Summary

1. Measurements have been made on the viscosity of solutions of barium chloride at 25° covering the range 0.005 to 1.0 molal.

2. The fluidity (reciprocal of the viscosity) of these solutions can be computed within the limit of error of the data from the equation

$$\varphi = 1 - 0.02013\ \sqrt{c} - 0.20087c$$

3. It is shown that an equation of the form $\varphi = 1 + A\ \sqrt{c} + Bc$ can be made to fit the data by proper choice of the values of A and B in the case of many other salts for which precise data are available extending to low concentrations.

4. The value of A is negative for all strong electrolytes for which accurate data are available. This term probably represents the stiffening effect on the solution of the electric forces between the ions which tend to maintain a space lattice structure. The value of A is zero for non-electrolytes.

5. The value of B may be either positive or negative. Most salts resemble barium chloride in causing an increase in viscosity or a decrease in fluidity at all concentrations giving a negative value to B. In such cases the equation is apparently valid up to about 1 molal.

6. Some salts cause an increase in the fluidity or a decrease in the viscosity over a wide range of concentration, so that the value of B in our equation is positive. In such cases the equation is apparently valid up to nearly 0.2 molal.

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[Contribution from the Chemical Laboratory, Michigan Agricultural Experiment Station]

THE DETERMINATION OF ALUMINUM IN PLANTS. II. ALUMINUM IN PLANT MATERIALS[1]

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The biological significance of the use of aluminum in food materials, water purification, cooking utensils, etc., has been a live problem during the last one or two decades. Because of this, the aluminum content of plants has been considered of importance, even though the amount present may be small.

Langworthy and Austin,[2] Gonnerman,[3] Bertrand[4] and more recently

[1] Published by permission of the Director of the Experiment Station as Journal Article No. 11 n.s. from the Station and No. 49 from the Chemical Laboratory.

[2] Langworthy and Austin, "The Occurrence of Aluminum in Vegetable Products, Animal Products and Natural Waters," New York, **1904**.

[3] Gonnerman, *Biochem. Z.*, **88**, 401 (1918).

[4] Bertrand, *Bull. soc. hyg. aliment.*, **8**, 49 (1920).

Myers and Voegtlin,[5] Gray,[6] McCollum, Rask and Becker,[7] and others have made quantitative determinations of aluminum in plant materials. All of these analysts, with the exception of McCollum, Rask and Becker, found aluminum present in these materials. The differences in the results obtained by these analysts, however, indicate that there is considerable variation in the aluminum content of some of the materials analyzed or that some of the materials were contaminated more than others. Because of these variations and because of the present interest in the aluminum content of foods, a number of plants and plant materials were analyzed for this element by the colorimetric method[8] described in an earlier article. The work herein presented gives the method used for preparing the samples for analysis and also the results of aluminum determinations.

Experimental Part

Preparation of the Material.—Since the real problem at hand was to determine the amount of aluminum in the materials as they are used for food, the samples were prepared in practically the same way as in the ordinary preparation for table use. The impurities were removed when possible by carefully washing the materials with water and a brush. When the impurities were not readily removed by this method, as in the case of some roots, the contaminated spots were scraped with a knife and then washed. All fresh materials were dried at approximately 35°. The moisture was determined. The dry materials were ground so as to pass a 20-mesh sieve and stored in stoppered bottles.

Preparation of the Sample.—From 1 to 30 g. of material (depending on the amount of aluminum present) was placed in a platinum dish in an electric muffle, the temperature was raised to just below redness and allowed to remain overnight. Any unburned carbon at this point was ignored, since it could be ignited later. The ash was digested with hydrochloric acid, centrifuged, the supernatant liquid decanted and the residue washed once with about 5 cc. of water by means of the centrifuge and decantation. Since it was found that the aluminum in the ash was not always entirely dissolved by hydrochloric acid, the residue was washed into a platinum crucible by means of a fine jet of water, the water evaporated, the residue ignited if necessary, fused with 0.5 g. each of sodium and potassium carbonates, taken up with hydrochloric acid and added to the original solution.[9]

Determination of Aluminum.—After adding a few drops of nitric acid and boiling to oxidize the iron and removing the silica by dehydration, the solution was transferred to a centrifuge tube of about 25-cc. capacity with marks at 15, 20 and 25 cc. The iron

[5] Myers and Voegtlin, "U. S. Weekly Public Health Rep. 29," Part 1, Nos. 1–26, 1625 (1914).

