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TITANIUM, BARIUM, STRONTIUM
and LITHIUM IN CERTAIN PLANTS

By WM. P. HEADDEN



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TITANIUM, BARIUM, STRONTIUM AND LITHIUM IN CERTAIN PLANTS

By WM. P. HEADDEN

In Bulletin 35 of the Colorado Experiment Station, (1896), page 92, I mentioned, in a footnote, the presence of strontia in the ash of our alfalfa, also the absence of lithia. The latter fact struck me as peculiar, for I knew that lithia is of common occurrence in our waters. Subsequent work has shown that it is seldom, if ever, absent from the ground-waters of this section. I have never failed, so far as I can recall, in finding this element in either a ground- or river-water which I have examined for it. That lithia is usually present in micas, felspars and many other minerals, and is very widely distributed in small quantities is common knowledge. When it is considered that our soils are rich in felspar fragments with some mica, it is no cause for surprise that lithia is present in the waters. This judgment is not simply an inference from the fact that felspars often contain lithia, but it is an experimentally obtained fact that the pink felspar commonly occurring in our soils yields lithia when finely ground and treated for some days with water and carbon dioxid. The same is true in regard to strontia, to such a degree, that the strontia can be easily detected in the residue obtained on evaporating the aqueous solution to dryness. This does not exclude the possibility of other sources, but it presents itself as one sufficient to account for the very general, if not universal, presence of lithia in the waters of the section and for the presence of strontia in the ash of the alfalfa growing in soils so abundantly provided with this source of it.

The statement made in the note referred to was based on the results of the ordinary determinations of the alkalis in the course of an ash analysis, and the question has frequently suggested itself whether it is true that lithia is absent from the ashes of our alfalfa, or whether I had simply not taken enough of the ash to find it. The statement of the note was evidently not intended to exclude the possibility of the presence of spectroscopic traces, though such might not have been observed when operating with one gram of ash. This fact made it all the more reasonable that I should examine larger amounts of ash with special regard to the presence of lithia. This has been done several times in the intervening years with the result that in only one sample of alfalfa have I found a fair amount of lithia and in many of them only a faint trace.

Some of the samples tested have been obtained from other sections of the state, with whose soils I am not so familiar as with those of this section, but the origin of the soils in many cases is essentially the same, if not identical in character, and I believe it entirely reasonable to assume that the samples examined were entirely comparable.

The statement made in the note is justified in this far, that alfalfa

takes up a very little lithia even from soils presenting a good supply of this element, both in the rock particles comprising a rather large percentage of the soil itself, and in the ground-water.

Further, there are traces of lithia present in the water used to irrigate the land during the growing season of alfalfa, which facts have been stated in various bulletins of this Station, and yet the ash of alfalfa shows the presence of only very small amounts of this element.

The absence of lithia under these conditions is suggestive that alfalfa may not assimilate lithia readily, but is no more striking than the presence of baryta and strontia in determinable quantities. This contrast is very marked in the case of our alfalfa. That barium and strontium must both be present in the soil if they appear in the ash of the plant is evident unless they had been applied to the plant, which, of course, was not the case. The quantities of these elements present in our soils has not been determined in many instances, so far as I know, but their presence can be easily demonstrated. I have referred to the presence of pink orthoclase fragments as constituting a considerable proportion of our soil, and have already mentioned the fact that it contains strontia and lithia in sufficient quantities to account for the presence of these compounds in the river- and ground-waters. It also contains traces of both baryta and titanitic acid. The trace of baryta present is not very heavy. I used 10 grams of the mineral in testing for it and obtained a very small amount of baric sulfate.

REASONS FOR ASSERTIONS THAT ELEMENTS ARE IN SOILS

We have several grounds for asserting the presence of these elements in the soil, their presence in the plants grown on them, their presence in some of the constituent minerals of the soil and their presence in the river-waters used in irrigating the land and in the drainage- and ground-waters.

Their relative quantities in the soil have not been determined, either in connection with this or incidentally in connection with other work, although we shall present some data pertaining to this point.

The ample supply of lithia in the waters and its almost total absence from the alfalfa plant, while strontia, which is no more abundantly supplied, occurs constantly in our alfalfa, struck me as an interesting fact. Baryta is apparently always present in the ashes of our plants and in relatively large quantities.

It is unfortunate that in the work I have done in this connection, I have had to use crude ashes which are always contaminated, sometimes very badly so, with soil particles and I have devised no way to avoid the objections that the presence of such material justifies.

The presence of a large percentage of such contaminating material cannot, in many cases, be avoided, and it does not necessarily indicate carelessness in gathering the sample nor in preparing it. If samples be grown under natural conditions, not in a house, they will gather more or less dust and dirt, according to the character of their leaves, the frequency of winds, the fineness of the surrounding soils, etc. This is marked in the case of the tobacco and similar plants with leaves favoring the adherence of dust.

I was surprised in attempting to analyze a crude ash to find almost 30.0 percent of insoluble, which was so good as wholly sand. I had grown and gathered these plants and had dried them on boards to prevent their accumulating dirt of this character. This was dust that the plants had gathered by having it blown upon them. In another case, that of some tobacco that was given to me. This contamination was very strong. The appearance of the tobacco, which, I suppose, had been grown for the market, was all that one could desire and yet the crude ash from this sample carried 55.0 percent insoluble in hydrochloric acid after the carbon had been burned out. The insoluble in this case appeared to be made up wholly of very small angular fragments of a colorless, transparent quartz. This contaminating material cannot be removed mechanically nor by washing, which is wholly inadmissible.

