[CONTRIBUTION FROM THE CHEMICAL SECTION, IOWA AGRICULTURAL EXPERIMENT STATION.]

ESTIMATION OF CALCIUM IN ASH OF FORAGE PLANTS AND ANIMAL CARCASSES.

BY S. B. KUZIRIAN.

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An accurate as well as a rapid method for the estimation of calcium in forage plants and animal carcasses in agricultural experiment stations is of prime importance in studying the relationship between the growing plant or animal on the one hand and the soil or food supply on the other.

Having had occasion in this laboratory to make a large number of calcium determinations on samples of forage plants and animal carcasses, the disadvantages and inconveniences of the methods in common use soon became apparent. In the course of these analyses the method described in this paper was found to be superior both in regard to accuracy and convenience.

Thompson and Morgan[1] attempt the precipitation of calcium as oxalate in the presence of large excess of phosphoric acid in acetic acid solution. McCrudden[2] likewise tries to estimate the calcium without first removing the phosphoric acid.

The separation of phosphoric acid as mercurous,[3] stannic,[4] bismuthic,[5] silver,[6] etc., phosphates with the subsequent removal of these precipitants by some suitable analytical operations is too tedious, requiring prolonged time for execution. These methods are, therefore, out of consideration for general use in experiment stations.

The basic acetic method is the one which has come into most common use, having been adopted as official by the Association of Official Agricultural Chemists. The conditions to be observed with this method are of such a nature, that it is difficult to get concordant results in determinations of manganese, calcium, magnesium and the alkalies. The main objection to this process is the prolonged evaporation which is necessary to reduce a large volume of filtrate into 50 to 75 cc. The action of ammonia salts upon the glass beaker at 80 to 90° is not altogether negligible.

A More Accurate and Rapid Method.—Shedd's[7] method, though more convenient and rapid, tends to give higher results due to contamination

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[1] *J. Ind. Eng. Chem.*, **3**, 398.

[2] *J. Biol. Chem.*, **10**, 187.

[3] H. Rose, *Pogg. Ann.*, **76**, 218.

[4] W. Reissig, "Zur quantitativen Bestimmung der Phosphorsäure," *Ann. Chem. Pharm.*, **98**, 339–344 (1856).

[5] *Compt. rend.*, **50**, 416; *Chem. Zentr.*, 1860, 272.

[6] Fresenius' *Quant. Chem. Anal.*, **1**, 458.

[7] O. M. Shedd, referee in inorganic plant constituents for the A. O. A. C., Bur. of Chem., *Bull.* **152**, 64, 65.

with molybdenum. When, however, the following procedure, which is a slight modification of Shedd's process, is adopted, excellent results are obtained. The modification consists essentially in boiling the calcium oxalate precipitate for 30 minutes on a hot plate, and filtering through a Gooch; then, instead of dissolving this precipitate with hydrochloric acid and reprecipitating with dilute ammonia, which operation seems to be insufficient completely to remove adhering traces of molybdenum,[1] it is ignited to convert the oxalates into oxides, preferably in an electric furnace. It is then dissolved in dilute hydrochloric acid, filtered, some ammonium chloride and ammonia added, and boiled until the odor of ammonia is faint. The precipitated iron and aluminium are removed and the calcium precipitated as oxalate, at this stage of the process, calcium being entirely free from molybdenum salts.[2]

The results shown in Table I were obtained with solutions containing known amounts of calcium and phosphorus. The phosphorus was removed in each case as ammonium phosphomolybdate, according to directions given in the Official Methods[3] (Volumetric Optional) and titrated to make sure that its removal was complete. The estimation of calcium according to the above method was then attempted and the following results were obtained:

TABLE I.—ANALYSIS OF KNOWN SOLUTION FOR CALCIUM AND PHOSPHORUS.

No. of the experiment.	P_2O_5 taken (as Na_2HPO_4), g.	CaO taken (as $Ca(NO_3)_2$), g.	CaO found, g.	Error, g.
1	0.0207	0.0283	0.0283	0.0000
2	0.0207	0.0283	0.0285	+0.0002
3	0.0207	0.0283	0.0283	0.0000
4	0.0207	0.0283	0.0283	0.0000
5	0.0207	0.0283	0.0283	0.0000
6	0.0207	0.0566	0.0566	0.0000
7	0.0207	0.0283	0.0282	—0.0001
8	0.0207	0.0283	0.0283	0.0000

The ease with which closely agreeing duplicates can be obtained when ash of forage plants is analyzed for calcium is shown in Table II. Numbers 1 and 2 in each case are duplicates of the same sample.

