

ELECTROLYSIS OF HUMUS SOLUTIONS.

BY

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The term "humus" is used in this article to signify that portion of the organic matter of the soil dissolved by ammonia after the removal of lime and magnesia by washing with dilute hydrochloric acid.

Grandeau's¹ work on the ammonia-soluble organic matter of the soil is the basis of the method of the Association of Official Agricultural Chemists² for the estimation of humus. Grandeau mixed ten grams of soil, freed from lime and magnesia by washing with acid, with coarse sand and placed them in a small funnel, at the bottom of which were fragments of porcelain. This was moistened with ammonia and allowed to digest for several hours. The ammonia was then displaced with water and the filtrate evaporated and dried to constant weight, ignited and weighed again. The loss on ignition is termed humus and the residue in the dish, "humus ash."

Grandeau's method was used by Hilgard³ with modifications. Hilgard placed the soil on a paper filter and covered it with a disc of filter paper, then washed it with dilute hydrochloric acid and then with distilled water. The soil was then extracted with 4 per cent ammonia until the extract was colorless.

Huston and McBride⁴ further modified the Grandeau method and their modification is substantially the official method of the Association of Official Agricultural Chemists. In this method 10 grams of the sample are placed in a gooch crucible and extracted with 1 per cent hydrochloric acid to remove the lime, and then washed with water to remove the acid. The entire contents of the crucible are washed into a glass-stoppered cylinder with 500 c.c. of 4 per cent ammonium hydroxide and allowed to remain with occasional shaking for twenty-four hours. The soil is then allowed to settle twelve hours. The supernatant liquid is filtered, and an aliquot evaporated, dried at 100° C., and weighed. It is ignited, and weighed again. The loss on weight on ignition is termed humus. Considerable clay is brought into suspension with this method. This clay on ignition loses water, which causes an error in the humus determination. In one soil used by the writer nearly a third of the sample was held in suspension after the soil had been allowed to settle a week. Filtration does not remove the clay and continued settling will not remove it. Recent work (5, 6, 7 and 8) has proved this method to be entirely unreliable for certain soils on account of the clay present.

Snyder⁹ proposed a method which differs little⁶ from that of Huston and McBride. In this method the soil is treated with successive portions of acid in a flask, and washed with water in the same way. It is then treated with successive portions of ammonia, made up to volume, and an aliquot evaporated, dried and weighed, ignited and weighed again.

As early as 1901¹⁰ it was pointed out that the official method was unreliable on account of the clay, which lost its water of combination on ignition, which was thus calculated as humus. Cameron and Breazeale,¹¹ in 1904, used the Pasteur filter to remove the suspended clay, although

they did not propose the method as quantitative. This method modified⁵ has given fairly satisfactory results, but is long and tedious.

Peter and Averitt¹² proposed a correction by subtracting from the humus 10 per cent of the so-called "humus ash." They admitted that this correction was uncertain, but it is certainly better than none. Fraps and Hamner⁶ have shown that the average correction would be more nearly correct if placed at 8 per cent.

Mooers and Hampton⁷ have introduced a modification of the official method to remove the clay. "The ammoniacal humus extract, containing clay in suspension, is evaporated to dryness over a steam bath, by which means the clay is flocculated so that during extraction with 4 per cent ammonia it can be retained by an ordinary filter paper. Two evaporations are necessary, as a rule, in order to get a clear filtrate, in which the humus is determined as usual." They compared their method with that of Huston and McBride, that of Cameron and Breazeale, and that of Peter and Averitt. They concluded that the Huston and McBride method gave results far too high. The Cameron-Breazeale method gave low results, and a 14 per cent correction was thought better than 10 per cent. The method of Mooers and Hampton is open to the objection that some of the humus might be decomposed by the continued baking necessary to flocculate the clay. The method also requires several days to complete a determination.

Stoddard¹⁵ precipitated the clay with ammonium sulphate and acidified the alkaline solution of humus. He filtered the resulting precipitate on a gooch, evaporated, dried and weighed. Fraps and Hamner⁶ have shown that this method gives low results, the average recovery being 64 per cent. Buthelot and Andre¹³ found that one-half of the carbon of the soil, soluble in dilute alkalis, was not precipitated on the addition of acid.