If one attempts to determine baryta or titanitic acid in such an ash, the results are discouragingly questionable in value and there is no way to avoid the difficulties that present themselves. If one evaporates the ash to dryness with an acid, as one is almost compelled to do, the whole or the major part of the baryta, if present at all, will remain with the insoluble, for there is enough sulfuric acid present in all ashes to effect the precipitation of baric sulfate; one is not quite certain about strontia and knows that titanitic acid, if present, is divided between the solution and the insoluble residue. However one may proceed in treating the insoluble residue, the question as to the source of the titanitic acid or baryta or strontia that may be present presents itself: i. e., was the titanitic acid, baryta or strontia derived from the ash or from the soil particles in the insoluble? If the insoluble be rejected, the whole of the baryta, certainly a part of the titanitic acid and possibly a part of the strontia will be rejected with it.

ASSUMPTIONS MADE

In the work here presented, the following assumptions are made: first, that all lithia soluble in hydrochloric acid belongs properly to the ash of the plant; second: that quartz sand contains neither baryta nor strontia, and as the insoluble portion of the ash is very largely composed of this, the amount of baryta or strontia derived from soil particles is negligible; third: owing to the fact that titanitic acid occurs in quartz sand, no importance can be attached to its appearance in the statement of an ash analysis in cases where the insoluble portion makes up any considerable portion of the ash and has been fluxed or otherwise manipulated as a part of the ash.

My reasons for the last assumption are simply the well-known facts pertaining to the occurrence of titanitic acid in a very large range of minerals, including clays and soils. Quartz is included in the minerals in which titanitic acid occurs. This is true not only of rutilated quartz, in which the needles of rutile or sagenite are visible, but in quartz sand that appears white and pure. I washed a quantity of sand out of one of the heavily contaminated ashes and determined the titanitic acid in it. I found a quantity, that, calculated on the crude ash, corresponded to 0.252 percent of titanitic acid. Determinations made on the crude ash itself ranged from 0.268 to 0.288 percent. I am convinced that the titanitic acid found in the

crude ash was wholly carried by the quartz sand in it. I have another sample of sand furnished by the Berkshire Glass Sand Company, Cheshire, Mass. This sand was obtained for the purposes of filtration and I take it to be simply sized, ground quartz. This sample contains 0.05 percent titanic acid. These facts, together with the known common occurrences of titanic acid in clays and minerals, seem to me to necessitate the assumption made relative to its source even though the amount found in the ash may not be proportional to the amount of the insoluble present. As a matter of fact, we have no data to show how the titanic acid actually varies in the different insoluble portions. It does not seem necessary to state that this assumption, i. e., that the titanic acid found belongs to the sand and soil particles and not to the ash proper, pertains only to the samples presented and does not question the occurrence of this substance in other ashes, or to deny the possibility that it may occur partly in the ash proper and partly in the insoluble portion, and I have no reason to assert that the latter is the case and believe that it is wholly contained in the insoluble portion.

METHODS USED IN THIS WORK

Owing to the fact that this work has been done from time to time, as circumstances permitted, it has not all been done by the same method; for instance, lithia has been separated both by alcohol-ether and by amylic alcohol. Both amylic alcohol and absolute alcohol and ether have been used in separating lime, strontia and baryta.

The general method was to obtain a solution containing the basic elements of the ash. This was accomplished by evaporating the ash to dryness with hydrochloric acid and taking up again with hydrochloric acid. The solution contained the phosphates, soluble sulfates, etc.; the insoluble portion contained the carbon, sand, silica and insoluble sulfates. The loss obtained on igniting this residue was considered as carbon, which is not strictly correct, and the residue as sand, etc., although it always contains some sulfates. This sand, etc., was fused with sodic potassic carbonate, molecular mixture, disintegrated in boiling water and washed with a dilute solution of sodic carbonate. The filtrate and wash waters were rejected. I tested this filtrate for titanic acid and only occasionally found a trace present. The insoluble portion of the melt was dissolved in hydrochloric acid in which it is easily and completely soluble, evaporated to dryness with hydrochloric acid to separate silica, as in a silicate analysis. The filtrate from this silica was added to the main hydrochloric acid solution and the united filtrates were evaporated down to a small volume. The silica was dissolved in hydrofluoric acid with the addition of sulfuric acid, evaporated down, and some of the sulfuric acid driven off by heating on a sand bath; this sulfuric acid solution containing some of the titanic acid was added to the united hydrochloric acid solution which was, as a rule, already turbid, due to the separation, principally, of calcic sulfate. The volume of the filtrates was less than 100 c.c. and strongly acid with the hydrochloric acid, sufficiently so to hold all of the phosphates in solution. To this acid solution I added usually about two and one-half volumes of 95 percent alcohol and allowed it to stand over night. The precipitate contained all of the baryta, strontia and some, or all of the lime as sulfates and the

titanic acid as a phosphate. I did not in this work take particular pains to make the precipitation of the lime complete. The precipitate contained the whole of the baryta, strontia and titanic acid; the filtrate contained the whole of the lithia. The precipitate was filtered off and washed at first with 50 percent alcohol acidulated with hydrochloric acid to get rid of all iron salts, and subsequently with 50 percent alcohol, dried and fused with sodic potassic carbonate to decompose the sulfates. After the sulfuric acid was thoroughly washed out, for which I used a dilute sodic carbonate solution to avoid loss of baric carbonate, the precipitate of carbonates containing also the titanic acid, largely a phosphate, was treated with hydrochloric acid which dissolved the lime, baryta and strontia but only a small part of the titanic acid. This titanic acid ran through the filter very badly and had to be separated from the lime, etc., by precipitation with ammonia. Enough of the titanic acid goes into solution in hydrochloric acid to form the characteristic flocculent precipitate of hydrated titanic acid to carry the whole of the undissolved titanic acid down with it. This titanic acid precipitate can be ignited and weighed, but the results will be too high, by a great deal. This titanic acid can be brought into complete solution, but with difficulty.

