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To cite this article: J. Denham Smith Esq. (1845) XII. On the composition of some varieties of South American Guano; with the description of a new mode of estimating Ammonia, and of a process for separating Lime from Magnesia, when these earths exist in combination with phosphoric acid , Philosophical Magazine Series 3, 26:171, 123-141, DOI: [10.1080/14786444508562683](https://doi.org/10.1080/14786444508562683)

To link to this article: <http://dx.doi.org/10.1080/14786444508562683>



Published online: 30 Apr 2009.



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object-glass of a telescope were analysed by absorption (which might be done by putting a piece of blue glass before the object-glass), I fancy that some insight into this subject might be gained. I can show, I think, that exactly the same mixture of colours may possibly take place in the spectrum produced by diffraction, as in the common prismatic spectrum.

Balham, Surrey, December 27, 1844.

M. O'BRIEN.

[To be continued.]

XII. *On the Composition of some varieties of South American Guano; with the description of a new mode of estimating Ammonia, and of a process for separating Lime from Magnesia, when these earths exist in combination with Phosphoric Acid.* By J. DENHAM SMITH, Esq.*

THE results of the following examinations of guano, necessary as a matter of business to myself, may prove of some interest to the Society, as they serve to confirm, in most points, those arrived at by previous analysts, especially with respect to the variableness of the composition of this substance. When I commenced these analyses I had but one sample of guano in my possession, which came through the hands of a broker in 1842, of the purity of which I could not be certain before analysis. Subsequently I was successful in obtaining genuine samples of South American guano direct from the warehouses of the importers, the bulks from which these specimens were taken being at the present time in the course of consumption in this country.

South American guano, as imported, presents itself in three distinct states, although these varieties are often mixed together in the same bag. The larger proportion of it consists of a damp pulverulent substance of various tints of brown, intermixed with nodules, usually of a lighter colour than the powder; some of these nodules are soft, easily crushed by the finger, and often present light brown silky crystals when broken; others are much harder, of a dirty white and uniform texture throughout.

The second variety exists as large concretions, often weighing several pounds, presenting various aspects when broken; sometimes appearing merely to be the first variety in a coherent, instead of a pulverulent state; at other times as a regularly stratified deposit of different shades.

The third description of guano occurs in irregularly shaped masses, very heavy in comparison with the other varieties, and

* Communicated by the Chemical Society; having been read May 6, 1844. On the composition and chemical history of guano, see also Phil. Mag. S. 3. vol. xxi. p. 385, and vol. xxiv. p. 317, 395, 470.

termed "stones" by the labourers; when broken, this variety presents a crystalline fracture, resembling a fused salt of a brown colour; it appears to exist in large quantities in the guano when imported, for at the warehouses whence I obtained my samples, I was told that at least a hundred tons of it had been picked from the guano they had hitherto sent out for consumption. For the sake of distinguishing this variety, I shall term it "Saline Guano," whilst the second kind I shall call "Concrete Guano."

After a preliminary qualitative examination of these varieties of this manure, the utility of another and probably more exact mode of estimating ammonia than by condensing the gas in hydrochloric acid and evaporating the solution to dryness, and a more economical and less troublesome plan than by a salt of platina, became obvious. I therefore had recourse to an indirect method of analysis, that of estimating the ammonia from the quantity of carbonate of barytes obtained. I preferred a salt of barytes to any other substance forming a true neutral carbonate, on account of the high atomic number of barium, and its consequent capability of expressing with exactness the quantity of ammonia, as well as the great delicacy of a salt of barytes in evidencing the existence of carbonate of ammonia, for which purpose this substance is superior to a salt of lime, or even to lime water.

The point which appeared most likely to occasion error was, that the carbonate of ammonia might not be obtained as a true neutral carbonate; as a basic carbonate would of course vitiate the results, and the frequency of the occurrence of such combinations we all know since the publication of Rose's excellent paper on this subject. Experiment showed that the neutral carbonates of potash and soda, distilled with a solution of an ammoniacal salt, afforded a basic carbonate of ammonia, the solution being alkaline after a salt of barytes had been added until no further precipitate fell, and that a current of carbonic acid gas produced a precipitate in such a solution when filtered. The acid carbonates of soda and potash answered well enough where the ammonia existed in small quantities, but when a large proportion of the volatile alkali was present in the liquor subjected to distillation, the distilled solution evidently contained a basic carbonate, as when the ordinary carbonates of soda and potash were used. It now remained to be proved whether the acid carbonates of ammonia would afford correct results. To determine this point, 59 grs. of sesquicarbonate of ammonia, taken from the centre of a lump, were dissolved in cold water and precipitated by excess of nitrate of barytes, the solution being exposed to the air in an open

dish for twenty-four hours: this precipitate, collected, washed and dried, weighed 98·07 grs., indicating an excess of '012 in estimating ammonia, merely an error of experiment to this trifling amount. The solution when gently heated evolved a little carbonic acid, but did not deposit any carbonate of barytes. Satisfied by this experiment that the acid, as well as the neutral carbonates of ammonia, precipitate a barytic salt equatomically as respects the bases, and therefore that the proposed plan of indirect estimation of ammonia was an accurate one, I subjected 54 grs. of muriate of ammonia to distillation with an excess of a solution of the ordinary carbonate of soda, carrying on the distillation until about one-half of the liquid had passed into the receiver, in which distilled water was of course placed; long before this quantity of liquid was distilled a slip of turmeric paper suspended from the tubulure of the retort ceased to be reddened; the contents of the receiver, a solution of a basic carbonate of ammonia, were added to a solution of nitrate of barytes, and then subjected to a stream of carbonic acid gas until the precipitate became arenaceous and the solution slightly affected litmus paper; this exposed to the air for a day, and the precipitate collected, and dried, gave 97·63 grs. of carbonate of barytes. As in the former case, the filtered solution when gently heated gave off a little carbonic acid gas, but deposited nothing. These results being so favourable, and the process simple, the trifling deficiency evidently being traceable to defective manipulation alone, I have adopted this process for estimating ammonia in the analyses subsequently detailed, considering it susceptible of greater accuracy than the hydrochloric acid method, and as accurate as, and far less troublesome and expensive than, the employment of salts of platinum, and of alcohol for this purpose.

