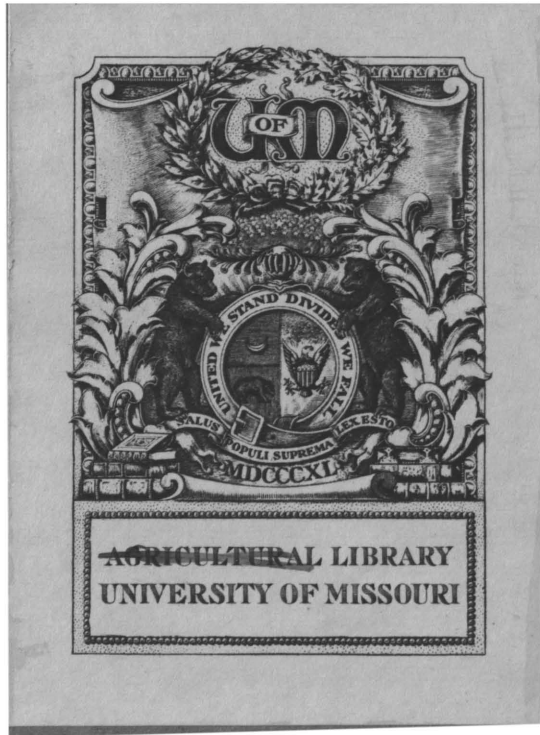


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THE REMOVAL OF LIME  
FROM THE ASH OF COW FECES.

by

*revised*  
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INTRODUCTORY.

While employed in the Government Dairy Research Laboratories at Columbia, Missouri, the writer had occasion to conduct the analytical work in a mineral nutrition experiment conducted on dairy cattle. The principal constituent (and the one with which this paper is to deal) was lime. Rations high and low in lime were fed and the milk, urine and feces were analysed to determine the calcium eliminated. It was in the analysis of the feces-ash that the trouble was experienced that prompted the following investigation.

It was found that in cases where the cow had been fed on certain hays and especially on dirty hays, the ash of this feces ran abnormally high, as high in fact as 20.55%.<sup>1</sup> This abnormally high ash was obtained when the cow was fed on dirty alfalfa hay. When this ash was subjected to treatment with acid, there remained behind in every case, a large acid insoluble residue. Upon looking up the literature on ash analysis, nothing could be found relating to any special methods of analysis of feces-ash. Wherever an analysis of feces-ash has been

1. Dr. P. F. Trowbridge of the Missouri Experiment Station informs the writer that in his experiment on steer feeding he has found the ash to run as high as 39%.

conducted, the regular methods of ash analysis have been employed as applied to plant ashes. Mineral nutrition is a comparatively recent phase of nutrition. Previous investigators have confined themselves almost exclusively to the organic phases of nutrition. The reason for the scarcity of analytical methods regarding the analysis of ash of feces is due to the fact that the percentage of such ash in general is seldom high and does not usually contain much silica. Under ordinary conditions, therefore, there would apparently be little reason for thinking that methods used in analysis of plant ashes would not be applicable to feces-ash.

After noting the evident lack of literature relating to this particular problem, the writer then turned his attention to the methods of ash analysis as applied to feeds and fodders, as stated in the literature.

Leach,<sup>1</sup> in his methods of ash analysis for cereals, feeds and fodders, advises that the ash should be boiled at least ten minutes with hydrochloric acid to remove all constituents.

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1. "Food Inspection and Analysis." Leach. pp 301





Standard methods of analysis<sup>1</sup> are less specific and direct that the material be "treated" with acid until dissolved. It was noted that the time of treatment with acid and dilution of acid were not emphasized. However, with reference to soils in the "Official and Provisional Methods of Analysis," Department of Agriculture,<sup>2</sup> the time of acid digestion is placed at ten hours.