The filtrate from the titanic acid precipitate was boiled with the addition of sodic carbonate until the ammonia salts were wholly destroyed, the carbonates were filtered off, eventually converted into nitrates and the calcic nitrate dissolved out by means of absolute alcohol and ether; the baryta was separated from the strontia as chromate and finally thrown down as sulfate, in which form it was weighed. The strontia was thrown down as chromate from the filtrate from the baric chromate by the addition of ammonia to faint alkaline reaction and alcohol. Other methods were tried but none were more satisfactory in my hands than this. This strontia determination is the most unsatisfactory of the determinations made; still, when really weighable quantities of strontia are present, this method works fairly well.

To return to the titanic acid, the precipitation as a phosphate seems to be complete if the solution be not too strongly acid, so strongly acid that the calcic sulfate will not come down completely. The precipitate as thrown down from the solution obtained by dissolving the carbonates of the alkaline earths in hydrochloric acid contains phosphoric acid, even after fusion with sodic carbonate or sodic potassic carbonate. Rose suggests that the titanic phosphate may be decomposable by fusion with this reagent, and Fresenius asserts that it is; but my precipitates were not decomposed. The only advantageous way that I found to work this precipitate was to fuse it with potassic acid sulfate and determine the titanic acid colorimetrically, observing the well-known, necessary precautions.

In the lithia determination, the alcoholic filtrate from the precipitate of calcic sulfate, etc., was evaporated down to a small volume, principally to get rid of the excessive acid, diluted to a convenient volume, milk of lime added in excess and boiled. The precipitate is voluminous, but filters and washes easily, which is not the case if ammonia be used to effect this precipitation. After the filtrate and wash waters had been evaporated down to a volume of about 400 c.c., I precipitated the lime by adding

ammonic oxalate to the boiling solution. I find that if the lime be thrown down as carbonate it carries easily detected quantities of lithia with it and no amount of washing and no number of reprecipitations will remove it. I had this repeated 17 times in the case of a solution to which I had added only a small amount of lithic chlorid, and the calcic carbonate obtained in the seventeenth precipitation showed the presence of lithia strongly. This does not seem to be the case with the oxalate. The ammonia salts in the filtrate were destroyed by concentrated nitric acid, and the remaining magnesia removed as phosphate, and the lithia, after the removal of the excessive phosphoric acid and destruction of the ammonia salts, was extracted with strong alcohol and hydrochloric acid and finally separated by alcohol saturated with hydrochloric acid and ether and weighed as sulfate. No attempt was made to make quantitative spectroscopic determinations.

As previously stated, the determination of strontia is the most unsatisfactory; beside, in most instances, it occurs in very small quantities.

THE SCOPE OF THE WORK PRESENTED

The presence of barium and strontium in the alfalfa ash in fairly large quantities and the very sparing occurrence of lithium under soil conditions favorable to the assimilation of lithium by the alfalfa suggested the question of the relative quantities of the elements in the ashes of other plants grown under similar conditions. Inasmuch as the occurrence of lithium is often mentioned in connection with tobacco, and in such a way that one is led to infer that, at least, some sorts of tobacco, if not a great many varieties of this plant, are remarkable for this occurrence, the idea occurred to me that this might be a good plant to grow beside the alfalfa to ascertain whether its ash would be rich in lithium, while that of the alfalfa grown under the same conditions would be poor in this element; and further, to see whether they would take up the same elements. Of course reference here is had to the rare or accidental constituents, specifically to barium, strontium and lithium. We have already indicated that we believe that but little or no importance can be attached to the titanitic acid that appears in our statements of analytical results. In other words, the statements concerning the occurrence of lithium in the ash of tobacco led us to adopt it as a standard for the maximum occurrence of this element in plant ashes. Subsequently we shall have occasion to see to what extent this choice was justified, or what purpose it served.

Perhaps we should state, in order to avoid misapprehensions, that the occurrence of these rarer substances in plant ashes has been known for a long time. For instance, Scheele mentioned the occurrence of barium in the ash of certain trees as early as 1788, and it has been found in very many ashes since that time; so, too, the occurrence of strontium, lithium, titanitic acid and a number of other rare elements has been mentioned by various investigators. There is nothing new in their occurrence, and their distribution seems to be very general. This, too, is common knowledge, but a citation indicating this may not be out of place. "Lastly, rubidium has been found in the ash of many plants and in the saline or crude potash obtained from the residue of the beet root sugar manufacture. According

to Grandeau, the salin of the north of France contains 1.8 grams of rubidium chloride in a kilogramme. The amount of this salt annually abstracted from the soil amounts to about 260 grams per hectare, although the proportion of rubidium existing in the soil is too small to be detected even by spectral analysis. Rubidium has also been detected in tobacco leaves, in coffee, tea, cocoa and crude tartar. In minerals and mineral waters rubidium and caesium are always associated with lithium, and generally also with potassium and sodium, but plants have the power of assimilating two or three of these metals to the exclusion of the rest. Thus tea, coffee and the salin of beetroot contain potassium and rubidium, but not a trace of lithium." (Watts Dictionary of Chemistry, Vol. 5, p. 127. New edition 1877.)

Again we find, "One has found the following rarer elements in the sugar beet caesium, rubidium, manganese, titanium, vanadium and boron." (Ruempler, Manual of Sugar Manufacture, 1906, p. 149). Ruempler makes no mention of lithium as occurring in the beetroot, from which we infer that he considered it as absent.

The statement made in Watts' Dictionary of Chemistry that no trace of lithium occurs in the beetroot is in harmony with this assumption.

This statement is not true of Colorado beets, for lithium occurs in the ash both of the tops and the roots. This must be attributed to the different soil conditions and not to the varieties, for our beets were grown from German, French or Hungarian seed.