Several comparisons of these methods have been published. Alway et al.⁵ and Leavett⁸ find the Mooers and Hampton method satisfactory, but it has been shown by Fraps and Hamner that in many soils of the Southwest the method does not remove all the clay. The Pasteur filter as used by the latter failed to give satisfactory results. Some of the clay was removed, but a part of the humus failed to go through the filter. Mooers and Hampton failed to get good results with the Pasteur filter.

In a recent bulletin⁶ of the Texas Experiment Station, Fraps and Hamner mentioned an attempt to use electrolysis for the removal of the suspended clay. It was to ascertain if the electric current could be used for this purpose and to study its effect on the humus that the work here presented was undertaken.

Cushman and Hubbard¹⁴ have shown that feldspars, when slimed with water, can be removed from suspension by means of the electric current. It is a well-known fact that most colloids migrate toward the anode upon electrolysis. Since humus is a colloidal, it is possible that both the clay and the humus would be affected by the current.

EFFECT OF ELECTROLYSIS ON THE CLAY.

Six soils high in clay and low in humus were selected. The solutions of humus were prepared according to the method of the Association of

Official Agricultural Chemists. However, instead of filtering, the solutions were decanted, allowed to settle a week and then decanted again. They were shaken thoroughly before each aliquot was removed. The following four methods were tested on these solutions:

(a) Humus and ash were determined in 100 cubic centimeters by evaporation, drying to constant weight and subsequent ignition.

(b) Humus and ash were determined in 100 c.c. according to the method of Mooers and Hampton, the solution being twice evaporated to dryness, and taken up in 4 per cent ammonia, filtered, evaporated, dried, weighed, ignited and weighed again.

(c) Humus and ash were determined by the electrolytic method adopted after a number of preliminary experiments to study the conditions which should prevail in this work. One hundred and thirty-five cubic centimeters were placed in an electrolytic cell and a current of .05 amperes (28 volts) was passed for sixteen hours. The solution was decanted through a filter into a dry flask and 100 c.c. taken for determination of humus and ash by direct evaporation and ignition.

The electrolytic cell used was a 200 c.c. cylinder. The electrodes were platinum and were attached to platinum wires sealed in glass tubes. The tubes were supported by means of a perforated tin plate which covered the top of the cylinder and the electrodes were adjusted by means of sections of rubber tubing fitting the glass tubes above the plate. The anode was placed at the bottom of the cylinder and the current was regulated by moving the cathode, no resistance box being necessary. After sixteen hours the clay was found in a compact mass around the anode and the solutions were in all cases clear and nearly colorless, showing that the humus was precipitated to a considerable extent, or else oxidized. When the upper electrode was made the anode, the precipitation was not complete. On four of the determinations corrections were made for volatile and nonvolatile solids found in the ammonia used.

(d) The clay in 300 c.c. was flocculated with 0.3 gram and 0.6 gram ammonium chloride and an aliquot subjected to electrolysis as described above, another aliquot being used for the determination of clay by direct evaporation and ignition.

Results.—The results by these methods as regards ash are shown in Table 1. A very large amount of clay remained in suspension in the case of soil No. 823. This amount of clay would lead to a serious error if the official method (a) were used to determine humus. A large part of the clay was removed by the method of Mooers and Hampton. In only two cases, however, was it reduced to less than 1 per cent.

Electrolysis removed more suspended clay than the Mooers and Hampton method. The results, with one exception (823) are fairly uniform and average less than half those of the Mooers and Hampton method. Electrolysis following the partial removal of clay by ammonium chloride, in the proportion of 1 gram per liter, removed some clay but was not as effective as electrolysis in the absence of this salt.

When the clay was first precipitated with 2 grams of ammonium chloride per liter, there was no clay removed by subsequent electrolysis. The amount of humus "ash" left by these two methods is greater than by electrolysis alone. It appears that the current is a more efficient pre-

cipitant for clay than 1 gram per liter of ammonium chloride, but less efficient than 2 grams ammonium chloride per liter.

Cushman and Hubbard¹⁴ have shown that feldspars in suspension in water are decomposed by the electric current. It is probable that a portion of the ash remaining after ignition consists of substances other than clay.