#### Preliminary Experiments.

Owing to the fact that the acid insoluble residue from the ash of cow feces was so large, it was necessary to establish for a certainty the factors influencing the removal of the mineral constituents, for unlike the ashes of plants, cereals, etc., the appearance of the residue after acid treatment revealed nothing. Digestion of the feces-ash with acids of varying strength from ten to thirty minutes was found to give varying results. It was not known at first whether the discrepancies were due to insoluble compounds formed by the high heat of ashing or whether the

1. "Handbook of Inorganic ANALYSIS," Wöhler.  
 "Quantitative Analysis." Olson.  
 "Quantitative Chemical Analysis." Cairus.  
 "Quantitative Chemical Analysis." Talbot.  
 "Official and Provisional Methods." (U.S. Dep't Agr),  
 Bulletin 107.  
 "Aschen Analysen." Abderhalden.
2. "Official and Provisional Methods". (U.S. Dep't of  
 Agr.) Bulletin pp. 107.



time of acid treatment was insufficient.

Fusions were made on some of the acids insoluble residues and it was found that the calcium might serve as an index for all the other constituents, for when the calcium had been entirely removed, all other constituents had then been also eliminated. In a few cases phosphorous was found with the calcium after making fusions of the acid insoluble residues. This seems to be in accordance with the views of Fleurent and Levi,<sup>1</sup> that in the heat of ashing, acid phosphates often act upon the silica.

Owing, therefore, to the fact that calcium was the constituent removed with the greatest difficulty, all other constituents can be considered as having been eliminated when calcium has been completely extracted from the ash. As the volatile constituents, such as sulphur and chlorine, were not determined, the heat of ashing was not conducted at a low temperature for most of the ash.

The reason for the use of dirty hay in this problem was to find as abnormal conditions as possible, so that the methods proposed for use as a result of this investigation would be applicable to all feces high in silica.

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1. "Compt. Rendu." Academy of Science. (Paris)

Vol. 152 (1911-No. 11) pp 55.



These feces were air dried in a large open dish and when dry were ground to a fine powder. A large amount of this powdered sample was ashed to a cream white ash in a platinum dish and the ash placed in a ground glass-stoppered bottle for analysis. For the digestions and boilings, the samples of ash were all weighed out at one time in order that no error due to moisture absorption could creep in.

Ashes of plants have been classified both as to their composition and solubility in acids. Fresenius<sup>1</sup> has divided them into three classes. The division is more or less arbitrary as no well defined line of demarkation can be drawn.

#### Class I.

Ashes in which the carbonates of the alkalies and alkaline earths predominate. Such ashes are afforded by woods, herbaceous plants, etc.

#### Class II.

Ashes in which phosphates of the alkalies and alkaline earths predominate. To this class belong all seeds.

---

1. "Quantitative Chemical Analysis." Fresenius.

Vol. II. pp 799.





## Class III.

Ashes in which silica predominates. These are yielded by the Graminae and Equisetaceae, etc. Alexander Classen divides the ashes of plants into but two divisions.<sup>1</sup>

## Class I.

Ashes decomposed by acids.

## Class II.

Ashes not decomposed by acids.

If one attempts to apply the system proposed by Fresenius, the exact classification of the ash of cow feces would be somewhat difficult. It might possibly come within the limits of Class III., although it would seem better to place it in a class by itself. It is evident, of course, that according to the classification of Alexander Classen it would fall in Class II.

## PLAN OF PROBLEM.

The conditions governing an exact determination of the calcium in ash of cow feces which it seemed necessary to determine may be outlined as follows:

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1. Text Book of "Quantitative Chemical Analysis."

Alexander Classen.



7.

1.

The time necessary to remove the lime by

(a) Digestion of ash with acid over steam.

(b) Boiling the ash with acid on a hot plate.

11.

The comparison of the efficiency of dilute and concentrated acid. (It was finally concluded to use concentrated hydrochloric acid, concentrated nitric acid and dilute hydrochloric acid of the specific gravity of 1.11. This dilution may be made by mixing equal parts of concentrated hydrochloric acid and water.)

111.

The determination of which acid (nitric or hydrochloric) is most efficient.

1V.

The effect of leaching the ash with hot water before treatment with acid.

V.

The effect of the heat of ashing.

VI.

The effect of dilute alkalis to break up silicates not decomposed with acid.

VII.

