

TABLE III—RELATION EXISTING BETWEEN THE SULFUR, PHOSPHORUS AND MANGANESE IN THE GEOLOGICAL AREAS OF KENTUCKY

| VIRGIN SURFACE | | | CULTIVATED SURFACE | | | VIRGIN SUBSOIL | | | CULTIVATED SUBSOIL | | |
|----------------|------------|-----------|--------------------|------------|-----------|----------------|------------|-----------|--------------------|------------|-----------|
| Sulfur | Phosphorus | Manganese | Sulfur | Phosphorus | Manganese | Sulfur | Phosphorus | Manganese | Sulfur | Phosphorus | Manganese |
| D | T | T | T | T | Q | St L-C | T | T | T | T | T |
| C | D | C | RA | RA | RA | RA | RA | RA | RA | RA | RA |
| T | C | Q | D | D | C | T | ECF | ECF | RA | ECF | RA |
| S | RA | RA | C | RA | RA | S | S | St L-C | S | S | Q |
| RA | ECF | WCF | S | ECF | WCF | ECF | WCF | Q | WCF | Q | K-W |
| ECF | Q | St L-C | WCF | Q | D | WCF | St L-C | WCF | ECF | St L-C | WCF |
| WCF | WCF | S | St L-C | WCF | ECF | Q | K-W | D | K-W | St L-C | D |
| Q | St L-C | D | ECF | K-W | K-W | D | D | Q | Q | D | D |
| St L-C | K-W | K-W | K-W | St L-C | St L-C | K-W | D | D | Q | D | D |

Quaternary, Eastern and Western Coal Fields and finally the Keokuk-Waverly, which is generally regarded as the poorest of all.

In a majority of the samples, the cultivated surface as well as the subsoils show considerable losses of manganese when compared with the corresponding virgin. Furthermore, the surface soils of both generally contain more of this element than their respective subsoils.

The counties in which the soils were collected for this work were Wolfe, Graves, Warren, Henderson and Madison; also Nos. 813 to 820 from Metcalfe and Jefferson, or a total of forty samples. The above holds true in all with respect to the manganese content of the surface compared with its subsoil, while in three instances the virgin surface contained less and in two the same amounts of manganese as the cultivated samples.

The remainder of the samples were generally selected from those sent in by the residents of the state for chemical analysis and as it is sometimes difficult to obtain the accurate history of a field for several years past, since in certain sections much of the land is rented to tenants, it would have been better to collect all for this work, but this would have caused considerable delay.

In the Keokuk-Waverly area, commercial fertilizers were used while in some of the others it is very probable that commercial fertilizers or manure had been used in former years. This may partly account for the fact that the manganese content has been maintained in the soils of this area as well as in some of the others.

The large losses of manganese in some of the cultivated soils are hardly to be explained as due to the amounts removed by the different crops grown on them for the accumulated analyses show that the ordinary crops do not contain sufficient amounts of this element to justify this conclusion. It may be that cultivation converts the manganese compounds into soluble forms which are readily leached out and thus lost in the drainage water. This is a matter that needs further investigation, and the writer desires, as soon as an opportunity affords, to examine some of the surface and deeper drainage waters of the different areas in order to determine to what extent this element is present.

SUMMARY

I—It has been proven by different observers that manganese is universally present in soils, plants and many animals.

II—The majority of the experiments show that the application of certain manganese compounds, particularly the sulfate, to some crops, is decidedly beneficial. These experiments have further shown that while small applications are in many cases beneficial to plants, large applications are generally harmful.

III—In a large majority of the soils examined, the writer found considerably less manganese in the cultivated surface than in the corresponding virgin samples. The same holds true for the subsoils.

IV—In practically every case, the surface soils of the virgin and cultivated areas contain larger amounts of this element than their respective subsoils.

V—When some former work on these samples is considered, it is found that a majority of the soils contain considerably more manganese than phosphorus, but many samples have much less, while the losses of manganese in the cultivated areas are usually greater than of phosphorus.

VI—There are large differences in the manganese content of the soils of the different geological areas and sometimes in those from the same area. The amounts found in the surface soils vary from 0.005 to 0.331 per cent, and in the subsoils from 0.002 to 0.264 per cent.

VII—As a rule, the better agricultural areas contain much larger amounts of manganese than the inferior areas.

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ON THE COMPOSITION AND VALUE OF BAT GUANO

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At various points in this country, especially in the warmer regions, caves exist which are frequented by bats in such numbers that their excrement or "bat guano" has accumulated in amounts sufficient to give it some commercial importance as a fertilizer.

Generally, the amount of guano is rather limited in any one deposit and in the aggregate, the entire quantity now in sight, or probably to be discovered in this country, is not sufficient to appreciably affect the fertilizer industry. On the other hand, such a deposit may represent a considerable fortune to the individual discoverer or owner, and the frequency with which these small deposits occur, justifies a short discussion of their composition and value.

The following table containing the results of analyses of bat guano samples sent to this Bureau from time to time, shows their composition as well as the locality from which they were taken.

| BAT GUANO ANALYSES | | | | | |
|---|-------|-------------------------------|------------------|----------|----------------|
| Results in percentages, based on air-dry sample | | | | | |
| LOCATION | N(a) | P ₂ O ₅ | K ₂ O | VOLATILE | ANALYST |
| Near Carlsbad, N. M. | 4.24 | 2.31 | 1.28 | .. | J. A. Cullen |
| Guadeloupe Mts., N. M. | 1.77 | 2.68 | 0.41 | 40.0 | C. F. Miller |
| Torreón, N. M. | 10.82 | 1.08 | 1.01 | .. | W. H. Waggaman |
| Oregon Co., Mo. | 8.10 | 2.06 | 0.58 | .. | B. E. Brown |
| San Juan, Porto Rico(b) | 1.00 | 3.40 | 0.21 | .. | W. H. Waggaman |
| San Juan, Porto Rico(b) | 0.50 | 2.40 | 0.29 | .. | W. H. Waggaman |
| El Fondo, Santo Domingo, Haiti | 11.84 | 4.80 | 1.61 | 90.0 | C. F. Miller |

(a) Determined by Mr. T. C. Trescott, of the Bureau of Chemistry.