TABLE NO. 1.
PERCENTAGE OF HUMUS ASH IN SOILS, ESTIMATED BY DIFFERENT METHODS.

Laboratory Number.	Kind of Soil.	Official (direct evaporation.)	Moore and Hampton (evaporation and solution 2 times.)	Electrolysis (0.05 amperes 16 hours.)	Precipitation of clay with ammonium chloride.			
					1 gram per liter		2 grams per liter	
					Electrolysis.	Alone.	Electrolysis.	Alone.
					(d)	(e)	(d)	(e)
114	Travis gravelly loam.....	8.80	0.41	0.57			0.27	0.28
823	Orangeburg fine sandy loam.....	28.20	1.23	0.87			0.39	0.43
982	Cameron clay.....	4.59	1.73	0.37	0.80	1.26		
993	Orangeburg clay.....	2.66	0.41	0.37			0.37	0.34
978	Lufkin clay.....	6.69	1.12	0.35	0.85	0.94		
1203	Houston clay.....	5.36	1.98	0.36	0.58	1.38		
	Average.....	9.38	1.16	0.45	0.74	1.17	0.35	0.35

Results on Humus.—The humus determinations made as already described are presented in Table 2. The results by the Moore and Hampton method average one-half of those of the A. O. A. C. method. This is probably due to the water lost on ignition of the clay. This is in accord with the work of others (5, 6, 7 and 8), who have shown that the official method is unreliable when the solutions contain much suspended clay. Soil 823 contains very little humus (0.86 per cent) but gives 5.65 per cent by the A. O. A. C. method, which shows that this method is misleading for such soils.

The Moore and Hampton method does not remove the clay completely. When the results are corrected for water in the clay by the Peter and Averitt method, they are considerably lower in some cases and average about one-tenth of 1 per cent less, on account of the clay present.

The humus left after removal of the clay by electrolysis was apparently higher than before. But it was evident to the eye that humus had been precipitated to some extent or else oxidized, for the solutions were nearly colorless, in most cases. An examination showed that nitrates were present after electrolysis, though absent from the original solutions. Apparently the current had produced nitric nitrogen. Nitrates were determined colorimetrically by the phenolsulphuric acid method, a blank on the original solution being run with each determination and the results are given in the table.

When the nitrogen in nitrates is calculated as ammonium nitrate, and subtracted from the apparent humus found after electrolysis, the humus in solution is found to be less in all cases than the humus by the Moore and Hampton method. On an average, 0.34 per cent humus disappeared from the solution in electrolysis, either by precipitation or by electrolysis.

Cushman and Hubbard, as mentioned on a preceding page, have shown that potassium hydroxide is formed when feldspars are decomposed by the electric current. Hence it is possible that there is some potassium nitrate in the alkaline humus solutions after electrolysis, but most of the nitric nitrogen must be combined with ammonia.

TABLE NO. 2.
PERCENTAGE OF HUMUS ESTIMATED BY DIFFERENT METHODS.

Laboratory Number.	Kind of Soil.	Official (direct evaporation.)		Moers and Hampton (evaporation and solution 2 times.)		Electrolysis 0.05 amperes 16 hours.	Nitric nitrogen in solution after electrolysis.	Nitric nitrogen calculated to ammonium nitrate.	Solids in solution after electrolysis less nitrate.
		Direct.	Corrected.	Direct.	Corrected.				
		(a)	(b)			(c)			
114	Travis gravelly loam.....	1.98	0.79	0.75		0.87	0.08	0.46	0.41
823	Orangeburg fine sandy loam.....	5.65	0.98	0.86		1.33	0.13	0.74	0.59
982	Cameron clay.....	1.59	1.44	1.26		2.16	0.20	1.14	1.02
993	Orangeburg clay.....	0.61	0.57	0.53		1.55	0.20	1.14	0.41
978	Lufkin clay.....	1.75	1.47	1.36		1.56	0.15	0.86	0.70
1203	Houston clay.....	1.14	1.13	0.93		1.87	0.25	1.43	0.44
	Average.....	2.10	1.06	0.95		1.56	0.17	0.96	0.60

EFFECT OF ELECTROLYSIS ON THE HUMUS.

