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THE CHEMICAL NEWS.

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THE COMPOSITION OF THE CANARY-YELLOW ARSENITE OF SILVER.

By J. ALFRED WANKLYN,
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THE canary-yellow arsenite of silver which every school-boy knows, and which is described in chemical text-books as "the tetrargentic salt, $2Ag_2O \cdot As_2O_3$," has been recently analysed in my laboratory. The result of the analysis has astonished me, and is certainly interesting.

The following are the details and the figures of the analysis:—

The arsenite of silver, as is well known, is produced when the gas from the Marsh's apparatus is led into solution of nitrate of silver. It separates from the filtered solution (the reduced silver having been left on the filter-paper) on the cautious addition of dilute ammonia to the filtered solution.

A quantity of the arsenite of silver prepared in that manner was washed and dried in the water-bath and analysed.

1.0135 grms. gave 0.966 grm. of AgCl and 0.277 grm. of As_2S_3 . The formula $3Ag_2O \cdot As_2O_3$ requires—

	Calculated.		Found.
Ag	648	72.48	71.73
As	150	16.78	16.66
O	96	10.74	—
	894	100.00	

The formula was confirmed by a synthetical experiment. A weighed quantity of As_2O_3 was dissolved in water, and an insufficient quantity of ammonia added, and then the observation was made that, on mixing with this solution a known quantity of nitrate of silver (excess of nitrate of silver being taken), the solution became powerfully acid during the precipitation of the yellow arsenite of silver. Dilute ammonia was then carefully added so as just to saturate the acid, and the resulting canary-yellow arsenite of silver was separated by filtration, washed, slightly pressed, dried at $212^\circ F.$, and weighed. The theoretical figures were experimentally obtained.

It is noteworthy that, in this experiment, the yellow colour of the precipitate was not lost on drying.

The Laboratory, New Malden, Surrey,
April 12, 1902.

ON MINERALS OCCURRING IN AUSTRALIAN BAT GUANO.

By R. W. EMERSON MACIVOR, F.I.C., &c.,
Formerly Assistant Professor of Chemistry, Anderson's College,
Glasgow; Consulting Chemist to the Royal Agricultural
Society of Victoria, Australia; &c.

SOME years ago I contributed a paper to the CHEMICAL NEWS (vol. lv., p. 215), in which I described the bat guano which forms extensive deposits in certain basaltic caves in the vicinity of Skipton, 30 miles south-west of Ballarat, and also gave an account of a number of interesting and well-defined minerals which occur in it. I propose in this communication to supplement the statements I then made by some new facts, particularly in respect to the two new magnesium-ammonium phosphates which I had named Dittmarite and Muellerite respectively, but which at the time I had not fully examined.

Struvite, $MgNH_4PO_4 \cdot 6H_2O$, previously a rare mineral, occurs in great abundance in the form of large orthorhombic crystals in the moist depths of the guano, but rarely in the upper or drier portion of the deposits. It is sometimes associated with beautifully defined triclinic crystals of the more complex hydrous ammonium-magnesium phosphate, $Mg_2H_2(PO_4)_2 \cdot MgH_2(NH_4)_2(PO_4)_2 \cdot 8H_2O$. Indeed, as stated in my earlier paper, the crystals of the latter are occasionally found adhering to those of the struvite in such a way as almost to suggest that they had grown out of the latter. Bat hannayite, the hydrous magnesium hydrogen phosphate, $MgHPO_4 \cdot 3H_2O$, to which I gave the name newberyite, and the other well-defined minerals hereafter described, occur most abundantly in the seemingly older—or, at all events, drier—parts of the deposits containing the white indistinctly crystalline nodules of what appears to be altered struvite, and which approximate in composition to the normal tribasic magnesium phosphate, $Mg_3(PO_4)_2 \cdot xH_2O$. I may mention, in passing, that the aqueous extract of the guano contains, among many other salts, sodium-ammonium-hydrogen phosphate, $NaNH_4HPO_4$, which I succeeded in separating in a pure state by repeated crystallisations.