The process for separating the phosphate of lime from the phosphate of magnesia depends upon the insolubility of the oxalate of lime in very dilute acetic acid, and the solubility of the magnesian salt in that menstruum. Thus, when a solution of these mixed phosphates in hydrochloric acid is treated with ammonia slightly in excess to precipitate the characteristic gelatinous precipitate, and acetic acid is gradually added till such precipitate is redissolved, the solution being acid to litmus paper, but only faintly so to the taste, oxalate of ammonia produces the characteristic precipitate of oxalate of lime, which base is completely thrown down; the filtered solution, when evaporated and treated with a little phosphate of soda and ammonia, affording the ammoniacal magnesian phosphate, which contains no lime. I do not give this process as one which is necessarily rigidly accurate, for if the

acetic acid be in too great excess, more than completely sufficient to redissolve the precipitate produced by ammonia, the clear solution, although containing no magnesia, will at times, as I have found, give indications of the existence of lime on supersaturation with ammonia; but the quantity under such circumstances held in solution is too small to be of importance except in cases where a scientific point is involved. Where oxalate of lime is in solution together with the magnesian and calcareous phosphates, this process requires some modification, which it may be better to explain in the details of the mode I have adopted in the analysis of guano, than at present—that recapitulation may be as much as is possible avoided.

It may be advantageous here to describe the mode of analysis pursued in the examination of these samples of guano, as each analysis, in fact, consists of three separate ones, viz. of those portions soluble in cold water; the substances which dissolved on boiling the residue insoluble in cold water, in abundance of water; and the portion which remained insoluble in either menstruum. This division I found to be a very convenient one, as the solutions obtained were far less complex than if the portions of the guano soluble in water cold and hot, and in acids, had been mixed together; and it of course gives a pretty correct idea of the salts as they actually are presented to the roots of plants manured with guano. My reasons for combining the bases and acids as I have done in the results of these analyses are, that in some cases the proportional quantities of acid and base have tallied, and also that I have obtained by crystallizing the hot and cold solutions, oxalate of ammonia, oxalate of soda, muriate of ammonia, chlorides of potassium and of sodium, sulphates of soda and potash, urate of ammonia and free uric acid, from the various samples of guano; and also that by microscopic examination crystals of the chlorides and of sulphate of soda have been readily observed in the mass of the guano. As I have also given the amount of bases and acids obtained without reference to the state of combination in which they exist, those who differ from me in this respect, can combine them as they think proper.

The mode adopted for determining the respective amounts of the fixed alkaline bases is open to many objections. It is complex; a very slight error in weighing is liable to considerably vitiate the result: if the whole numbers I have adopted as representing the combining equivalents of the various acids and bases are incorrect, so also must the results be. On the other hand, I have tried this method upon an

actual mixture of soda and potash salts, and the results approximated very closely to the truth; and upon the whole, weighing the advantages of this indirect system of Griffin's with the positive modes of estimating the potash, either by perchloric acid, tartaric acid or platina salt, I believe this indirect mode to afford, in careful hands, at least as accurate returns, if not more so, than the direct modes of estimating the potash, and ascertaining the soda from the loss. I may be wrong in attributing this process to Mr. Griffin, as Barreswil and Sobrero assign it to M. Mayer, with a date anterior to Griffin's description in the *Philosophical Magazine*.

With respect to the neutral phosphate of lime stated to exist in the sample of "Concrete Guano, No. 6," and also in No. 2, I may state that it precipitated as neutral phosphate; and if I had estimated it as bone-phosphate, the sum of the analysis would have fallen very far short of the quantity employed; whilst by estimating it as I have done, the loss was most trivial, amounting only to a common error of analysis. Of the solubility of the phosphate of lime, and of the ammoniacal magnesian phosphate in boiling water, it is simply necessary to refer to the already established solubility of these salts in neutral solutions containing organic animal matter, and also to state that these solutions were invariably faintly acid to litmus paper.

I was led to suspect the existence of a volatile acid in guano, but I in vain tried to isolate it, if indeed it exists, and the acid odour and reaction are not truly to be attributed to the reaction of the sulphuric or phosphoric acids, the agents made use of in the attempt, upon the organic portions of the guano.

The quantity submitted to analysis was in each case either 300 or 500 grs., and the results were calculated to 1000 parts for the convenience of ascertaining the per-centage, and for greater readiness of comparison.