The object of this work was to study the effect of electrolysis upon the organic matter in solution. Six soils were selected which gave solutions higher in humus and lower in clay than the soils used in the work just described. The humus solutions were prepared as previously described. Humus was determined by the methods following:

(a) The humus was determined in 100 c.c. by the method of Moers and Hampton (evaporation and solution).

(b) Humus by electrolysis. Three hundred cubic centimeters were treated with 2 grams per liter of ammonium chloride and allowed to stand over night. The clay was then filtered off. One hundred cubic centimeters were then diluted to 200 c.c. with water and the current passed through as described on a preceding page. The precipitated humus was filtered on a gooch crucible, washed with 1 per cent hydrochloric acid and dried to constant weight at 100° C.

(c) Humus by precipitation with acid. One hundred cubic centimeters of the solution freed from clay as described in (b) were acidified with hydrochloric acid, filtered on a gooch, washed with 1 per cent hydrochloric acid, and dried to constant weight at 100° C.

Results of the Work.—The results are shown in Table 3. The “ash” remaining in the solution purified by the Moers and Hampton method was considerable, and the corrected humus ranges from 0.05 per cent to 0.17 per cent less than the uncorrected humus.

The humus precipitated by acid was less in all cases than the corrected humus by the evaporation and solution method and averages

about half of it. There does not appear to be any relation between the total humus and the humus precipitated by acid.

The humus by electrolysis varies from 0.10 per cent to 0.27 per cent and averages 0.18 per cent. This is about one-fifth of the humus precipitated by acid, and one-tenth of the total humus. In this case also there appears to be no relation between the amount as determined by the different methods.

The current alone precipitated twice as much humus as when ammonium chloride was present. (See Table 1.) In the latter case the solutions were only slightly lighter and the cathode was blackened by some substance which could only be removed by burning. Ammonium sulphate, ammonium nitrate and sodium chloride were used to precipitate the clay before electrolysis, but they also interfered with the precipitation of the humus by the current. The current was increased but the amount of humus precipitated did not appear to be greater and the solution remained dark colored. It appears that salts interfere with the precipitation of the humus by electrolysis.

TABLE NO. 3.
PERCENTAGE OF HUMUS PRECIPITATED BY ELECTROLYSIS AND BY HYDROCHLORIC ACID AFTER THE REMOVAL OF CLAY BY MEANS OF AMMONIUM CHLORIDE.

Laboratory Number.	Kind of Soil.	Moore and Hampton Method (evaporation and solution 2 times.)			Humus by hydrochloric acid.	Precipitated by current .05 amperes.
		Ash.	Humus.	Corrected for water in 10 per cent clay.		
334	Houston loam	1.66	1.82	1.65	1.33	0.16
829	Houston loam	1.39	2.52	2.38	1.21	0.10
896	Norfolk fine sandy loam.....	0.84	1.58	1.50	0.87	0.26
845	Wabash silt loam.....	0.49	2.16	2.11	1.05	0.17
941	Houston loam.....	0.55	1.25	1.19	0.60	0.11
1121	Hagensport loam.....	1.22	1.32	1.20	0.32	0.27
	Average.....	1.03	1.78	1.67	0.89	0.18

EFFECT IN NEUTRAL SOLUTION.

One hundred cubic centimeters of humus solution were evaporated in a 150 c.c. Jena beaker to a volume of about 25 c.c. and made up to 100 c.c. with water. The current was then passed as already described. The humus and clay were precipitated almost completely as before. Only a trace of nitrates (0.3 mg. per 100 c.c.) was found after electrolysis, showing that the nitric nitrogen produced is principally from the free ammonia. When it was found that the humus was precipitated with the clay, the work on neutral solutions were discontinued after the following experiment had been made. One hundred cubic centimeters were evaporated to 25 c.c. and placed inside of a diffusion shell of parchment. (C. S. & Schull.) The shell was placed in a beaker of water, the cathode of the electrolytic apparatus was placed inside the shell and the anode outside. A current of .05 amperes (28 volts) was passed for sixteen hours. The humus collected on the walls of the cell, and the water outside the shell remained colorless.