Again we find concerning the occurrence of lithium: "In smaller quantities it is very widely diffused, being found in sea-water, in many micas, felspars, in the ash of various kinds of tobacco and in many mineral springs." (Watts' Dictionary of Chemistry, Vol. III, p. 727.) Tobacco is again indicated as a lithium assimilating plant.

I grew some tobacco, White Burley, alongside of some alfalfa plants. The plants were not more than 15 inches apart so soil differences, but not the differences in the root systems and feeding areas of the plants, were eliminated. I also grew *nicotiana affinis* on the same little patch of ground. Other plants were included from time to time until the following have been examined: Alfalfa, first, second and third cuttings, alfalfa hay from another place, alfalfa grown in the mountains and general samples of alfalfa hay, two loco weeds, *Astragalus alba* fl. pl., and *Aragallus Richardsonii*, sweet clover, *Melilotus alba*, three samples, corn leaves, pea vines, tobacco from Colorado, Connecticut, Pennsylvania, Kentucky and Texas.

Originally I intended to study the occurrence of barium, strontium, and lithium only. The titanic acid that appears in the analysis was not originally included in my plan, but it was determined simply because it had to be separated from the alkaline earths. Its percentage in most cases is too high, due to the presence of phosphoric acid in the precipitate as previously stated.

Any data given regarding the soils are incidental and no complete analyses of the soils have been attempted. The soil of my garden for instance contains 0.573 percent titanic acid, 0.0319 percent baryta and 0.0105 percent strontia. No test was made to show the presence of lithia, but its presence is thoroughly well established by the fact that it is present

in the plants grown on it, and the supply was the same for alfalfa and the tobacco except in so far as their feeding areas may have differed. An analysis of the surface foot of this soil would not help in proving that the plants had absolutely the same supply of lithium or of barium. We can only assert that the lithia supply in the soil available to the plants was probably not materially different, and no more can be said concerning the supply of baryta or strontia.

TITANIUM, BARIUM, STRONTIUM AND LITHIUM IN CERTAIN PLANT ASHES

ALFALFA*						
	Sand	Carbon	TiO ₂	BaO	SrO	Li ₂ O
1st cutting	2.410	0.106	0.343	0.0240	0.0210	0.005
2nd cutting	7.868	4.893	0.327	0.0341	0.0225	Trace
3d cutting	2.996	4.941	not detd.	0.0302	0.0195	Trace
Rist canyon, mountain grown	4.774	5.126	0.0164	0.0164	0.0028	Trace
Sample grown on college farm	not detd.	0.0578	0.0239	Trace
Sample hay	0.0515
Sample grown on college farm **	not detd.	0.0550	0.0142	Trace
Hay (Paonia)	0.0719

These samples represent different soils which I have not analyzed, but they vary greatly. The Rist canyon sample, for instance, was grown on a mountain soil. This soil was evidently quite shallow and lay on the gneiss of the region which was the source of the soil itself. The farm samples were grown on a different soil, a deep one, with different conditions in regard to the ground-water, and the soil itself was partially derived from younger rocks.

SWEET CLOVER, MELILOTUS ALBA

Soldier Canyon, near stone quarry, sample in bloom but second growth, as plants had been badly attacked by grasshoppers.

	Sand, etc.	Carbon	TiO ₂	BaO	SrO	Li ₂ O
1st sample	6.679	6.132	not detd.	0.0825	None	0.0104
2nd sample	2.921	1.764	not detd.	0.0844	Trace	Trace
W. A. Martin (hay).....	***2.0485	10.938	0.463	Trace	Trace	0.032

*Percentages are calculated on crude ash.

**Determinations made by R. H. Gustavson, Associate Professor of Chemistry.

***Largely calcic sulfate.

The first two samples were grown on a red clay soil derived from the Jura-Triassic formation. The third sample was grown on a somewhat marshy soil on the horizon of the Niobrara shales. Further, these plants were the first season's growth, cut when in full leaf. The variation in these results is great, but the absence of barium and strontium in the Martin sample, except in traces, was established by a repetition of the analysis.

NICOTIANA AFFINIS

	Sand, etc.	Carbon	TiO ₂	BaO	SrO	Li ₂ O
Sample grown 1918.....	0.037	0.020	Abundant
Sample grown 1919.....	present	0.006	Abundant
Sample grown 1920.....	23.43	3.13	0.0369	0.024	Abundant
Sample grown 1920.....	25.918	4.007	0.475	0.0857	0.0135	0.0496

TOBACCO

Grown at Ft. Collins.....	9.73	2.67	0.390	0.0158	None	0.0328
Dark leaf, Kentucky.....	9.814	2.214	0.303	None	None	Trace
Seed leaf, Conn.....	26.520	12.312	0.250	0.062	None	0.0190
Seed leaf, Conn., stalks..	9.141	6.561	0.169	0.067	None	0.0111
Big Cuba, Texas.....	55.046	1.940	0.288	0.0069	Trace	0.0189
Big Cuba, stalks.....	19.883	3.870	0.191	0.2004	None	0.0031
Seed leaf, Penn.....	16.010	1.360	0.158	0.0299	None	0.00497
Seed leaf stalks, Penn....	14.88	4.850	not detd.	0.0164	None	0.00497

We have a tobacco grown at Fort Collins, Colo., one from Connecticut, one from Kentucky, one from Pennsylvania and one from Texas. I am indebted to Dr. Jenkins, of Connecticut Station, Dr. Peter of Kentucky Station, Dr. Frear of Pennsylvania Station, also to Mr. Olson of the substation at Ephrata, to the authorities of the Texas Station, and Mr. McNess of the sub-station at Nacogdoches for these respective samples.