The water was determined approximately, by drying till the portion lost no more weight, without any sublimation taking place. Water and ammonia were volatilized. This estimation of the water was corrected by subtracting the sum of the weight of the soluble salts, and portions insoluble in cold water, ascertained during the subsequent process, from the original weight of guano employed. A given weight of the sample of guano to be examined was ground up with cold distilled water; when the insoluble portions had subsided, the solution was passed through a filter and the residue washed with two or three successive portions of distilled water; the insoluble residue was then placed on the filter, and treated with distilled water until salts of lime and barytes, being added to a

few drops of the solution, gave no precipitate, or but a faint trace of one. The insoluble residue was dried at 212° , its weight was noted, and the aqueous solution, which usually amounted to about a pint and a half, was accurately measured, and its quantity made up to exactly 32 or 40 fluid ozs. This solution, when freshly prepared, was generally neutral or slightly acid; in no one instance have I found it alkaline, but it became so when kept in a stopped bottle for some days.

One-sixth or one-eighth of this solution acidified with nitric acid and treated with nitrate of silver gave the amount of chlorine—hydrochloric acid. The same quantity similarly treated, but with barytes instead of silver, indicated the quantity of sulphuric acid.

Another portion, slightly acidified with acetic acid (a few drops are sufficient), and treated with hydrochlorate of lime, gave, if any oxalic acid were present, the amount of that acid, the precipitate of course being treated in the usual way; to this filtered solution, having previously boiled it and taken care that an excess of lime salt was present, was added excess of ammonia, which precipitated the phosphoric acid as bone-phosphate; this result was corrected by the weight of phosphate of silver obtained during a subsequent operation.

The quantity of ammonia was determined by distilling one-fourth or one-sixth of the solution in the mode described in a foregoing part of this paper.

If potash and soda were both found to exist in the solution by previous experiment, the following operation was carried completely out; if one only of these alkalies were present, the process was discontinued when the weight of the alkaline sulphate had been determined. One-fourth at least of the solution was gently evaporated, by which it became markedly acid; this evaporation was carried to dryness till no more water was given off, taking care to avoid volatilization of any salt of ammonia, although uncombined ammonia had been liberated during the evaporation; when quite dry it was confined for a few hours over a mixture of powdered lime and sal-ammoniac, then the vessel containing the residue of the evaporated solution was gently warmed and weighed; this afforded the quantity of solid matter contained in the cold aqueous solution, together with traces of water combined with salts and organic matter. This residue was then ignited, the organic matter and ammoniacal salts were expelled, and the loss, deducting from it the weight of the salts of ammonia, was estimated as organic matter with a little water; the fused residue was dissolved in water and precipitated by nitrate of silver; this precipitate, when collected, fused and weighed, and the fused salt of silver treated

with nitric acid and its loss of weight noted, expressed the quantities of phosphoric acid and chlorine contained in the fused saline residue. To the original solution hydrochloric acid in slight excess was added; the chloride of silver thus formed was separated, and the clear solution was evaporated with so much diluted sulphuric acid, as would have been sufficient to convert the whole of the fused saline residue into sulphate of soda, had it consisted entirely of chloride of sodium; this evaporation being very carefully conducted and the residue transferred to a platinum crucible, in which it was heated to full redness until no more acid fumes were given off, the crucible with its contents was accurately weighed, and the weight noted; if one alkali only was present, its weight was calculated from that of the sulphate; but if both potash and soda were contained in the specimen of guano under examination, the mixed sulphates thus obtained were dissolved in water, the solution was treated with a salt of barytes in the usual way, and the resulting sulphate of barytes was weighed with the most scrupulous care. The respective weight of each alkaline sulphate contained in the solution was then calculated by the following formula, which I subjoin, as the steps in the calculation are much more readily perceived in figures than expressed in words:—

$\text{KOSO}_3 \text{ BaOSO}_3 \text{ KOSO}_3 \text{ BaOSO}_3 \text{ NaOSO}_3 \text{ BaOSO}_3 \text{ NaOSO}_3 \text{ BaOSO}_3$

88 : 116 :: 1 : 1·31818 . 72 : 116 :: 1 : 1·61111
 —1·31818 = 0·29293 the difference. Let the weight of the mixed sulphate be 48·54 grs., then $1·31818 \times 48·54 = 63·984 - 70·525$, weight of sulphate of barytes obtained by experiment = $6·541 \div 0·29293 = 22·33$ sulphate of soda — $48·54 = 26·21$ sulphate of potash, and from these weights the respective proportions of the bases may be calculated*.

The actual amount of the chlorine or hydrochloric acid, the sulphuric, phosphoric and oxalic acid, of the ammonia, potash, soda, organic matter, &c., contained in the cold aqueous solution, were ascertained by calculation, as well as that of the water.

The residue insoluble in cold water was then ground to powder, and a known weight of it was boiled with three or four successive half-pints of distilled water, for about an hour after each addition of water; the mixture was then allowed to deposit the undissolved portions, the solution being kept hot during this subsidence and filtered whilst still at that temperature. When water boiled upon this residue came off colourless, and

* See Phil. Mag. vol. xiii. pp. 132 *et seq.* and Barreswil and Sobrero's *Appendice aux Traités d'Analyse Chimique*, p. 41.

contained only minute traces of soluble matter, the insoluble portion was collected on a filter, dried at 212° and its weight noted. The mixed solutions being gently evaporated to dryness, the product was weighed and treated with cold water, the weight of the matter insoluble in the cold water was noted, and the substance reserved; the solution obtained by thus treating it, being again evaporated to dryness, was weighed, ignited, and the loss of weight noted, indicating the organic matter, with traces of water and ammonia; the fused residue was treated with water, the filtered solution precipitated with nitrate of silver, and the weight of the phosphate of silver was ascertained; this was assumed to be due to the presence of phosphate of soda, but the quantity was always too small to ascertain whether this alkali or potash was present; the portion insoluble in water was then dissolved in a little hydrochloric acid and treated in the manner before described, to estimate the proportion of phosphate of lime and phosphate of magnesia.