(b) Both of these samples contained considerable calcium carbonate.

Both potash (K_2O) and phosphoric acid (P_2O_5) were determined by the official method for fertilizers, the former by treatment with concentrated sulfuric acid, ignition and extraction with dilute hydrochloric acid; the latter by treatment with a solution of magnesium nitrate, evaporation, ignition and a similar extraction.

A glance at the table shows that a wide variation exists, not only in the percentages of the fertilizer constituents present, but also in the ratios of nitrogen to phosphoric acid, nitrogen to potash or phosphoric acid to potash. This large variation is attributable to either one, or both of two things: (1) The presence of considerable extraneous matter such as rock debris, etc., or (2) the removal of some of the more available constituents by leaching, or, in the case of nitrogen, by decomposition of the material and subsequent volatilization as ammonia.

It may be said in this connection, that in the more recent deposits, nitrogen is the most valuable constituent, phosphoric acid and potash following in the order given; but on "aging," the nitrogen content decreases very rapidly since most of it is present in an available form.¹

The writer wishes to place particular stress on the sample from Haiti as it represents uncontaminated and practically undecomposed bat guano which is very likely of recent origin, since thousands of bats² spend their days in the cave at the present time. As received in the laboratory, it consists of a dry, dark brown powder, in which the wings and other parts of insects can be seen by the naked eye.³

Over 90 per cent of the phosphoric acid present is water-soluble as is also the greater part of the potash; and if the high percentage of nitrogen, together with the large amount of organic matter (as shown by the volatile determination), are reckoned with these facts, it is evident that the substance is very valuable.

It has been calculated from data concerning the Haitian cave (which had not been fully explored at the time) that it contains approximately seven hundred tons of bat guano. Based on the market prices of 20 cents per pound for nitrogen,⁴ and 5 cents per pound for phosphoric acid and potash, the material is worth (not considering the organic matter, which is a big factor) very close to \$40 per ton, or approximately \$30,000 for the entire deposit. Whether or not this is a representative example is a matter for conjecture, but very likely it is above the average in quantity and it certainly is in quality.

No specific data on the extent of the American deposits already discovered, are available. In several instances, however, they were reported as being of considerable size.

The facts given in this paper warrant the suggestion that a further search for bat guano be made, since

¹ Thompson, E., "Bat Guano in Burma," *Agr. J. India*, 4 (1909), 379-81.

² It has been reported that the "flight of the bats on leaving the cave, in rope-like formation, as large in diameter as an ordinary street car, requires over an hour, by actual timing."

³ For further description see, Tod, W., "Ueber Fledermausguano," *Landw. vers. Station*, 1 (1859), 264-268.

⁴ "Quotation on Nitrogen of Bat Guano," *Bull. Texas Exp. Station*, 160, July, 1913, p. 10.

there is a possibility, or even a probability, of the existence of other valuable, and as yet undiscovered deposits in this country.

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STUDIES IN SYNTHETIC DRUG ANALYSIS—I. ESTIMATION OF ACETANILIDE AND PHENACETIN IN ADMIXTURE

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INTRODUCTION

During the past few years, more particularly since the inception of both federal and State drug enactments, attention has been directed repeatedly to the dearth of adequately tested methods for detecting and estimating medicinal agents. The need of these methods was most keenly felt in connection with certain inhibited substances of synthetic character like acetanilide and its derivatives, antipyrin, cocaine, codeine, heroin and other similarly potent drugs, which find extended application in many of our proprietary medicines.

Aside from these considerations, however, there existed in the case of acetanilide and phenacetin (acet-phenetidin) additional cause, on the part of drug analysts at least, for desiring quantitative methods. The relatively low cost of acetanilide, taken in connection with its pronounced physical resemblance to phenacetin, has already suggested to the unscrupulous the possibility of partial or even complete substitution of the former drug for the latter, and indeed several flagrant instances of such practice are on record. Accordingly, much time and effort have been expended in various quarters in the hope of devising a quantitative separation, though hitherto apparently without marked success. It is evident, however, that any procedure, calculated to determine even approximately the relative proportions of acetanilide and phenacetin in admixture, thus blocking the ways of the sophisticator, must prove welcome to officials and chemists engaged in drug control.

Ordinarily, the preliminary or gross separation of these two drugs from complex mixtures presents no unusual difficulties, being easily effected by extraction with chloroform. It is in the subsequent quantitative partition of the mixture thus isolated where the real problem begins, since no purely physical method, involving, for example, water or any of the commonly available organic solvents, lends itself to a sharp separation. A partial separation may indeed be effected according to Will² with water about as follows: If 1 gram of a mixture of equal parts of acetanilide and phenacetin be shaken with 200 cc. of water, all of the acetanilide goes into solution together with 0.13 g. of phenacetin, the remainder being unaffected. This latter portion is then filtered and weighed. Its weight, corrected by the addition of 0.13, represents the phenacetin originally present in this particular

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² *Pharm. J.*, [3] 21, (1890), 377.