead-hydroxy arsenate.

3. A new basic lead arsenate, $Pb_5(PbOH)_2(AsO_4)_4$, which we have designated 5,2,4-lead-hydroxy arsenate, has been prepared and described.

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[1] *Am. J. Sci.*, **42**, 144 (1916).

[2] Since the publication of our work concerning certain of the arsenates of lead (THIS JOURNAL, **38**, 2027 (1916)) we have measured their indices of refraction by the method of immersion in liquids of known refraction, and found them to be as follows: Lead metarsenate, 2.05 (probably ω). Monolead arsenate, 1.74 and 1.82 (for the position in which the crystals usually lie). Pyrolead arsenate, $\beta = 2.03$. Dilead arsenate, $\alpha = 1.90$; $\gamma = 1.97$. Trilead arsenate (fused), 2.14 (probably ω).

The indices given in this paper refer in all cases to sodium light at about 20°.

We desire to thank Dr. H. E. Merwin, Geophysical Laboratory, Carnegie Institution of Washington, for advice in the preparation of the immersion liquids and assistance in the measurement of their indices.