[6] Gray, Hearings, Dochet 540, U. S. Federal Trade Commission *vs.* Royal Baking Powder Co.

[7] McCollum, Rask and Becker, *J. Biol. Chem.*, **77**, 753 (1928).

[8] Winter, Thrun and Bird, THIS JOURNAL, **51**, 2721 (1929).

[9] The wet method (digesting the sample with sulfuric and perchloric acids) used by Myers and co-workers was tried. The method proved entirely satisfactory when only a comparatively small sample was used, *e. g.*, 1 g. However, since the blank on the reagents was appreciable, in cases where only a small amount of aluminum was present, it was found much more satisfactory to ash a larger sample, carry it through to where the iron is separated and then take an aliquot of the solution.

and aluminum were precipitated and the iron was separated by the method of Myers, Mull and Morrison[10] (practically all of the materials analyzed contained sufficient iron to carry down the aluminum but did not contain phosphoric acid enough to insure complete precipitation of the iron and aluminum as phosphates; hence no iron but about 0.10 g. of ammonium hydrogen phosphate was added to each sample). The solution was made up to a volume of 25 cc. An aliquot was transferred to a 50-cc. volumetric flask, a small piece of litmus paper was added, then water to make a volume of about 20 cc., and finally hydrochloric acid until the litmus paper just turned red. The aluminum was determined by the colorimetric method previously mentioned.

The Blank.—Among the reagents used for making aluminum determinations, sodium hydroxide, sodium carbonate and potassium carbonate contain aluminum. Ordinary c. p. sodium hydroxide is not suitable for this work, but samples specially prepared from metallic sodium were obtained which contained very little of the element. The carbonates contained only a very small amount. In every case, however, it was found necessary to run a blank on all the reagents used and make a correction.

Comparison of Methods.—In order to check the method herein used for making aluminum determinations, the combined iron and aluminum were determined in each of three plant materials by the method described by Patten and Winter.[11] The iron was also determined colorimetrically by the method described in the same paper and the aluminum by the method herein referred to. The results of this work are found in Table I.

TABLE I

COMPARISON OF METHODS

Sample	$FePO_4 + AlPO_4$, %	Fe, %	Al, %	Calcd. to $FePO_4 + AlPO_4$, %
1	1.530	0.250	0.141	1.514
2	0.800	.104	.098	0.737
3	.860	.126	.107	.860

The data in Table I indicate that the method herein described gives fairly accurate results.

The Recovery of Aluminum Added to Materials.—In order to show whether or not the aluminum added to materials can be determined, different quantities of aluminum chloride solution were added to four samples of red beets. The samples were ashed and the aluminum was determined. The results are shown in Table II.

TABLE II

RECOVERY OF ALUMINUM

Material	Sample	S. + 0.01 mg. Al	S. + 0.02 mg. Al	S. + 0.03 mg. Al
Al found, mg.	0.0038	0.0130	0.0230	0.0325

These results indicate that added aluminum can be accurately determined.

Table III gives a list of plant materials on which aluminum determinations were made. Tap water and a few animal products used for food are

[10] Meyers, Mull and Morrison, *J. Biol. Chem.*, **78**, 595 (1928).

[11] Patten and Winter, *J. Am. Off. Agr. Chem.*, **11**, 202 (1928).

also included. Where the materials were sufficiently dry to be readily mixed and ground the results are expressed in parts per million of aluminum in the dry sample; otherwise the percentage of water and the parts per million of aluminum in the wet sample are also given. (In making these determinations corrections were made for all of the reagents used.)