The reserved portion, which was insoluble in the cold water, was then treated to ascertain the existence and proportion of free uric acid. It was boiled in successive small portions of water, four or five fluid ounces each time, until the solution ceased to become turbid on cooling; these solutions were mixed together, boiled, and allowed to cool very gradually: if free uric acid were present a few crystalline grains of this substance would be deposited, which, when weighed, were ascertained to be uric acid by means of potash and nitric acid. The portion left undissolved by these small portions of boiling water was then treated with a few drops of very dilute potash, the absence of ammonia was proved by test-paper, and the solution precipitated by sulphuric acid, which threw down the uric acid as a voluminous precipitate, which by repose was converted into crystalline grains; this was weighed, added to the weight of uric acid previously obtained, and the loss was estimated as organic matter: the solution of urate of ammonia was evaporated, its weight ascertained, then ignited, and the ashes, if necessary, analysed for lime and magnesia, in the manner before described.

The third division of the analysis was commenced by ascertaining, by means of potash, whether any uric acid or urate of ammonia was present in the residue left undissolved by the repeated boiling with water. If these substances were absent, care being taken at the same time to note whether the residue gave off any ammonia when thus treated, and the presence or absence of ammonio-phosphate of magnesia being thus ascertained, (supposing no urate of ammonia nor uric acid existed in the residue) a given weight of it was boiled with diluted muriatic

acid and filtered; in no one instance did any evolution of carbonic acid take place; the solution was then treated with ammonia in excess, which precipitated the oxalate and subphosphate of lime, perhaps the magnesia also; acetic acid was then rapidly added until it was distinctly acid to litmus paper, and a slight acidity could be detected by the taste; the insoluble precipitate being collected, thoroughly washed, dried, and ignited with the usual precaution, indicated the amount of the oxalate of lime; this precipitate was invariably examined for phosphate of lime; if it contained any, this was separated in the state of bone-phosphate and estimated as neutral phosphate, in which state of combination it existed mixed with the oxalate of lime.

To the acetic acid solution excess of oxalate of ammonia was added, this precipitated the lime present in the solution originally as bone-phosphate, sometimes mixed with neutral phosphate of lime, and from the weight of the resulting carbonate of lime, and the loss of weight sustained by ignition of another portion, correcting each other, the amount of the phosphate of lime was calculated. The filtered solution evaporated until a slight pellicle began to form, was treated with ammonia in excess, and a little phosphate of soda, observing the usual precautions recommended by Berzelius, and the resulting ammoniacal phosphate of magnesia was collected and weighed. The portion insoluble in hydrochloric acid being treated with potash gave a solution possessing the properties described to belong to an alkaline solution of the substance termed humus or humic acid; this was precipitated, collected and weighed; the residue insoluble in potash was weighed and ignited, the loss of weight noted, and the product treated with hydrochloric acid; if effervescence ensued on this addition from the presence of carbonate of lime, this was estimated as oxalate, and was added to the amount already obtained of that salt; by these means the proportion of the organic matter insoluble in potash, the humus, oxalate of lime (if any), sand, &c. &c. undissolved by hydrochloric acid, were obtained.

The proportions in which these substances existed in the guano were then ascertained by the necessary series of calculation.

Where the proportions of acid and base, as ascertained by analysis, did not exactly agree, the estimate derived from the quantity of the acid was preferred, as being far less subject to error than the process for estimating the respective amounts of the potash and soda; the requisite loss or gain was always placed to the soda, and this will account for the differences of the losses sustained between the constituents of these samples

of guano when combined, and the table, which shows the constituents according to the results of analysis.

I cannot deny that this mode of analysis is extremely tedious and complex, and I fear that this complexity, combined with a wish to avoid all unnecessary prolixity of description, has rendered its details in many places obscure. I could wish to have described a simpler and shorter mode; but in a product consisting of some fifteen to twenty substances in various states of combination, a simple mode and brevity of description of analysis are I fear impossible. For ordinary purposes of estimating the comparative value of a sample of guano, this mode of analysis is both unfitted and unnecessary, the estimation of the amount of uric acid, of ammonia, of phosphate of lime and magnesia, with the sand, &c., being quite sufficient for such purposes, and a more detailed analysis would, in the majority of cases, be both time and trouble thrown away.

Composition of a sample of South American Guano in my possession since 1842.—This guano was of the colour of Lundyfoot snuff, with dirty white lumps intermixed, varying in size from that of small shot to that of marbles. The quantity submitted to analysis was 500 grs.

No. 1.

Calculated Composition.		Constituents.		
Soluble in cold water.	Moisture with combined water	222.00	Moisture and combined water	222.00
	Muriate of ammonia	25.5	Hydrochloric acid ...	17.50
	Sulphate of potash, trace of sulph. soda	80.0	Sulphuric acid	36.40
	Oxalate of ammonia	74.0	Oxalic acid.....	50.30
	Phosphate of ammonia	63.3	Phosphoric acid.....	43.00
	Organic matter	15.0	Potash	43.71
Soluble in boiling water.	Urate of ammonia.....	154.18	Ammonia	52.05
	Uric acid	25.16	Organic matter	15.00
	Animal matter, with water and trace of ammonia.....	11.80	Uric acid	165.23
	Phosphate of magnesia and ammonia .	5.64	Ammonia	14.77
	Phosphate of soda ? .	1.20	Phosphoric acid.....	4.19
	Phosphate of lime...	1.86	Lime.....	1.00
Insoluble in water.	Oxalate of lime	25.60	Magnesia	0.77
	Phosphate of lime ...	197.50	Soda ?.....	0.57
	Phosphate of magnesia	20.30	Animal matter, water	13.31
	Sand, &c.....	15.60	Oxalic acid.....	14.40
	Humus	26.36	Phosphoric acid.....	102.03
	Other organic matter with combined water	34.56	Lime.....	118.72
Loss	0.44	Magnesia	7.25	
		Sand, &c.....	15.60	
		Humus	26.36	
		Water, with organic matter	34.56	
		Loss	1.28	
	1000.00		1000.00	