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AN IMPROVEMENT IN THE METHOD FOR ESTIMATING HUMUS IN SOILS.

As shown in the preceding article, the chief difficulty with the present method for the estimation of humus is the presence of clay, which loses water by ignition and thereby increases the apparent quantity of organic matter which is present.

It is well known that salts can coagulate clay and throw it out of suspension. Fraps and Hamner used non-volatile salts to precipitate the clay, but call attention to the fact that the salt used might be decomposed or otherwise lost on ignition. It occurred to the writer that if a salt could be found that volatilized below 100° C., its use would overcome this difficulty. Ammonium carbonate decomposes at 85° C., and was accordingly tested.

Experimental.—Twelve soils, some low and some high in humus, were compared by means of the methods described below. The solutions were prepared by the A. O. A. C. method referred to in the previous article.

1. Humus and ash were determined in 100 c.c. prescribed in the official method.

2. One hundred c.c. were evaporated two times and taken up with 4 per cent ammonia as in the method of Mooers and Hampton, evaporated, and completed as usual.

3. Carbon dioxide, obtained by heating sodium bicarbonate and washed with water, was passed through 130 c.c. of the humus in glass-stoppered 200 c.c. cylinders for five minutes. The solutions were allowed to settle over night and decanted through a filter, 100 c.c. taken and the determination completed as usual.

4. Carbon dioxide was passed through 100 c.c., as above described, for 3.5 minutes, the clay allowed to settle over night and the solution decanted through a filter. The clay was then washed five times by decantation with successive portions (20 c.c. each) of 4 per cent ammonia containing 10 grams ammonium carbonate per liter.

5. Ammonium carbonate (tested purity) at the rate of 5 grams per liter was added to the solutions, the precipitate allowed to settle over night, the clear supernatant liquid decanted through a filter, and an aliquot taken for analysis as described in the official method.

6. One hundred c.c. of the clay was precipitated with ammonium carbonate as in 5, and washed with ammoniacal ammonium carbonate solution as in 4. The solutions by the carbonate methods were in all cases perfectly clear. In all but two cases the Mooers and Hampton solutions were not clear.

The ammonium carbonate used was Eimer and Amend "tested purity," and was tested as follows: One gram was placed on a tared watch

glass and kept in a steam oven at 100° C., for three hours. The residue was unweighable.

All determinations were made on the same solutions. The time of drying of the humus in all cases was three hours, as numerous tests by us and by others in this laboratory showed that length of time to be quite sufficient.

Results of the Work.—The results are shown in Table 1. The “humus” by the official method¹ varied from 0.86 per cent (soil 993) to 6.20 per cent (soil 947). The “ash” by the official method varied from 3.97 per cent (soil 993) to 33.45 per cent (soil 823) and averaged for the twelve soils 10.20 per cent.

The humus by Mooers and Hampton’s method² varied from 0.58 to 5.77 per cent with an average of 1.69 per cent, about one-half of the A. O. A. C. average for humus. The “ash” by this method varies from 0.35 per cent (soil 993) to 3.94 per cent (soil 947) and averaged 1.37 per cent, about one-half of the average for ash by method 1.

TABLE NO. 4—PERCENTAGE OF HUMUS AND HUMUS ASH BY DIFFERENT METHODS.