I cannot give details concerning the soils in which these samples were grown, not even the soil at Fort Collins, for I have not made a sufficiently exhaustive analysis of the soil on which my sample was grown to be of any value in this connection. My sample of tobacco was grown beside some of my alfalfa samples for the purpose of ascertaining, if possible, whether the observation relative to the absence of lithium from the alfalfa ash and its presence in the tobacco ash would be corroborated. As this is a purely comparative method, even as complete an analysis as possibly can be made would add but little if anything to our knowledge of what causes the differences in the deportment of the plants.

ABILITY OF PLANTS TO SELECT CONSTITUENTS

I have no theory concerning the ability of plants to select the constituents that they take up, but there is certainly some other condition than the mere presence of the element that determines it, even if the element is an accidental one. If the element, lithium for instance, were actually absent from the soil, it, of course could not be taken up but when present some plants seem to take it up much more readily than others.

Given the presence of these accidental ash constituents, their assimilation by plants may be influenced by the composition of the soil, but I don't see how we can interpret our analytical results to explain the processes by which these accidental constituents vary in different plants.

Dr. Frear kindly furnished me with an analysis of a Pennsylvania tobacco soil, not identical however, with the one on which the Pennsylvania sample was grown. It, however, is the same class of soil, differing a little in texture, and it may be of interest in this connection.

ANALYSIS OF HAGERSTOWN SILT LOAM SOIL, PENNSYLVANIA
EXPERIMENT STATION

	Surface Soil	Sub-Soil
Moisture	2.42	2.22
Humus (Loss on ignition).....	4.88	4.75
Insoluble (Sand, etc.).....	67.54	66.77
Soluble silica	11.82	11.73
Dissolved in hydrochloric acid:		
Potash	1.62	0.67
Soda	Trace	Trace
Lime	0.61	0.62
Magnesia	1.25	1.19
Brown oxid of manganese.....	0.05	0.05
Ferric oxid	4.13	4.13
Aluminic oxid	6.57	8.00
Phosphoric acid	0.191	0.177
Sulfuria oxid	0.373	0.428
	<hr/>	<hr/>
	100.464	100.905
	<hr/>	<hr/>
	Surface Soil	Sub-Soil
Soluble in water.....	0.087	0.127
Sulfuric acid	0.001	0.002
Chlorin	0.042	0.049
Soluble in one percent Citric acid		
Potash	0.053	0.054
Percent of total potash.....	8.500	9.500
Phosphoric acid	0.044	0.042
Percent of total phosphoric acid.....	2.250	1.980
Total nitrogen	0.110	0.094
Available nitrogen	0.018	0.013
Nitrogen in nitrates.....	0.004	0.002
Proportion of nitrogen to humus.....	2.260	1.980

Dr. Frear mentions the work of Mr. J. W. White in connection with titanin acid, of which Mr. White found in the hydrochloric acid solution small amounts varying with the manner of extraction. Following the official method, Mr. White obtained 0.06 and 0.04 percent from the soil and sub-soil respectively, while the insoluble residue yielded 1.73 and 1.48 percent respectively.

Mr. Olson, in charge of the work at Ephrata, sent me a sample of the soil on which the sample of tobacco given in the table of analyses had grown. I determined the titanin acid, barium and strontium in this sample with the following results: Titanin acid 0.852 percent, baric oxid 0.0457, strontic oxid none. As the titanin acid that I obtained is much lower than the amount found by Mr. White, I had Mr. Tobiska, one of my assistants, check my determination; he obtained 0.884 percent. The determination of baryta was satisfactory and is probably correct for this sample. I used twenty grams for the determination of baryta and strontia and the latter is not present in sufficient quantity to give any indication of its presence in this amount of soil. No attempt was made to determine the lithia present, but it was sought qualitatively, using five grams of soil. It was present and could have been determined readily by gravimetric methods.

The absence of strontia from this soil is a sufficient explanation for its non-appearance in the ash of the tobacco grown on the soil, but this is not the case with the sample grown at Fort Collins, which carries titanin acid 0.573, baryta 0.0319 and strontia 0.0105 percent.

The presence of strontia in the alfalfa and *Nicotiana* ash really answers the question of the availability, whether it is soluble in water or not. Still the question suggests itself and though we have found strontia in easily determinable quantities in some residues obtained by evaporating ground-waters to dryness, I thought that it might be well to test a sample

taken at random from samples preserved from work of years past. The residue chosen was not one in which strontia had been reported in analysis, but it was abundantly present.

Mr. George S. McNess, Superintendent of the station at Nacogdoches, Texas, kindly furnished me the following data relative to the soil on which the Texas sample was grown: Surface soil, orangeberry fine sandy loam, sub-soil, a red clay.

MECHANICAL ANALYSIS

	Top Soil	Sub-Soil
Organic matter	0.58	0.29
Gravel, 261 m.m.	0.56	1.26
Coarse sand, 160.5 m.m.	1.34	1.40
Medium sand, 0.5 to 0.25 m.m.	4.52	2.74
Fine sand, 0.25 to 0.1 m.m.	30.84	18.86
Very fine sand, 0.1 to 0.05 m.m.	30.16	18.10
Silt, 0.05 to 0.005 m.m.	26.46	23.10
Clay, 0.005 to 0.0001 m.m.	6.04	34.54
Water—Soluble in parts per million.		

	Top Soil	Sub-Soil
Ca	5	5
Mg	16	15
K	19	64
SO ₄	52	102
Cl	37	43
HCO ₃	50	43
NO ₃
PO ₄	21	10
SiO ₂	41	36

In making a solution of the ash of tobacco grown on this soil, I was surprised to find that more than one-half of the ash consists of a fine sand which, after treating the ash with hydrochloric acid, appears as a fine white sand, apparently wholly made up of small, irregular, transparent quartz particles. While the titanic acid that appears in this ash is not materially higher than in some other samples, the fact that it is among the richest in titanic acid, though one-half of the ash is apparently a pure quartz sand, might be interpreted as showing that the ash proper must be unusually rich in titanic acid.