The next sample very much resembled the guano just described, in its physical character; some of the small lumps were of a dirty white colour, and when broken showed no appearance of crystalline structure; these were chiefly composed of phosphate of lime; others showed brown silky crystals in the interior, which, examined under the microscope, appeared to be sulphate of soda and oxalate of ammonia. This, as well as all the succeeding varieties of guano mentioned, was obtained in January last; this specimen was considered by the importers to be of a very superior quality. The quantity analysed was 500 grs.

No. 2.

Calculated Composition.		Constituents.		
Soluble in cold water.	Water.....	215·10	Water.....	215·10
	Organic matter with combined water...	61·74	Organic matter with combined water...	61·74
	Sulphate of soda	37·90	Sulphuric acid	21·06
	Phosphate of soda...	35·82	Phosphoric acid.....	55·02
	Phosphate of lime...	12·56	Oxalic acid	68·18
	Phosphate of ammonia with some bi-phosphate	30·06	Hydrochloric acid ...	24·14
	Phosphate of potash	20·02	Lime.....	6·56
	Muriate of ammonia	35·22	Ammonia	51·68
	Oxalate of ammonia	100·38	Potash.....	11·44
	Urate of ammonia...	25·12	Soda	33·70
Soluble in boiling water.	Phosphate of ammonia and magnesia .	4·04	Phosphoric acid.....	4·30
	Phosphate of soda ? .	1·28	Magnesia	0·56
	Phosphate of lime ...	2·88	Ammonia.....	2·66
	Animal matter	6·38	Soda ?.....	0·60
	Oxalate of lime.....	107·26	Uric acid	23·08
	Phosphate of lime ...	192·00	Lime.....	1·26
	Phosphate of magnesia, trace of ammonio-phosphate ...	19·84	Animal matter and water	7·40
	Humus	20·60	Oxalic acid.....	60·32
	Organic matter	11·40	Phosphoric acid.....	103·96
	Water.....	42·42	Lime.....	145·74
Insoluble in water.	Sand, &c.....	16·48	Magnesia	7·08
	Loss	1·50	Humus	20·60
			Organic matter.....	11·40
			Water.....	42·42
			Sand	16·48
		Loss, &c.....	3·52	
1000·00		1000·00		

Two other samples of a similar character, but much darker in colour, were qualitatively examined: one, No. 3, contained substances similar to No. 2, both soda and potash, some urate of ammonia and very little sand and dirt; the other, No. 4, was almost destitute of urate of ammonia or uric acid, the faintest trace being discoverable by nitric acid and ammonia, but in too small a proportion to enable me to isolate a particle

of the acid even when acting on 3 to 500 grs. This guano also contained 17 per cent. of sand, &c., consisting apparently of sea-sand mixed with little lumps of granite, and a very dense black sand, resembling Iserine or Menachanite.

The first lump of the "Concrete Guano," No. 5, was about the size of a human skull, soft enough to be readily shred with a knife, and uniform throughout, presenting the appearance of a dark brown mass containing a vast number of minute dirty white granulations. Its scent was very slight, and neither this nor any of the other samples had an ammoniacal odour, but merely the peculiar smell possessed by South American guano. When shred and thoroughly mixed the powder was damp, and almost as dark-coloured as Nos. 3 and 4; very different in this respect from the samples 1 and 2, the analyses of which have already been detailed; 500 grs. was the quantity analysed.

Concrete Guano. No. 5.

Calculated Composition.		Constituents.	
Insoluble in water.	Sol. in cold water.	Water	204.2
		Oxalate of ammonia	93.9
		Phosphate of ammonia	61.24
		Phosphate of potash	77.32
		Sulphate of soda	259.44
	Sol. in boil. wat.	Chloride of sodium	29.22
		Organic matter	6.68
		Phosphate of magnes. and ammonia, and trace of phosp. soda	7.84
		Organic matter	8.60
	Insoluble in water.	Oxalate of lime	109.58
		Phosphate of lime	62.70
		Phosphate of magnesia	8.74
		Humus	8.62
		Sand, &c.	7.20
Water		49.74	
Loss, &c.....		4.98	
• 1000.00			
Insoluble in water.	Soluble in cold water.	Water.....	204.2
		Oxalic acid.....	63.78
		Phosphoric acid.....	79.50
		Sulphuric acid	144.14
		Ammonia	50.00
	Soluble in boil. water.	Potash	38.42
		Sodium	11.09
		Soda	115.30
		Chlorine	18.13
		Organic matter	6.68
	Soluble in water.	Magnesia	1.08
		Ammonia	0.81
		Phosphoric acid.....	3.89
		Water and animal matter.....	10.66
Insoluble in water.	Lime	81.78	
	Oxalic acid.....	61.64	
	Magnesia	3.12	
	Phosphoric acid.....	34.48	
	Sand, &c.....	7.20	
	Water.....	49.74	
	Humus	8.62	
	Loss	5.74	
	1000.00		

The second sample of "Concrete Guano," No. 6, was much harder than the former, and appeared to have been deposited in strata; the colour was lighter than any of the preceding samples and the powder drier; 300 grs. were analysed.