The crystallographic features of struvite, hannayite, and newberyite were years ago minutely examined and described by G. vom Rath, to whom I sent, through the late Prof. Ulrich, some representative specimens of each mineral (*Ber. Nied. Ges.*, p. 11, January 7th, 1878; and January 13th, 1879; also Dana's "A Treatise on Mineralogy," p. 832). I may take this opportunity of correcting a slight—but to me not altogether unimportant—error in connection with the discovery of hannayite into which vom Rath was led by a misstatement made in writing to him by Professor Ulrich, and which is repeated in Dana's great work of reference in a manner that reflects somewhat upon myself as a mineralogical chemist. The mineral is described as having been "discovered by MacIvor, of Melbourne, . . . and recognised as new by Ulrich, as stated in a letter to vom Rath." Now the facts of the case were that, by the time Ulrich came to my laboratory to obtain the specimens for Professor vom Rath, I had not only repeatedly analysed the mineral and by other means identified it as new, but had actually named it after my old friend and early associate Mr. J. B. Hannay. Ulrich had nothing whatever to do with its identification as a new species.

The following are some later analyses of—(A) struvite, (B) hannayite, and (C) newberyite from Skipton guano:—

	(A).		(B).		(C).	
	Found.	Theory.	Found.	Theory.	Found.	Theory.
H_2O	44.09	44.03	28.51	28.69	36.31	36.21
MgO^*	16.51	16.38	18.76	18.87	22.96	22.99
$(NH_4)_2O$	10.58	10.61	8.10	8.18	—	—
P_2O_5	28.82	28.98	44.63	44.26	40.73	40.80
	100.00	100.00	100.00	100.00	100.00	100.00

* Including equivalent MgO for FeO and MnO present in the three minerals:—(A). FeO, 0.81; MnO, 0.16. (B). FeO, 0.310; MnO, 0.067. (C). FeO, 0.85; MnO, 0.021.

Dittmarite is met with in the form of small rhombic transparent crystals, which do not readily lose water on lengthened exposure to the atmosphere, but give up much of their water of crystallisation and lose transparency on being maintained for a time at $100-105^\circ$. On ignition, it yields magnesium pyrophosphate. Its composition indicates the somewhat extraordinary formula $MgNH_4PO_4 \cdot 2Mg_2H_2(PO_4)_2 \cdot 8H_2O$.

	Found.	Theory.
H_2O	23.42	23.65
MgO^*	26.13	26.28
$(NH_4)_2O$	3.94	3.42
P_2O_5	46.51	46.65
	100.00	100.00

* Including MgO equivalent to 0.38 FeO and 0.08 MnO.

This interesting mineral I named in honour of my old and esteemed principal, the late Professor W. Dittmar, F.R.S.

Muellerite is yet another remarkable ammonium-magnesium phosphate found here and there sparsely distributed in the older and moderately moist (about 18 to 25 per cent H₂O) guano deposits. It occurs in small flat crystals of somewhat indistinct character, and which are with difficulty freed from adhering and locked up guano. However, after the exercise of considerable patience, I succeeded in separating some fairly clean crystals, which on drying at 100° C. for two hours did not lose water of crystallisation, but at 120° C. commence to lose weight. On strong ignition the mineral left magnesium metaphosphate, Mg(PO₃)₂, and, on analysis, gave numbers indicating the formula Mg(NH₄)₂H₂(PO₄)₂ + 4H₂O:—

	Found.	Theory.
H ₂ O	27.55	27.77
MgO*	12.42	12.35
(NH ₄) ₂ O	16.15	16.05
P ₂ O ₅	43.88	43.83
	100.00	100.00

* Including MgO equivalent to 0.20 FeO and 0.05 MnO.

This mineral I called *Muellerite*, in compliment to the illustrious Australian scientist, the late Baron Sir Ferdinand von Mueller, K.C.M.G., F.R.S., with whom I was much associated during my eleven years' work at the Antipodes.

The chalk-like white nodules, incidentally referred to in my earlier paper and also in this note as being "altered" struvite, and which are found abundantly distributed throughout the mass of some of the drier guano deposits, appear to consist largely of imperfectly crystalline tribasic magnesium phosphate, Mg₃(PO₄)₂. However, neither the chemical nor crystallographic data at present in hand will permit of my stating that this nodular material is really a distinct mineral species, but I hope soon to have an opportunity of settling the point.

In order to show the general composition of the "drier" guano deposits, in which hannayite, newberyite, dittmarite, muellerite, and the nodular mineral most usually occur, I quote the following analysis:—

Water	19.80
Organic matter*	52.83
Ash†	27.37
	100.00

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METHOD FOR THE ESTIMATION OF THE TOTAL ALKALI, THE FREE ALKALI, AND THE CARBONATED ALKALI IN SOAPS.