As it is exceedingly easy to wash this sand out of the ash, especially with the aid of hydrochloric acid, I determined to ascertain whether the pure sand contained titanic acid or not. This was done with the result that I found the sand decidedly rich in titanic acid. I wrote to Mr. McNess asking if there were not bodies of white sand near the field where the tobacco was grown, whence the sand might have been blown upon the tobacco, and if so, to send me a few ounces of the sand. I proved to be correct that there is sand near this locality. It is, however, not white, but brownish. This is due to a thin coating of ferric oxid. The sand sent by Mr. McNess was quite interesting. It all passed a 1 mm. sieve except small concretions of clay ironstone, or clayey, hydrated oxid of iron. The sand itself was white or grayish white in mass after it had been boiled out with hydrochloric acid, and examination with a pocket magnifier, revealed only transparent fragments of quartz. This sand contained 0.286 percent titanic acid. The iron oxid dissolved out of the iron concretions contained only a trace of titanic acid, but the clayey material, insoluble in hydrochloric acid, amounting to 17.96 percent, carried 1.34 percent of its weight of titanic acid. This clayey residue from the iron oxid was rela-

tively very rich in titanitic acid, but only a trace of it went into solution with the iron. While I was a little surprised to find the sand so rich in titanitic acid, there was no reason why I should be, nor is there anything especially new in the fact, though it is not often mentioned, rutiled quartz is a well-known occurrence of the two minerals, rutile or sphenite and quartz. Dana cites Fuchs as having found 1 to 1.5 percent of titanitic acid in Rose quartz. It does not seem to have been common for investigators to examine quartz for titanitic acid, but it seems to be frequently present in this mineral. I have some quartz sand obtained from the Berkshire Glass Sand Company, Cheshire, Mass. I take this to be simply sized, pulverized quartz. It contains a heavy trace of TiO_2 . I also tested a sample of quartz broken out of a piece of our granite where it was associated with tourmaline. This contained only a slight trace of, if any, titanitic acid.

PLANTS NOT SOURCE OF TITANIC ACID

I believe that in all the cases presented in this work, the soil, clay, sand or other minerals constituting the insoluble residue, are to be considered as the source of the titanitic acid and not the plants. For this reason I have considered it of little importance that the titanitic acid determinations are in some cases too high, which I am aware is the case.

I did not examine the Texas soil for baryta, strontia or lithia. In fact, the sample of sandy soil that Mr. McNess was kind enough to send me was not supposed to represent the tobacco soil but simply to account for the fine sand present on the leaves in such quantity. The 30 percent of very fine sand in the soil itself might go very far toward accounting for its presence on the leaves. That this sand had reached the leaves as dust was suggested by the fact that the ash from the stalks contained only a little over one-third as much sand, etc., as that of the leaves.

The analysis of the Dark Leaf tobacco from Kentucky was made four times before I was willing to accept the results as established. This sample is certainly exceptional but it contains no barium and only the faintest trace of lithium.

The Connecticut sample was the best available one and answers the purpose for which it was used quite well; perhaps sufficiently so, as the titanitic acid is of little consequence and it is not especially rich in this constituent, which in this case, as in the other cases, probably came from the soil.

LOCO WEEDS

Astragalus alba fl. pl. collected at Fossil Creek.

Sand, etc.	Carbon	BaO	SrO	Li ₂ O
10.6500	0.570	0.0220	0.0096	0.007
<i>Aragallus Richardsonii</i>		Trace	Absent	Trace

The results obtained with the ash of the loco weed, *Aragallus Richardsonii*, really led to the analysis of the Rist Canyon sample of alfalfa to see whether the practical absence of barium, strontium and lithium was to be wholly explained by the character of the soil, or whether this loco weed was not an active gatherer of these constituents. The alfalfa grown on this soil contained less barium and strontium than some other

samples, but these elements were present in weighable quantities, whereas this particular loco weed had gathered none of either of them. The *Astragalus*, on the other hand, grew on the plains where there is an abundant supply of these elements available and its ash is not especially rich in them, less so than alfalfa. The only interest attaching to this fact is that at one time the loco disease was attributed to the presence of barium in the loco weed.

The *Aragallus* was very plentiful where we gathered the sample and some of it had been browsed by the cattle ranging in that section.

These plants, the *Astragalus alba fl. pl.* and the *Aragallus*, are plentiful in the respective sections, but I have not learned of any case of loco disease in either of them.

CORN LEAVES

Crude ash equaled 13.93 percent of the dried leaves. The crude ash contained,

Sand, etc.	Carbon	TiO ₂	BaO	SrO	Li ₂ O
54.230	10.475	0.723	0.0210	0.010	0.0197

Barium was found in the leaves of Egyptian wheat grown in the Nile delta many years ago, so there is no novelty in its occurrence in corn leaves. I was surprised at the titanic acid, and while this particular determination may be too high, it serves to indicate, in fact shows, that the amount of it actually present in this case is relatively large. The silica in this case is certainly not all sand, but whether the titanic acid is associated with the silica of the leaves, or the sand and dust accumulated on them may sometime be determined. At the present time I do not know.

PEA VINES

These were garden peas, tall growing varieties, well supported by a chicken wire fence, so the amount of dirt or soil appearing in the crude ash is rather unexpected, as the vines were cut and dried on a rack. Crude ash contained,

Sand, etc.	Carbon	TiO ₂	BaO	SrO	Li ₂ O
25.069	1.946	0.438	0.0398	Trace	0.040

The titanic acid is too high; of this I am certain, but it is very abundant and is probably not less than 0.350. This uncertainty in regard to the titanic acid arises from the fact that the phosphate of titanium is not readily decomposed by fusion with sodic potassic carbonate. The statement that the titanic phosphate is converted into Na₂ TiO₃ and Na₃ PO₄ by fusion with sodic carbonate is made in *Zeitschrift der Analytischen Chemie* Vol. 22, p. 561. I fused the phosphate for 20 minutes with NaKCO₃ and did not find this to be the case. The decomposition was very imperfect and it is from this fact that I am certain that those determinations of TiO₂ in which this reaction was depended on to decompose the titanic phosphate are too high, but I have no means of judging how much they are too high, as this will depend entirely upon the amount of titanic phosphate that remained unchanged by the fusion.