No. 6.

<i>Calculated Composition.</i>		<i>Constituents.</i>		
Insoluble in water.	Water.....	106.66	Water.....	106.66
	Muriate of ammonia	4.43	Chlorine.....	8.66
	Chloride of sodium.	9.50	Phosphoric acid.....	6.40
	Phosphate of potash	14.94	Sulphuric acid.....	6.80
	Sulphate of soda	12.23	Organic matter	2.40
	Organic matter	2.40	Ammonia	1.40
	Oxalate of ammonia	a trace	Potash and soda not separated	19.07
	Organic matter	10.00	Organic matter	10.00
	Phosphate of lime, trace of magnesia.	11.37	Phosphoric acid.....	5.25
	Phosphate of soda... a trace		Lime.....	6.12
Sol. in boil. wat.	Sand, &c.....	20.43	Organic matter, humus, &c.....	29.73
	Humus, organic matter, &c.	29.73	Sand, &c.	20.43
	Phosphate of lime...	664.47	Phosphoric acid.....	385.60
	Phosphate of magnesia	30.56	Lime.....	298.53
	Water.....	80.60	Magnesia.....	10.90
	Loss	2.68	Water.....	80.60
		1000.00	Loss	1.45
			1000.00	

Having previously described the characteristics of "Saline Guano," No. 7, it is needless to recapitulate them here: it is deliquescent, and the solution yielded crystals of oxalate and sulphate of soda, and the chloride of that base. 300 grs. afforded on analysis—

Saline Guano. No. 7.

<i>Calculated Composition.</i>		<i>Constituents.</i>				
Soluble in cold water.	Water.....	77.00	Water.....	77.00		
	Sulphate of soda	191.77	Sulphuric acid	106.54		
	Oxalate of soda.....	105.63	Oxalic acid.....	55.63		
	Phosphate of soda....	3.60	Phosphoric acid.....	23.1		
	Phosphate of potash .	49.47	Hydrochloric acid ...	20.76		
	Chloride of potassium	41.63	Chlorine.....	192.22		
	Chloride of sodium .	286.31	Soda	136.93		
	Muriate of ammonia	30.30	Sodium	114.52		
	Organic matter with combined water...	25.53	Potash.....	28.27		
	Phosphate of lime ...	1.10	Potassium	21.91		
Soluble in boil. water.	Phosphate of ammonia and magnesia .	1.33	Ammonia	9.54		
	Animal matter and water	7.56	Organic matter and combined water ...	25.53		
	Sand, &c.....	4.20	Soluble in boiling water.	Lime	0.60	
	Insoluble in water.	Oxide of iron and alumina		1.50	Magnesia	0.18
Phosphate of magnesia		25.80		Phosphoric acid.....	0.66	
Phosphate of lime...		131.13		Organic matter and water	7.90	
Humus, organic matter, water, &c.		18.36	Ammonia	0.15		
<u>1002.22</u>		Sand, &c.....	4.20	Insoluble in water. boiling water.	Oxide of iron and alumina	1.50
Insoluble in water.		Lime.....	71.63			
		Magnesia	9.21			
		Phosphoric acid.....	76.09			
		Organic matter, humus, &c.....	18.36			
<u>1002.22</u>				<u>1002.43</u>		

On comparing the results of these five analyses, the extreme variableness of the composition of guano is the first thing that demands attention; no two samples resemble each other: in one, potash salts, abundance of urate of ammonia, with free uric acid exist; in another, the salts of the mixed alkalies are present, but the soda salts in far larger proportion than those of potash, and the amount of urate of ammonia diminished from about 17 to 2 per cent.; here also free uric acid is absent; in another instance of ordinary guano, No. 4, no uric acid whatever is present, and this specimen contains a large proportion of sand. The amount of ammonia also varies very considerably in this description of guano, and even the proportion of those salts which are common to both seldom bear any relation to each other. The state of combination in which the phosphate of lime occurs is also dissimilar; that of sample No. 1 apparently existing wholly as bone-phosphate, whilst that of No. 2 is a mixture of the neutral with the sub-sesquiphosphate of lime: instances of dissimilarity may readily be multiplied by a glance at the results of these two analyses, the resemblance to each other being for the most part confined to the existence of some similar salts in both cases.

Then, again, the samples of concrete guano differ not merely from the common guano, Nos. 1, 2, 3 and 4, but also widely from each other; sample No. 5, concrete guano, containing large proportions of sulphate of soda and oxalate of lime, no uric acid, and but a very small quantity, when compared to any of the other samples, of phosphate of lime—this existing in this specimen as bone-phosphate; whilst the other kind of concrete guano, No. 6, affords very small quantities of soluble substances, the merest trace of ammonia salts, and consists almost entirely of water and phosphate of lime. The constitution of this salt again varies from that which exists in the specimen No. 5, being chiefly neutral phosphate instead of the bone-phosphate. The saline guano is the very opposite of this last description; the larger proportion consisting of soda salts and others soluble in water: here also the ammoniacal salts are almost absent, whilst common salt, a substance existing in comparatively small quantities in the other samples, and totally absent in two of them, is by far its most prevalent constituent.