Laboratory Number.	Kind of Soil.	Official.		Moers and Hampton.		Carbon dioxide alone		Carbon dioxide and washing		Ammonium carbonate alone		Ammonium carbonate and washing	
		Humus.	Ash	Humus	Ash	Humus	Ash	Humus	Ash	Humus	Ash	Humus	Ash
114	Travis gravelly loam.	3.35	19.43	0.78	0.95	0.70	0.22	0.72	0.30	0.58	0.21	0.73	0.37
823	Orangeburg fine sandy loam subsoil.	5.00	33.45	0.86	0.51	1.30	0.36	1.48	1.03	0.78	0.19	1.38	0.61
829	Houston loam surface.	1.85	4.50	1.54	0.72	0.89	0.26	0.87	0.40	1.33	0.27	0.95	0.41
830	Laredo gravelly loam surface.	1.70	4.81	1.11	1.18	1.15	0.55	1.11	0.69	0.90	0.28	1.19	0.74
896	Norfolk fine sandy loam surface.	1.28	0.66	1.32	0.69	1.15	0.55	1.11	0.69	1.20	0.57	1.10	0.94
978	Lufkin clay surface.	2.15	11.00	1.29	1.97	0.86	0.53	1.17	0.88	0.95	0.47	1.10	0.94
982	Cameron clay subsoil.	1.75	4.40	1.42	1.54	0.86	0.53	1.17	0.88	1.08	0.56	1.10	0.94
993	Orangeburg clay surface.	0.86	3.97	0.58	0.35	0.47	0.19	0.49	0.28	0.45	0.37	0.82	0.82
947	Soil from alfalfa field, North Dakota.	6.20	13.09	5.77	3.94	5.07	0.78	5.07	0.78	5.07	0.20	5.07	0.20
941	Houston loam surface.	3.14	11.95	1.25	0.55	1.00	0.55	1.00	0.55	0.83	0.45	0.83	0.45
1203	Houston clay subsoil.	2.18	9.51	1.00	1.53	1.00	0.55	1.00	0.55	3.06	1.03	3.06	1.03
949	Soil from old field, Edgely, N. Dakota.	3.81	5.67	3.40	2.53	3.40	2.53	3.40	2.53	1.44	0.45	1.44	0.45
	Average (12 soils, 3 methods).....	2.77	10.20	1.69	1.37	1.69	1.37	1.69	1.37	1.44	0.45	1.44	0.45
	Average (6 soils on which all methods were used)	2.14	9.73	1.12	0.90	0.90	0.35	0.97	0.60	0.90	0.36	1.03	0.65
	10 per cent correction	1.17	1.03	0.86	0.91	0.90	0.96
	14 per cent correction.	0.78	0.99	0.85	0.89	0.89	0.94

When carbon dioxide was used to precipitate the clay, without subsequent washing (method 3), the per cent of humus obtained was less than by the Mooers and Hampton method. The average for the six soils was 0.90 per cent, while for the Mooers and Hampton method, the average on the same soils was 1.12 per cent. Considerably more ash, however, was present when the latter method was used.

The humus by carbon dioxide and washing (method 4) averaged 0.97 per cent, only slightly higher than the result by carbon dioxide alone. The ash, however, was almost doubled (average 0.60 per cent), showing that some clay was carried through the filter by the washing.

Humus by ammonium carbonate alone (method 5) averaged 0.94 per cent for the six soils on which carbon dioxide was used. The "ash" averaged 0.36 per cent. The averages for the twelve soils were, humus 1.44 per cent and ash 0.45 per cent. The humus was less than by the Mooers and Hampton results by 0.25 per cent and the ash was one-third as much.

The results by ammonium carbonate and washing (method 6) average nearly the same as with carbon dioxide and washing, being 1.03 per cent humus and 0.65 for ash.

TABLE NO. 5.

PERCENTAGE OF HUMUS IN SOILS ESTIMATED BY DIFFERENT METHODS AND CORRECTED FOR WATER IN THE ASH.

Laboratory Number.	Kind of Soil.	Official.		Mooers and Hampton.		Ammonium carbonate.	
		No correction.	10 per cent.	No correction.	10 per cent.	No correction.	10 per cent.
114	Travis gravelly loam.....	3.35	1.41	0.78	0.69	0.58	0.56
823	Orangeburg fine sandy loam subsoil.....	5.00	1.65	0.86	0.81	0.78	0.76
829	Houston loam surface.....	1.85	1.40	1.54	1.47	1.33	1.30
830	Laredo gravelly loam surface.....	1.70	1.22	1.11	0.99	0.90	0.87
896	Norfolk fine Sandy loam surface.....	1.23	1.21	1.32	1.25	1.20	1.14
978	Lufkin clay loam.....	2.15	1.05	1.29	1.09	0.95	0.90
982	Cameron clay subsoil.....	1.75	1.31	1.42	1.25	1.08	1.01
993	Orangeburg clay surface.....	0.86	0.46	0.58	0.54	0.45	0.41
947	Soil from alfalfa field, North Dakota.....	6.20	4.89	5.77	5.38	5.07	4.99
941	Houston loam surface.....	3.14	1.94	1.25	1.19	1.07	1.05
1203	Houston clay subsoil.....	2.18	1.23	1.00	0.85	0.83	0.78
949	Soil from old field, Edgely, N. D.....	3.81	3.24	3.40	3.15	3.06	2.96
	Average (12 soils).....	2.77	1.75	1.69	1.55	1.44	1.39
	Average (6 soils highest in humus).....	3.01	2.34	2.45	2.28	2.14	2.08
	Average (6 soils lowest in humus).....	2.54	1.17	0.62	0.94	0.72	0.71