The data in Table III show that aluminum was found in all of the

TABLE III

ALUMINUM IN PLANT AND ANIMAL MATERIALS

Materials	H_2O, %	Al. p.p.m. Dry	Wet	Materials	H_2O, %	Al. p.p.m. Dry	Wet
Apples	87	8.4	1.1	Kohlrabi	92	27.5	2.2
Asparagus	93	50.0	3.5	Lemons	84	9.4	1.5
Alfalfa hay	..	99.0	..	Lettuce (roots)	85	850.0	127.5
Banana peels	87	26.9	3.5	Lettuce (tops)	92	155.0	12.4
Barley	..	11.3	..	Lettuce (whole)	88	246.7	29.6
Beans, green string	90	50.0	5.0	Linseed meal	..	73.0	..
Beans, yellow string	91	101.1	9.1	Mustard seed	..	67.0	..
Beans, light red kidney	..	7.0	..	Milk, dried skim	..	4.0	..
				Milk, dried buttermilk	..	28.0	..
Beans, dark red kidney	..	14.5	..				
				Milk, dried buttermilk	..	21.2	..
Beans, early prolific	..	9.0	..				
Beans, pea	..	10.5	..	Oatmeal	..	15.1	..
Beans, sulfur	..	7.0	..	Oranges	83	9.4	1.6
Beef, dried	54	30.2	13.9	Parsnips	80	21.0	4.2
Blood, dried	..	8.5	..	Parsnips	82	23.3	4.2
Beets	86	26.4	3.7	Parsnips	83	14.1	2.4
Beets	85	12.7	1.9	Peanut meats	..	7.6	..
Beet tops	92	293.8	23.5	Peanut shells	..	325.0	..
Cabbage	93	32.9	2.3	Pecan meats	..	4.2	..
Carrots	89	90.9	10.0	Peas, green	78	11.4	2.5
Carrots	91	28.9	2.6	Peas, yellow	..	5.8	..
Carrots	86	20.7	2.9	Peas, white	..	8.8	..
Carrots	91	22.2	2.0	Potatoes	80	11.0	2.2
Carrot tops	81	214.2	40.7	Prunes (pulp)	24	20.5	15.6
Cauliflower	89	66.4	7.3	Prunes (pits)	14.5	7.6	6.5
Celery	94	58.3	3.5	Radishes	94	80.0	4.8
Corn flakes	..	2.8	..	Raisins	17.5	20.4	16.9
Corn, flint	..	2.1	..	Raisins	17.5	24.2	20.0
Corn, popcorn	..	4.0	..	Rice	..	4.7	..
Cucumbers	96	67.5	2.7	Rhubarb (stems)	97	63.3	1.9
Dates (pulp)	17.5	12.9	10.7	Rhubarb (leaves)	93	34.3	2.4
Dates (pits)	10	11.1	10.0	Strawberries	93	44.5	3.1
Eggs, dried	..	12.0	..	Walnut meats (Eng.)	..	5.0	..
Eggs, dried	..	12.4	..	Walnut shells (Eng.)	..	22.0	..
Figs	20	23.0	18.4	Water, tap	..	..	0.04
Fish, cod	60	7.8	3.1	Wheat	..	4.5	..
Fish, white	81	15.8	3.0	Wheat bran	..	6.0	..
Fish, herring	20	11.0	8.8	Wheat middlings	..	3.3	..
Grape fruit	88	7.5	0.9	Wheat flour	..	2.0	..

materials analyzed in quantities ranging from 2.0 p.p.m. in wheat flour to 325.0 p.p.m. in peanut shells. It should be noted here that in all cases where the aluminum content ran unusually high (peanut shells, lettuce, carrot tops, beet tops, etc.) the sample was of such material that the adhering impurities could not be completely removed.

Since in the analyses made of the materials in Table III no special precautions were taken to remove the outer surfaces which undoubtedly were contaminated, samples of four different materials were cleaned and pared so as to remove all of the exterior portions. These were carefully dried, ground in an iron mortar and analyzed for aluminum. The results of these analyses and four blanks which were run at the same time are shown in Table IV.

Table IV

Aluminum in Four Specially Prepared Materials

Material	Sample, g.	Aluminum Mg.	Aluminum P.p.m. corr. for blank
Apples	1.00	0.0145	5.2
Red beets	2.50	.0240	5.9
Potatoes	2.50	.0197	4.2
Carrots	1.25	.0379	22.8
Blanks		0.0090 0.0098	
		0.0083 0.0102	
		Av. .0093	

The results in Table IV show that aluminum was found present in each of the materials analyzed or that some other element was present which reacted like aluminum with the dye. Since all elements known to interfere with this reaction had been removed, we conclude that aluminum was a constituent of these materials.

Summary and Conclusions

1. A method is given for the preparation of plant materials for making colorimetric aluminum determinations.
2. The results of determinations of aluminum in 76 samples of materials are presented.
3. Aluminum was found present in all of the samples examined.
4. Four samples which were carefully prepared by removing the external surfaces so as to avoid contamination were analyzed and aluminum was found present in each of them.

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