The efficiency of moist combustion as compared with ordinary combustion.



## PROCEDURE.

In all cases, five gram samples of feces and one gram samples of feces-ash were used. All digestions were conducted in beakers with watch glass covers to prevent loss of acid by evaporation. In the cases where boilings were made Erlenmeyer flasks were used. Little projections were blown in hard glass test tubes near their mouths, so that when these test tubes were filled with water they could be suspended in the mouths of the flasks, acting as condensers for the acid. In all cases, except the moist combustions, seventy-five cubic centimeters of acid were used. All of the work was conducted in guaranteed glassware such as is found in all experiment station laboratories.

After treatment with acid, each sample was filtered<sup>1</sup> and washed with hot water and the filtrate evaporated to dryness.<sup>2</sup> This residue was taken up with dilute acid and filtered and washed. The filtrate containing calcium

1. This acid solution was diluted with distilled water before filtering so that the acid would not attack the filter paper.
2. In a private communication, R.H. Collison of the Ohio Experiment Station advised several evaporations to dryness after treatment with acid, if gelatinous silica formed. In this ash no such trouble was experienced.





was made up to two hundred and fifty cubic centimeters and twenty-five cubic centimeter aliquots were taken for analysis. To these aliquots, ammonium hydroxide was added to alkalinity and the solution was then brought back to slight acidity with acetic acid. After boiling a few seconds to render them more easily filtered, the insoluble phosphates were filtered off and washed thoroughly. The Calcium in the acid filtrate was then precipitated with ammonium oxalate. The solution containing the calcium oxalate was then brought to a boil and set aside to cool. This causes the calcium oxalate to crystallize in larger crystals and therefore prevents any chance of its passing through the filter paper. When cool the calcium oxalate was filtered and washed.

The following method for removing the calcium oxalate from the filter paper was found to be most efficacious. A thin spatula is run carefully around the edge of the moist filter paper and the paper loosened from the funnel. It is then removed from the funnel and carefully opened out flat on the hand, the edge of the paper being placed in the funnel. The paper, being moist, will slide down into and cling to the funnel and remain open and in excellent position for washing with the dilute sulphuric acid.



This is much safer than the usual way of breaking a hole in the filter paper as there is no danger by using this method of any precipitate remaining unnoticed on the filter paper or within the folds.

The calcium oxalate is then dissolved in sulphuric acid and titrated hot, with potassium permanganate in the usual manner.

#### EXPERIMENTAL DATA.

Time required to remove calcium when ash is treated with dilute hydrochloric acid (specific gravity 1.11).

Table 1.

| A.                           |        | B.                           |        |
|------------------------------|--------|------------------------------|--------|
| <u>Digestion over steam.</u> |        | <u>Boiling on hot plate.</u> |        |
| Time.                        | % CaO. | Time.                        | % CaO. |
| $\frac{1}{2}$ hour.....      | 1.33   | 5 minutes.....               | 1.34   |
| 1 " .....                    | 1.33   | 10 " .....                   | 1.34   |
| 2 " .....                    | 1.37   | 20 " .....                   | 1.39   |
| 3 " .....                    | 1.37   | 30 " .....                   | 1.37   |
| 4 " .....                    | 1.37   | 40 " .....                   | 1.39   |
| 5 " .....                    | 1.38   | 1 hour.....                  | 1.44   |
| 6 " .....                    | 1.37   | 2 " .....                    | 1.47   |
| 10 " .....                   | 1.47   | 3 " .....                    | 1.46   |
| 15 " .....                   | 1.47   |                              |        |



Time required to remove calcium when ash is  
treated with concentrated hydrochloric acid.

Table 11.

| A.                           |        | B.                           |        |
|------------------------------|--------|------------------------------|--------|
| <u>Digestion over steam.</u> |        | <u>Boiling on hot plate.</u> |        |
| Time                         | % CaO. | Time                         | % CaO. |
| 1 hour.....                  | 1.44   | 10 minutes.....              | 1.36   |
| 5 " .....                    | 1.46   | 30 " .....                   | 1.40   |
| 8 " .....                    | 1.46   | 1 hour.....                  | 1.40   |
| 10 " .....                   | 1.47   | 2 " .....                    | 1.44   |
|                              |        | 3 " .....                    | 1.48   |
|                              |        | 4 " .....                    | 1.47   |





Arrangement of tables showing comparison of time required to remove lime from ash when ash is digested over steam with concentrated and dilute hydrochloric acid.