The lithia seems also to be high, but in this case the notes taken at

the time the analysis was made indicate the occurrence of a liberal quantity of this element.

POTATOES

The ash of some potatoes, Downings, grown without fertilizers, was examined. The tubers were washed with a stiff brush to remove any adhering soil particles, sliced, air-dried and burned at a very low temperature in an open vessel and not in a muffle. The total ash was 1.033 percent, so 20 grams of ash corresponded to almost exactly 2000 grams of fresh potatoes. In spite of the effort to remove all of the soil from the potatoes, it is readily conceivable that the ash might contain some soil particles. This statement is made because titanitic acid was present in the ash. Its quantity was not determined but it showed distinctly in the color of the ignited insoluble residue from the ash, being yellow while hot and colorless when cold. This, however, was not depended on for establishing the presence of titanitic acid. Barium was absent; strontium and lithium were present in traces only. I have a note on another sample of dried potatoes in which the absence of these elements is asserted. I do not know anything about the ash of potato vines.

BEETS

The sugar beet has been pretty thoroughly studied, especially in the various intermediate products obtained in the preparation of sugar from its juices. I have tested our beets, their ashes and the potash recovered by evaporating the Steffen's waste-waters to dryness, also the lime-cake from the filter presses, but I have found only lithium in the beet or its ash and titanitic acid and a trace of barium in the lime-cake.

I have cited in a previous paragraph the statement that lithia does not occur in beet ashes, also that manganese is classed as rare. Lithia is present in the ash of our beets, both of the leaves and the roots and so is manganese. This is, I think, present in all of the plants grown in our soils. I do not recall an exception to this statement. Quite recently an incident occurred that led me to test again a sample of ground, dried beets that had been kept in a Mason fruit jar for twenty years to see if our analysis of the ash of this sample was correct in giving manganese. The ash, where fused, was green and the reaction with ammoniac persulphate was very strong indeed. The portion of the potash obtained by evaporating down the Steffen's waste-water, that was insoluble in water, gave a good reaction for lithia. I, however, did not find any caesium or rubidium. The test for these was made with platonic chlorid. The double salts were treated with small portions of water repeatedly and finally the residual double salts were dissolved in hot dilute hydrochloric acid and the platinum precipitated as sulfid, simply because this was easier for me to do than to reduce them in hydrogen. The filtrate contained neither caesium nor rubidium.

I examined the lime-cake for barium and strontium, but only a trace of the former was found. The presence of this trace in the lime-cake has no significance whatever, as it may have been derived from other sources than the beets. The same applies to titanitic acid which was found, for it may have been contained in the limestone, or in the coke ash, or in the

beets themselves. Its source is uncertain and no importance attaches to its presence, only its total absence would be conclusive that it does not occur in the beet juices.

Concerning the occurrence of lithium in the tops and roots of our beets, I wrote in 1902 "Its (lithium's) presence was detected in the ash of the beets grown upon this plot and also in the ash of their leaves. This is peculiar for I have tested a number of ashes of alfalfa, some of it grown within this same swale and have never succeeded in finding it." Bul. 72, Colo. Exp. Sta., p. 34.

ALFALFA AND TOBACCO PRESENT GREATEST INTEREST

The two plants examined that present the greatest interest are the alfalfa and tobacco. I have used only Colorado alfalfa; this, however, is probably quite sufficient, for the elements with which we have concerned ourselves occur in these soils in sufficient abundance, if not in as great abundance, as in most other soils, either in the humid or semi-arid sections of our country.

If there were no barium, strontium or lithium in the soil these elements, of course, would not appear in the ashes of the plants grown on it. The contrary, however, does not appear to follow; that is, it does not necessarily follow that an element, though in solution in the soil, will appear in the ash of every plant grown on it. This was the feature in the composition of alfalfa ash, namely, the absence of lithium, or its presence in traces only, that directed my attention to this subject. It appeared to me remarkable that this should be so, for I had found lithia in the ground-waters of this section, also in all of our river-waters. Strontia is also present in these waters, and it appears in the alfalfa ash, whereas the lithia is so good as wholly absent. The felspar that occurs abundantly in our soils carries traces of strontium, lithium and also of barium. While strontium seems to be always present in an alfalfa ash, lithium is present in traces only though this element is present in the ground-waters, the drain waters, our river- and many spring-waters, and certainly in our soils carrying felspar. We assume that an element present in solution is assimilable by one plant as well as by any other, provided that the plant does not exclude it.

When we turn to the tobaccos, we find *Nicotiana affinis* grown here carrying all three of the elements barium, strontium and lithium in each of the three years that I grew it. Barium and lithium are plentiful, especially the lithium. The plants analyzed grew within a few feet of the alfalfa and *Nicotiana tabacum* grew between them. The tobacco plants contained barium and lithium but no strontium. I became curious to learn whether it is generally true of tobacco that it assimilates lithia but no strontia. Through the courtesy of the officials of the respective experiment stations I obtained samples from Texas, Kentucky, Pennsylvania and Connecticut and I grew some in my garden, so we have five states represented. In only one sample did I find a trace of strontium and in none of them did I fail to find at least a trace of lithium. The *Nicotiana affinis*, however, was much richer in lithium than the *N. tabacum* and it carried some strontium.