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[1] On testing qualitatively a series of 8 results obtained according to Shedd's method, all gave indications of molybdenum. The sulfide test was found to be most satisfactory, being sensitive to a small fraction of a milligram of MoO_3. In all cases calcium oxides were dissolved in hydrochloric acid, made ammoniacal, colorless ammonium sulfide added, digested, filtered and the filtrate made acid with hydrochloric acid. Sometimes a development of a blue coloration on addition of ammonia sulfide indicates a reduced condition of molybdenum.

[2] When two series of eight each were tested for molybdenum similarly, tests were negative in all cases.

[3] Bur. Chem., *Bull.* 107 (1910).

Table II.—Analysis of Forage Plants[1] for Calcium.

Lab. No. of sample.	Gram CaO found in aliquots.			% Ca in original sample (according to aliquots).		
	No. 1.	No. 2.	Diff.	No. 1.	No. 2.	Diff.
1072	0.0090	0.0095	0.0005	0.450	0.475	0.025
1073	0.0165	0.0165	0.0000	0.825	0.825	0.000
1074	0.0100	0.0100	0.0000	0.500	0.500	0.000
1075	0.0117	0.0120	0.0003	0.585	0.600	0.015
1076	0.0430	0.0430	0.0000	2.150	2.150	0.000
1077	0.0435	0.0440	0.0005	2.175	2.200	0.025
1079	0.0395	0.0390	0.0005	1.975	1.950	0.025
1086	0.0080	0.0080	0.0000	0.400	0.400	0.000
1089	0.0495	0.0495	0.0000	2.475	2.475	0.000
1090	0.0550	0.0545	0.0005	2.750	2.725	0.025
1091	0.0585	0.0590	0.0005	2.925	2.950	0.025
1092	0.0340	0.0340	0.0000	1.700	1.700	0.000
1095	0.0085	0.0080	0.0005	0.425	0.400	0.025
1097	0.0112	0.0113	0.0001	0.560	0.565	0.005
1098	0.0143	0.0145	0.0002	0.715	0.725	0.010
1100	0.0445	0.0450	0.0005	2.225	2.250	0.025
1101	0.0475	0.0480	0.0005	2.375	2.400	0.025
1102	0.0483	0.0478	0.0005	2.415	2.390	0.025
1103	0.0055	0.0052	0.0003	0.275	0.260	0.015
1104	0.0400	0.0403	0.0003	2.000	2.015	0.015
1105	0.0080	0.0080	0.0000	0.400	0.400	0.000

The carcasses of some newly born pigs were ashed after air drying and dissolved in nitric acid, the phosphoric acid precipitated as ammonium phosphomolybdate and the filtrate analyzed for calcium in the same way. Following are the results obtained:

Table III.—Analysis of Pig Carcasses[2] for Calcium.

Lab. No. of sample.	Gram CaO found in aliquots.			% Ca in original sample[3] (according to aliquots).		
	No. 1.	No. 2.	Diff.	No. 1.	No. 2.	Diff.
1255	0.0377	0.0377	0.0000	7.54	7.54	0.00
1256	0.0372	0.0372	0.0000	7.44	7.44	0.00
301	0.0370	0.0360	0.0010	7.40	7.20	0.20
303	0.0413	0.0407	0.0006	8.26	8.14	0.12
308	0.0408	0.0408	0.0000	8.16	8.16	0.00
309	0.0348	0.0352	0.0004	6.96	7.04	0.08
310	0.0345	0.0345	0.0000	6.90	6.90	0.00
315	0.0352	0.0348	0.0004	7.04	6.96	0.08
316	0.0403	0.0405	0.0002	8.06	8.10	0.04
317	0.0388	0.0382	0.0006	7.76	7.64	0.12
321	0.0418	0.0420	0.0002	8.36	8.40	0.04

[1] 2-gram samples taken.

[2] Ashing of the pig samples was done in platinum dishes. No calcium acetate or magnesium nitrate was added during ashing as it was found to be unnecessary.

[3] The weight of the air-dried sample taken in each case was 0.5 g.

When iron and aluminium were removed according to the description of Shedd[1] and tested for molybdenum in a series of four determinations the test was positive. Because of the fact that iron is titrated with permanganate after fusion with potassium bisulfate and reduction with nascent hydrogen, some complications may arise, preventing accurate results.