Table 111.

| A.                               |        | B.                                     |        |
|----------------------------------|--------|--|--------|
| <u>Dilute hydrochloric acid.</u> |        | <u>Concentrated hydrochloric acid.</u> |        |
| Time                             | % CaO. | Time                                   | % CaO. |
| $\frac{1}{2}$ hour.....          | 1.33   | 1 hour.....                            | 1.44   |
| 1 " .....                        | 1.33   | 5 " .....                              | 1.46   |
| 2 " .....                        | 1.37   | 8 " .....                              | 1.46   |
| 3 " .....                        | 1.37   | 10 " .....                             | 1.47   |
| 4 " .....                        | 1.37   |  |        |
| 5 " " .....                      | 1.38   |  |        |
| 6 " .....                        | 1.37   |  |        |
| 10 " .....                       | 1.47   |  |        |
| 15 " .....                       | 1.47   |  |        |



Arrangement of tables showing time required to remove the lime when the ash is boiled on a hot plate with concentrated and dilute hydrochloric acid.

Table IV.

| A.<br>(sp.gr.1.11)<br><u>Dilute hydrochloric acid.</u> |        | B.<br><u>Concentrated hydrochloric acid.</u> |        |
|--|--------|--|--------|
| Time   | % CaO. | Time   | % CaO. |
| 5 minutes.....   | 1.34   | 10 minutes.....                              | 1.36   |
| 10 " .....   | 1.34   | 30 " .....                                   | 1.40   |
| 20 " .....   | 1.39   | 1 hour.....                                  | 1.40   |
| 30 " .....   | 1.37   | 2 " .....                                    | 1.44   |
| 40 " .....   | 1.39   | 3 " .....                                    | 1.48   |
| 1 hour.....  | 1.44   | 4 " .....                                    | 1.47   |
| 2 " .....  | 1.47   |  |        |
| 3 " .....  | 1.46   |  |        |



## 14.

Table showing effect of evaporating to dryness with dilute Sodium Hydroxide after boiling two hours with concentrated hydrochloric and nitric acids respectively. This treatment with alkali is the Fresenius-Will method and is designed to break up any silicates that have not been decomposed by the acid. Table V-A is where the sample of ash was boiled two hours with concentrated hydrochloric acid and the residue evaporated to dryness with dilute NaOH. Table V-B was treated in exactly the same manner as V-A except concentrated nitric acid was used.

Table V.

| A.                        | B.                  |
|---------------------------|---------------------|
| <u>Hydrochloric acid.</u> | <u>Nitric acid.</u> |
| 1.5 % CaO.                | 1.49 % CaO.         |

Table VI. shows the amount of lime removed from the original feces(not from the ash) by moist combustion. This was done by boiling the feces in Kjeldahl flasks with acid until the organic matter is entirely decomposed.

| A.                               | B.                                      |
|----------------------------------|---|
| <u>Nitric acid concentrated.</u> | <u>Nitric &amp; hydrochloric acids.</u> |
| .304 % CaO.                      | .300 % CaO.                             |



Table VII. shows the amount of lime removed when feces are ashed with low heat and the ash is leached with hot water and the residue ashed with high heat and boiled three hours with concentrated hydrochloric acid.

Table.VII.

% CaO.-- .326

Table VIII. shows the amount of lime removed when the feces are ashed with high heat and the residue is boiled with concentrated hydrochloric acid for three hours.

Table VIII.

% CaO. .309

Table IX shows the amount of lime removed when feces are destroyed by moist combustion with concentrated nitric acid and the residue is treated with dilute alkalie.

Table IX.