Can we then wonder that such widely differing results should have been obtained by various farmers and experimentalists who have used the substance termed guano; even when its application has taken place under almost identical circumstances, as respects quality of land, description of crop, time of application, &c. &c., and differing only in the guano used by either party

being obtained through different sources? Putting aside all considerations of the mode of application to the soil, it is obvious that the effects of such manures must vary almost as widely as their composition; and that whilst the employment of such guano as No. 1, or even No. 2, would be in all probability attended with highly successful results, the use of the others, or even of these mixed with several lumps of Nos. 5, 6 and 7, would, on the contrary, completely disappoint the expectations of the agriculturist, and probably in some cases, especially where such a kind as No. 7 exists in quantity, or has deliquesced and been absorbed by the other portions of the guano, its application would be attended with positive injury.

The analyses of the ordinary guano detailed in this paper do not differ so considerably from Voelckel's analysis in composition, and the salts which they respectively contain, as to render many observations on this the most complete analysis I have met with necessary. In no one instance of the seven specimens of guano examined by me could I detect carbonate of ammonia in sufficient quantity to affect lime-water, although in two cases out of the seven, nitrate of barytes indicated a faint trace of this substance. The solutions in cold water were either neutral or slightly acid: these solutions distilled afforded a solution which was distinctly alkaline to test-paper, and contained a considerable quantity of ammonia, but it was in an uncombined state, not as carbonate; the residual solution in the retort subsequent to distillation was markedly acid, so that this ammonia arose from the decomposition of the phosphate of ammonia by boiling the solution containing it. Some portions of guano, gently dried and then sublimed, gave off ammoniacal fumes, and a white sublimate from the oxalate, muriate and other ammonia salts, but the sublimate contained no carbonate of ammonia. In this respect my results differ from those of Girardin, Bidard and some others, who describe carbonate of ammonia to exist in considerable quantities in the South American guano analysed by them. May they not have assumed that the ammonia liberated by heat existed as carbonate, as I did myself until these analyses obliged me experimentally to determine the question? Carbonate of ammonia is a substance, which, considering the composition of guano, does not appear unlikely to be produced; so that whilst I admit the possibility and even the probability of its presence on these grounds, yet experiment on seven distinct samples shows that it is absent.

The existence of the free uric acid which separated from the solution in boiling water of No. 1, may be questioned as
Phil. Mag. S. 3. Vol. 26. No. 171. *Feb.* 1845. L

to whether it ought not to be considered as a product arising from the decomposition of a portion of urate of ammonia by the presence of a stronger acid, rather than as existing in the specimen of guano in an uncombined state. This I cannot consider to have been the case; for although, like the other solutions made by boiling water, it was faintly acid, yet in No. 2 no free uric acid was discovered, although the urate of ammonia in that specimen existed under precisely the same circumstances as in the analysis of the first sample; and if uric acid had been evolved in the first instance from its combination with ammonia, this salt surely ought not to have escaped decomposition in the second case. I am therefore induced to consider it as highly probable that, when the dung of which guano is composed is freshly deposited, the uric acid which it contains is not wholly in a state of combination with ammonia, but that a portion exists as free uric acid.

I must now allude to the production of the oxalate of ammonia which is so constantly found in guano, being compelled on this point to differ with Dr. Fownes.

I am no friend to the hypothetical deductions which are now so constantly employed in organic chemistry. They may have their uses in leading the experimenter to the selection of the right path and the proper mode of investigating organized substances; but the abuses they are apt to engender, too often, I fear, more than counterbalance their advantages. Instances of the elevation of hypothesis to the rank and consideration due to ascertained and undoubted facts, and the erection of other theories upon the first hypothesis, are to be found thickly strewn throughout nearly every chemical publication of the present day; nor are the works of some of the most distinguished chemists free from this objection, but rather might be referred to as furnishing the most flagrant instances of this indulgence of a luxuriant imagination. In accordance with this usage, the sole requisite conditions to produce any given organic compound which may be known or imagined to exist, is to commence with a something which need contain but two elements, carbon and azote, and these are almost superfluous; add to this substance the oxygen of the atmosphere and water, as much as may be sufficient, liberate hydrogen, ammonia, oxygen, carbonic acid or azote, as may be necessary, and there is the substance sought for—*on paper*.

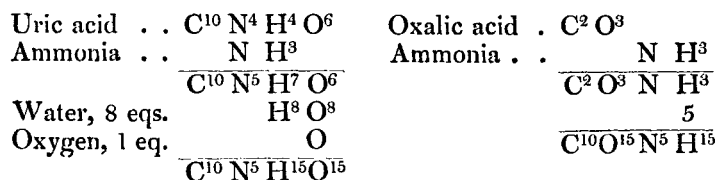
To return, however, to the formation of the oxalate of ammonia: it must, I presume, be formed from the urate of ammonia, because guano does not contain any other substance, except by such a process as is detailed above, which can produce it; in this, I believe, all chemists are agreed.