When a correction is applied to the results on the six soils on which all methods were used for water in the clay lost on ignition, the results by methods 3, 4, 5 and 6 are nearly the same. Washing increased the ash without noticeably increasing the humus, and carbon dioxide has no advantage over ammonium carbonate. The washing, therefore, appears to be unnecessary, as the use of ammonium carbonate is the easiest method, and reduces the clay to a minimum. It was the method finally adopted. In Table 5 we correct the results for humus by subtracting 10 per cent of the ash, as suggested by Peters and Averitt. The corrections reduce the amount of apparent humus obtained by the official

method enormously in some cases. "Humus" in soil 823 was reduced from 5 per cent to 1.65 per cent; with soil 114 the difference is almost as great, the humus being reduced from 3.35 per cent to 1.41 per cent.

The Mooers and Hampton results were also reduced considerably by correction, averaging 0.14 per cent less. When the results by ammonium carbonate were corrected they were only slightly lower (0.05 and 0.06 per cent) than before. It is doubtful if a correction should properly be made here because this ash is practically free from clay.

The average after correction is 1.75 (A. O. A. C.), and 1.55 (Mooers and Hampton) and 1.39 (ammonium carbonate). The results by the ammonium carbonate method were lower in all cases than by the Mooers and Hampton method and the corrected results average 0.16 per cent less. The corrections applied are purely arbitrary and represent averages. Fraps and Hamner have shown that the amount of water in the clay varies from 8 per cent to 20 per cent. These differences are not great and would possibly disappear if the evaporation and solution (Mooers and Hampton method) were continued until the clay were entirely removed. But the evaporations take considerable time and the ammonia is liable to absorb acid fumes from the laboratory. In addition, the continued baking is liable to oxidize or decompose some of the constituents of the humus.

There is possibility of precipitation of some of the humus, for in clay precipitated by ammonium sulphate, Fraps and Hamner found carbon in varying amounts, a portion of which must be in organic combination. At the same time the clay by the Mooers and Hampton method contains humus. If enough ammonia is used to get all the humus, most of the clay comes with it, and vice versa.

SUMMARY AND CONCLUSIONS.

Electrolysis of Humus Solutions.

1. Electrolysis removed most of the suspended clay from humus solutions and precipitated some of the humus.
2. Electrolysis removed more clay than the Mooers and Hampton method.
3. Electrolysis precipitated more clay than 1 gram per liter of ammonium chloride, but less than 2 grams per liter of the salt.
4. After precipitating the clay with 1 gram per liter of ammonium chloride, the current used did not complete the precipitation of the clay. The presence of the salts interfere with the precipitation.
5. Nitric nitrogen was formed by the current in the presence of free ammonia.
6. Only a small amount of humus was precipitated by the current in the presence of 1 gram per liter of ammonium chloride, much less than by hydrochloric acid. In the absence of ammonium chloride about a third of the humus was precipitated.
7. All of the humus was not precipitated by hydrochloric acid.
8. Humus and clay are precipitated from neutral solution by the current.
9. The electrolysis can not be used as a quantitative method for removal of clay or of estimation of humus.

Estimation of Humus.

1. Clay in humus solutions may be precipitated by ammonium carbonate or carbon dioxide, and the precipitant disappears on evaporating and drying the residue.
2. Evaporation and solution does not remove the clay completely.
3. Precipitation of the clay with ammonium carbonate is more nearly complete than by evaporation and solution, and is a much shorter method.

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