% CaO. .314





## DISCUSSION OF DATA.

It will be seen in Table I. that where the dilute acid was used, the boiling on the hot plate removed the lime in one fifth the time required when the ash was "digested" on the steam bath. In Table II. we find that where the ash was treated with concentrated hydrochloric acid, the lime was removed in about one-half the time when the ash was "boiled." In the case where the ash was "digested" over steam (Table III) with both the dilute and concentrated acid, it is found that comparatively all the lime is removed in five hours with the concentrated acid while ten hours are required for its removal in the case of the dilute.

In Table IV. we have the data so arranged as to show the difference in time of the removal of lime when the ash is "boiled" and the data shows that in the case of the concentrated acid, the time required to effectively remove the lime is between two and three hours while the dilute acid accomplished the same task in two hours. This shows that a certain dilution of the acid is not detrimental; on the other hand, seems to hasten the removal of the lime. The efficiency of the two strengths of acid when boiled is however practically the same for both, when the ash is



boiled for three hours with concentrated hydrochloric acid and concentrated nitric acid respectively and the acid insoluble residues treated with dilute Sodium Hydroxide (Table V.) it is found that slightly higher results are obtained. The difference is very slight, being only .03% higher than when the ash is not treated with alkali, but it shows that silicates are present in cow feces in a very small amount which are not decomposed with acid.

When feces, instead of ash, were used for the determination of calcium, the percentage of CaO naturally dropped to a lower figure. These figures, however, are compared with the figures in Tables I., II., III., IV. and V. as the percent of ash in the feces is known to be 20.55 % and from this fact, the figures were found to agree closely in every case.

The first determination of lime made from feces direct was when the feces had been destroyed by moist combustion (Table VI.). The percent of lime removed by concentrated nitric acid did not differ from that removed by nitric and hydrochloric acid. In both cases the percent of lime was .30 %. The highest percent of lime removed by any method was when the feces were ashed at a low heat and the ash



leached with hot water and the water insoluble residue burned to a white ash, after which the ash was boiled three hours with concentrated hydrochloric acid. As it is shown in Table VI, the lime content was .326%. When the feces were ashed with high heat and not water leached and were boiled with concentrated hydrochloric for three hours (Table VIII) the percent CaO was found to be .309.

If feces were destroyed by moist combustion with nitric acid and the insoluble residue treated with dilute alkali, the CaO is .314%. It will be seen by the foregoing data that moist combustion has no advantage over the regular method and that no insoluble compounds are formed in the high heat of ashing.

#### SUGGESTIONS.

In order to insure complete removal of the mineral constituents the following method is suggested:

Ash about five to ten grams of the finely ground feces in a platinum dish at a dull red heat. Allow to cool, take up with hot water and filter thru an ashless filter paper. Dry the filter paper and contents and then burn to white ash. Take up this ash with about 75 cc of concentrated hydrochloric acid and boil for three hours at a slow boil. A condenser should be



used to prevent loss of acid. This may be done by suspending hard glass test tubes full of water in the flasks. Dilute the acid solution with water and filter and wash. Evaporate the residue to dryness with dilute NaOH and take up with acid and filter and wash. These washings are added to the acid filtrate and the solution made up to volume for analysis.

#### SUMMARY.

The facts gleaned from the experimental data show:

1. That ash of cow feces is in a class by itself when referred to other ashes.
2. That the ash of cow feces requires special treatment to completely remove the mineral constituents.
3. That the mineral constituents are removed in a shorter period of time when the ash is boiled than when it is digested over steam.
4. That ash must be boiled for about three hours to insure complete removal of the lime.
5. That in digestion, concentrated acid is more efficient than dilute.
6. That, in boiling, there is very little difference between the length of time required to remove the lime with concentrated hydrochloric acid and hydrochloric acid





specific gravity 1.11.

7. If the feces are ashed at low heat and then leached with hot water, the water soluble material is removed. If then the water insoluble residue is burned to a white ash and treated with acid as specified, and the acid added to the water solution, it is found that slightly higher results are obtained.
8. In cases where silicates not decomposable by acids are present, the residue should be treated with dilute Sodium Hydroxide.
9. That moist combustion shows no advantages over the regular methods of combustion.

- - -



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