Now Dr. Fownes supposes that the uric acid of the urate of ammonia combines with eight equivalents of water and two of oxygen from the air, and produces four equivalents of oxalate of ammonia and two of carbonic acid, which of course unites, although it is not so stated in the note I refer to*, with the equivalent of ammonia before combined with the uric acid, producing the bicarbonate of ammonia, not the most volatile nor soluble of its salts, and which, if formed, surely ought to be found in every sample of guano. Now various specimens of guano have been examined, seven in number, in what we may suppose to be all the progressive stages of this conversion of the urate into the oxalate of ammonia; one containing uric acid, urate of ammonia and oxalate of ammonia; a second containing the two salts only; and others in which the uric acid and urate of ammonia have wholly disappeared, and oxalate of ammonia alone remains: yet in no one of these specimens of the guano has the substance, bicarbonate of ammonia, which is required by Dr. Fownes's theory, been detected; its presence would not necessarily have proved the theory to be correct, as it might fairly and possibly be attributed to the decay of azotized animal matter: but I respectfully submit that the absence of this ammoniacal salt proves this hypothesis of the conversion of urate into oxalate of ammonia to be erroneous. After the opinions I have uttered respecting the employment of hypothetical deductions, it is certainly vastly inconsistent on my part to have recourse to them, but it will tend to prove the truth of my former remarks on the readiness with which a theory in organic chemistry may be constructed, when no inconvenient nor insurmountable facts are opposed to it. In detailing this theory of the conversion of the urate into the oxalate of ammonia, I am more than indifferent to its fate; for gladly will I lend a helping hand to put an extinguisher upon it, if one based upon the actual and experimental conversion of the one salt into the other, a result I have endeavoured in vain to effect, is propounded.

Since Coindet's observation, that the uric acid in the excrement of birds existed as binurate of ammonia, the equivalent number of uric acid seems by general consent to have been doubled, so that this acid salt, according to Coindet's view, must now be considered as neutral urate of ammonia. Like Dr. Fownes's, my hypothesis of this conversion is an absorption of water and very slight oxidation, differing from his only in the proportions of these convenient substances, and in the conversion of the urate into the oxalate of ammonia without the formation of carbonate of ammonia or any other secondary

* Memoirs of Chemical Society, part 3, p. 38.

products,—one equivalent of urate of ammonia combining with 8 equivalents of water and 1 of oxygen, and producing 5 equivalents of oxalate of ammonia.



This theory has simplicity to recommend it, and is in accordance with observed facts, so far as they go; but after all it is merely hypothesis, and rests upon no experimental proof whatever; and I neither have faith in it myself, nor recommend it as worthy of credence by others. A more legitimate subject of speculation than the mode in which the oxalate of ammonia found in guano is produced, is the origin of guano itself and of its varieties. The large lumps found in the bags of guano, which I have termed “concrete guano,” appear to me to have been taken from the oldest portions of the beds of this substance, and in which decay of the organic salts and animal substances has proceeded further than in common guano, and that concrete guano is merely ordinary guano in an advanced stage of decay agglomerated by pressure and long contact. This remark applies chiefly to sample No. 5. I consider it probable that samples 6 and 7 are formed from the action of sea water on a bed of guano somewhat deficient in ammonia salts and containing no urate of ammonia; in short, one of the oldest beds on the lower ledges of the coast and rocks. The spray of the sea falling upon a bed of guano in this position mixes with it, the insoluble portions subside in regular horizontal strata, which again dries and hardens, giving rise to the formation of masses consisting chiefly of insoluble substances, as in the specimen No. 6, whilst the solution collecting in the crevices and hollows is subsequently dried by evaporation in a dry atmosphere, and forms the saline guano, No. 7, in which common salt so greatly predominates, the oxalate of ammonia being converted by double decomposition into oxalate of soda and muriate of ammonia; the disappearance of the larger portion of the latter salt I can only account for by its well-known tendency, when in a damp state, as existing as a saturated solution, to creep over the sides of the vessels which contain it, by which means it may have separated itself from the sea-water solution previously alluded to before that became quite solid and dry, and thus extending itself over the ledges of rock, assisted in its progress by noc-

turnal dews, has been finally washed away by the sea-water. This is rather an unsatisfactory mode of accounting for the absence of the muriate of ammonia, which from what we know of guano, and the existence of oxalate of soda in the saline guano, we may fairly conclude must have been formed, but which in the sample I have examined contains but little more than one equivalent of muriate of ammonia to three of oxalate of soda, so that nearly two equivalents have disappeared.

As to the respective hypotheses of the coprolitic or recent nature of these deposits, I have never held but one opinion, the one I believe generally entertained, that this manure is deposited by sea-fowl inhabiting coasts where no rain falls, and which consequently is never washed away. This view is supported by all ancient and most modern authorities, and has recently received additional confirmation from Mr. Teschemacher of Boston, who has presented specimens of Peruvian guano to the Philosophical Society of that town, containing *feathers*; and after quoting the accounts given by the old Portuguese historian respecting the formation and preservation of this manure, very justly remarks, that the beds of the greatest thickness hitherto observed might, without any extravagant calculation, and at the rate only of two to three inches a year, or less, be deposited in about three thousand years; whilst the theory of its coprolitic origin not merely requires a considerable exercise of the imagination, but is opposed by the direct testimony of eye-witnesses.

P.S. The May Number of the Philosophical Magazine, which has just come into my hands, contains an analysis of African guano by our Foreign Secretary, Mr. E. F. Teschemacher, in which he finds humic acid to exist in a soluble state in the African specimen, but no urate of ammonia. The humus described to exist in the Peruvian specimens analysed by me was extracted by dilute potash from the residue insoluble in water; and if it be true humus, and it possesses all the characters assigned to that substance, the South American varies from the African guano, amongst other differences, in containing uncombined humus.

XIII. *On certain Results relating to Quaternions.* By ARTHUR CAYLEY, Esq., B.A., Fellow of Trinity College, Cambridge.
To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

IN his last paper on Quaternions, Sir William R. Hamilton has alluded to a paper of mine on the Analytical Geometry of (*n*) dimensions, in the Cambridge Mathematical