Barium is present in practically all of the plants. I have not found it entirely absent except in one case, and it would be interesting to know whether that soil chanced to be free from barium, a condition that would be unusual. The sample of tobacco in which I failed to find any barium was the Kentucky Dark Leaf, of which I made four analyses before I was convinced of its absence. Sweet Clover hay, i. e., the first year's growth of Sweet Clover grown by W. A. Martin, was as much of a surprise as the tobacco in that it contained only a trace of barium whereas a sample grown in the red soils of the Jura-Trias was very rich in barium. There seems to be no doubt but the explanation for this difference is to be found in the soils themselves. We have the same variety of plant, and other conditions the same, unless it be their age. My samples are very unlike in the amount of these three elements they contain.

Concerning the titanitic acid, I have indicated the reasons why I attach no importance to its presence in these samples, and had it not become necessary to separate it from the barium and strontium I would not have done so. The only purpose that is served by giving the results obtained is to show its presence and approximate quantity. The only instance in which it has any further significance is its occurrence in the ash of the potato tuber. In this case it is probably, almost certainly, an integral part of the ash, for the tubers were washed so clean that there is no probability that the titanitic acid was derived from soil particles. Just what effect washing the potatoes may have had on the ash content and its composition is in no sense up for consideration. We assume that it is entirely negligible, but for the present purpose it was necessary that they should be free from soil particles, and they were as free as we could wash them. In all other cases, it is not only possible and probable that the titanitic acid came largely from the dust on the plant, but it is almost certain that it did.

SUMMARY

Our soil conditions are favorable for the assimilation of barium, strontium and lithium by plants. The first seems to be present in the soil in an insoluble form as it isn't present in ground-waters and I do not recall having found it in the aqueous extracts of the soil, but it is present in the plant ashes whether it is present in a more soluble form than the sulfate or not.

Felspar particles, even larger fragments, are plentiful in our soils. The felspar common in our rocks contains all four of the elements considered in this bulletin. Two of these elements go into solution when the felspar is treated with water and carbonic acid, for I have found them in such a solution; the other two were not looked for and may possibly go into solution but in a smaller measure.

Strontium and lithium are present in our ground- and river-waters and being in solution are assumed to be readily assimilable by plants.

The presence of lithium in alfalfa ash in the merest traces, or its absence when the plants were grown under these conditions, suggests the subject of this bulletin.

ASSUMPTIONS

This bulletin is based on the following assumptions:

That an element present in the soil and soluble in water is available for all plants alike.

That all lithia in a plant ash and soluble in hydrochloric acid belongs to the ash proper and not to the soil or sand contaminating the ash.

That soil and sand particles contaminating a crude ash contain only negligible quantities of barium and strontium.

That quartz and other minerals, constituting the sand and soil particles that contaminate a crude ash, contain so much titanitic acid that no importance can be attributed to its determination especially in cases of a heavy contamination.

Samples of quartz and quartz-sand, four samples, were examined for titanitic acid with results establishing its presence in apparently pure quartz.

Tobacco was adopted as a plant assimilating more lithium than ordinary plants which seemed justified by statements in chemical literature.

Alfalfa is relatively rich in barium and strontium and very poor in lithium. A sample of alfalfa grown on a shallow mountain soil derived from the granites and gneisses of the immediate neighborhood contained barium, strontium and lithium, but especially barium, while lithium was present as a trace only. The presence of barium and strontium seems almost characteristic. This feature is persistent in all of our samples, though they were grown on a variety of soils.

Sweet clover, *Melilotus alba*: Samples of this plant were gathered from two places only. It seems to excel alfalfa in its ability to take up barium. The samples examined carried only traces of strontium and varied in regard to lithium.

Tobacco, *Nicotiana affinis*: Samples of this plant were grown three years in succession. The ashes were relatively rich in the three elements considered, perhaps more so in lithium than in the others, but the absolute amount of barium was much higher. Only one other sample examined, a sample of tobacco stalks, carried a larger amount of barium.

Tobacco, *Nicotiana tabacum*: Nine samples of this plant, leaves and stalks, were examined. Eight of them carried barium; only one carried a trace of strontium, while they all carried lithium, but only one carried more than a very moderate amount of it. The *Nicotiana affinis* grown in my garden was richer in lithium than any other sample of tobacco. The sample of *Nicotiana tabacum* that was the richest in lithium grew beside this. The largest amount of barium was found in the stalks of a sample grown at Nacogdoches, Texas.

Only one tobacco carried so much as a trace of strontium, but they all carried more or less lithium.

This difference in the ashes of these plants persists, even when the plants are grown side by side, eliminating the questions of culture, climate and soil, and even the forms in which the respective elements existed in the soil.

Loco Weeds: Only two samples are given, neither of which present any points of particular interest. The *Astragalus*, generally supposed to be a dangerous plant, is not so rich in barium and strontium as some other plants and is poor in lithium. The *Aragallus* sample was obtained in the mountains and is of no interest except for the negative results obtained. A sample of alfalfa grown at the same place differed from samples grown on the plains only in the amounts of barium and strontium present.

Corn Leaves: This is the only representative of this class of plants that we have to present. The sample was fairly rich in barium, strontium and lithium and unusually so in titanium. Unfortunately the crude ash was strongly contaminated with sand and we cannot judge whether the large amount of silica in the leaves had any influence on the amount of titanium found or not.

Pea Vines: The only sample analyzed was rich in barium and lithium, but very poor in strontium.

Potatoes—tubers: Barium was absent, strontium and lithium present in traces only. This is the only case in which the titanium found belonged wholly to the ash proper.

Beets: The leaves and roots were not examined for barium and strontium. The potash obtained by evaporating the Steffen's waste-water and lime-cake was examined. Lithium and manganese occur in the tops and roots. The former is considered absent and the latter rare in beets. We did not find either rubidium or caesium.