By R. HENRIQUES and O. MEYER.

ONE single process can be used for determining the free and carbonated alkalis, which are usually present in small quantities only (2 to 5 per cent), at the same time as the alkalis of the fatty acids, in most household soaps. This process is based on the use of absolute alcohol, which dissolves the alkaline soaps and the free alkali, while

* Nitrogen (nearly all nitrates), 2.98.

† The ash contained—

Silica (and insol. in HCl 1:11 sp. gr.) ..	3.65	K ₂ O	1.79
Fe ₂ O ₃ ·Al ₂ O ₃	5.23	P ₂ O ₅	5.38
CaO	2.00	SO ₃	1.57
MgO	0.58	SiO ₂ (sol.)	1.06
Na ₂ O	2.93	CO ₂	2.00

The ash contained only a mere trace of manganese—a remarkable fact when we note the more than appreciable quantity of that substance contained in each of the minerals occurring in the guano.

apparently leaving the carbonated alkali intact. Unfortunately, this latter also is fairly soluble in absolute alcohol, and, further, the large percentage of water present in all soaps does not allow of the direct application of the method in question to soap. It is indispensable to thoroughly dry the soap under examination, and many other difficulties have also to be surmounted. Again, and this is the weakest point of the method, the free alkali becomes partially carbonated, which leads to results altogether erroneous.

The small apparatus, of which the following is a description, enables us to determine in a very simple manner and with great accuracy, not only the free and carbonated alkali, but also a certain number of other constants, in such a way that a complete analysis of a soap can be effected very rapidly and without difficulty. It consists of an Erlenmeyer matras of about 400 c.c. capacity, fitted with a cork pierced with three holes. One of these holes takes a small funnel, of about 100 c.c., furnished with a tap, the others take respectively the inlet and outlet air tubes. The air passing through the inlet tube is previously freed from its carbonic acid by being passed through a wash-bottle filled with strong soda-lye; the air is next passed through a drying flask filled with concentrated sulphuric acid. This apparatus is completed by a chloride of calcium tube, and a tared potash tube to retain the carbonic anhydride resulting from the decomposition of the soap. Finally, a 3 litre aspirator fitted with a syphon and pinchcock completes the apparatus.

The following is the method of working we adopted:—From 5 to 10 grms. of the soap are placed in the Erlenmeyer matras; this is dissolved in about 100 c.c. of warm water, and allowed to cool; the matras is then connected with the rest of the apparatus, and after making sure that the whole system is air-tight, dilute hydrochloric acid is run in through the funnel. Some excess of acid may be used when only the carbonated alkali is to be estimated; but if we also wish to determine the proportion of free alkali present, it is necessary to use an accurately measured volume of demi-normal acid. In all cases, however, this volume must be more than that actually needed for the complete decomposition of the soap. If the sample taken is 5 to 10 grms., 50 c.c. of demi-normal acid will suffice. The acid is run into the soapy liquor, the funnel rinsed, the tap closed, and a slow current of air allowed to pass through the apparatus. The matras is then heated gently, and it is the intensity of the heat which governs the regularity of the decomposition of the soap. The flame of the Bunsen burner should be regulated to about the size of a nut. After from thirty to forty-five minutes, provided the decomposition has proceeded regularly, the fatty acids ought to collect in a clear melted layer, and the whole of the liquid should be almost boiling.

As soon as the first drops of condensed steam reach the outlet tube the flame is removed, and the current of air allowed to pass for thirty or sixty more minutes, to completely drive out all the carbonic anhydride and bring it to the potash apparatus. It then suffices to weigh the latter to determine the weight of carbonate.

If, at the same time, we wish to determine the free alkali, we must continue in the following manner:—After absorbing the whole of the carbonic anhydride, the apparatus is disconnected, the funnel is well washed, the wash-water being allowed to run into the soapy liquor, which is once more brought almost to the boiling-point, and we continue the determination by Hehner's method; that is to say, the insoluble fatty acids are collected on a filter, and washed with warm water until the washings are no longer acid. The total aqueous solution is then titrated with demi-normal soda, taking into account the amount of demi-normal hydrochloric acid used for the decomposition of the soap.

In this manner we arrive at the *total alkalinity*.

The insoluble fatty acids are now dissolved in warm alcohol, and the alcoholic solution obtained is titrated