More reliable and accurate results of all basic ions in ash of forage plants and animal carcasses are obtained if the excess of molybdenum after the removal of P_2O_5 as ammonium phosphomolybdate, is removed as sulfide according to Fresenius.[2] In short, the filtrate is made slightly ammoniacal, digested with colorless ammonium sulfide, carefully acidified with 12% hydrochloric acid, warmed to 45° to flocculate the molybdenum sulfide and filtered through a Schleicher & Schüll filter (blue label). The clear filtrate thus obtained is boiled to expel hydrogen sulfide and after further filtration is ready for basic analysis. The fact that a perfect separation and gravimetric estimation of iron and aluminium can be effected with the use of this method, makes it highly commendable. Moreover, if manganese is present in traces, it may easily be tested for and estimated. Some work was undertaken in this laboratory to show the advisability of substituting this method for the separation and estimation of basic ions in ash in place of the official methods, giving special consideration to the time required and also accuracy. Aliquots of a solution of calcium nitrate of known strength were mixed with a solution of disodic hydrogen phosphate and the phosphorus removed as phosphomolybdate. From the filtrate thus obtained, molybdenum was removed as sulfide according to directions given above. The calcium was precipitated as oxalate and ignited into oxide. Following are the results obtained under these conditions:

TABLE IV.—ESTIMATION OF CALCIUM AFTER REMOVAL OF MOLYBDENUM AS SULFIDE.

No. of the experiment.	Gram CaO taken as $Ca(NO_3)_2$.	Gram CaO found.	Error, g.	No. of the experiment.	Gram CaO taken as $Ca(NO_3)_2$.	Gram CaO found.	Error, g.
1	0.0536	0.0535	—0.0001	11	0.0524	0.0525	+0.0001
2	0.0536	0.0537	+0.0001	12	0.0524	0.0520	—0.0004
3	0.0536	0.0534	—0.0002	13	0.0524	0.0522	—0.0002
4	0.0536	0.0539	+0.0003	14	0.0524	0.0523	—0.0001
5	0.0536	0.0540	+0.0004	15	0.0524	0.0522	—0.0002
6	0.0536	0.0534	—0.0002	16	0.0524	0.0522	—0.0002
7	0.0536	0.0540	+0.0004	17	0.0524	0.0520	—0.0004
8	0.0536	0.0530	—0.0006	18	0.0524	0.0515	—0.0009
9	0.0536	0.0532	—0.0004	19	0.0524	0.0521	—0.0003
10	0.0536	0.0532	—0.0004				

The time required in this case is much shorter than when basic acetate method is used, three hours being sufficient to bring one series of six, each

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[1] O. M. Shedd, Bur. of Chem., *Bull.* **152**, pp. 63, 64.

[2] Fresenius' *Quant. Chem. Anal.*, **1**, 464.

having one duplicate, to the condition where calcium is ready for precipitation as oxalate.

Summary.

A more rapid and accurate method is recommended for the determination of calcium in the ash of agricultural products. It consists essentially in removing the phosphorus as ammonium phosphomolybdate from an acid solution of the ash, and precipitation of calcium from the filtrate as calcium oxalate, either directly or after the removal of the excess of molybdenum as sulfide. Since no advantage was found in removing the molybdenum, it is recommended that this step be omitted.

A comparison of this method with the so-called basic acetate method in common use brings out the following points in its favor:

1. It yields more accurate and concordant results than the basic acetate method.
2. No attention need be given to the maintenance of exact neutrality of the solution.
3. The volume of the filtrate resulting from the precipitation of phosphorus can be kept reasonably small, so that no evaporation is necessary.
4. The time required for the determination is greatly shortened.
5. Phosphorus and calcium may be determined in the same aliquot.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

A SYSTEMATIC SEPARATION OF THE ANIONS OF GROUP I. ANIONS WHOSE SILVER SALTS ARE INSOLUBLE IN NITRIC ACID.[1]

BY H. C. P. WEBER AND H. A. WINKELMANN.

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The customary methods for the examination and separation of the acids depend mainly upon various group reactions, followed by specific tests for one or the other anion, combined with a process of elimination based upon the results of the analysis for the cations. For a limited number of anions special methods of separation have been worked out in detail, as for instance for certain of the acids containing sulfur. The literature on the separation of the halogens Cl, Br, I, is quite voluminous and in this particular case a choice of various satisfactory methods of separation is possible. On the whole these methods are, however, limited in scope and very little work has been done upon systematic methods for the separation of the anions.[2]

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[1] Portions of this work were submitted by Mr. H. A. Winkelmann in partial fulfilment of the requirements for the degree of Master of Science in Chemistry in the Graduate School of the University of Illinois, June, 1915.

[2] The lack of such a systematic procedure is shown particularly by the errors and confusion resulting from the customary method of attack in the hands of students