

A Routine Method for the Determination of Soluble Ash in Plant Material.

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THE growing prominence of pasture studies in agricultural research in this country has resulted in a great extension of the work reported on by du Toit and collaborators (1932). With a limited staff it became more imperative to reduce the time factor wherever possible in all methods employed for the analysis of samples of natural pasturage, without, however, unduly sacrificing accuracy. Although all the more important inorganic constituents had been determined in the past it was thought advisable to include soluble ash or silica-free ash for future work. Generally a figure for total ash is included with the mineral analysis of feeds and fodders. But when results for the total ash are given they also include silica which is not considered an essential element in nutrition, although it is present in considerable quantities in the ash of plant material.

A. PRINCIPLE OF THE METHOD.

The ash of the herbage is treated with concentrated hydrochloric acid on the steam-bath so as to convert all the bases into chlorides, decompose the silicates and render the silica insoluble. The soluble salts are leached out with dilute hydrochloric acid and the soluble ash determined by difference in weight of the original ash before and after leaching.

B. DESCRIPTION OF METHOD.

Approximately 6 gm. of finely ground material in a platinum dish of known weight are dried for at least three hours at 103° C. After 20 minutes in the desiccator the dish and contents are weighed on a "Bunge-quick-precision" balance and ignited in an electric muffle for 2 hours at about 450° C. The dish is then transferred to a desiccator and weighed after 20 minutes. The ash is moistened with distilled water and 3 c.c. concentrated HCl added. The acid is evaporated on the steam-bath and the ash allowed to dry for another hour on the steam-bath, whereby the silica derived from the decomposition of the plant silicates by concentrated HCl is rendered insoluble. 20 c.c. distilled water and 2 c.c. concentrated HCl are then added and the contents heated for a few minutes on the steam-bath, allowed to cool and filtered quantitatively through Whatman No. 40 filter paper into a 100 c.c. measuring flask. The filter is carefully washed with distilled water up to the mark on the flask. This filtrate of a 100 c.c. is used for the determination of Ca, Mg, K and Na. The insoluble residue, consisting of silica, carbon and often sand contaminating the sample, is washed back into the platinum dish with distilled water, evaporated to dryness on the

steam-bath, transferred to the electric muffle to dry for another 15 minutes at 300-350° C., allowed to cool in a desiccator and weighed. The difference between this weight and that for total ash gives the weight for soluble ash.

C. EXPERIMENTAL.

(a) *Decomposition of Plant Silicates and rendering Silica Insoluble.*

In order to test the reliability of the process of decomposing silicates in the ash of plant material with concentrated HCl and of the procedure for rendering the silica precipitated insoluble in the routine procedure described above, results thus obtained were compared with the figures obtained by treating the ash of the same specimen according to the method employed by Treadwell and Hall (1924) for the analysis of silicates decomposed by acids. Briefly, the powdered silicate is decomposed with 50 c.c. 3 N.HCl on the steam-bath, evaporated and heated for at least one hour at 120° C. in a closet to dehydrate the silica. The insoluble residues were in each case dried at 300-350° C. In the table below average percentages obtained for the soluble ash of each of three different plant specimens are presented.

TABLE 1.

Plant Specimen.	Soluble Ash. Treadwell & Hall.	Soluble Ash. Routine Method.
1. Green grass.....	6.32	6.24
2. Green grass.....	6.90	6.86
3. Bush.....	7.10	7.07

(b) *Drying the Insoluble Residue.*

According to Mellor (1922) silica retains about 3 per cent. of water when dried at 300° C., the anhydrous compound being obtained only when heated to 500° C. Admittedly, then, the silica in the insoluble residue is not completely dehydrated in the routine procedure described. However, a more serious error is introduced by simply igniting the insoluble residue together with the filter at 500° C. and computing the soluble ash figure from the weight of the residue thus obtained and the weight of the original ash, because after the soluble material has been leached out any residual carbonaceous material will readily ignite at 500° C. In the case of old mature grasses and the leaves of bushes a negligible amount of carbon is left over in the ash when ignited for 2 hours at 450° C. However, this does not apply to green grasses. Even if ignited at higher temperatures where there is danger of volatilizing alkali chlorides, etc., a considerable amount of carbon remains with the ash. This carbon does not, however, seriously interfere with the quantitative extraction of the soluble ash as is apparent from Table 3 further on in this paper, but, if the insoluble residue is ignited at 500° C. this residual carbon will be included with the figure for soluble ash.

The temperature to which charcoal has been heated and its resultant physical condition largely determines the temperature at which it will ignite. Consequently, in the case under consideration it may be assumed that a negligible amount of the residual carbon will ignite if heated for 15 minutes at 350° C., the upper limit for drying the insoluble residue.

Soluble ash figures obtained by drying the insoluble residue at 300-350° C. as described in the routine method and by igniting the insoluble residue together with the filter at 500° C. are tabulated below. Column 3 gives figures for residual carbon calculated as percentages of the original plant material and obtained by treating the ash of the same specimens according to the method for determining carbon, sand and silica of the Association of Official Agricultural Chemists (1920). Column 4 gives the difference between columns 2 and 3. An error which is negligible for routine purposes is indicated by these differences representing true percentages soluble ash when the insoluble residue has been dried at 500° C.

TABLE 2.

	Per cent. Sol. Ash Insol. res. dried at 300-350° C.	Per cent. Sol. Ash Insol. Res. ignited at 500° C.	Per cent. Residual Carbon.	Column 2 minus Column 3.
1	6.383	7.105	0.620	6.485
2	6.889	7.239	0.338	6.901

(c) *Recovery of Soluble Ash.*

Davidson (1931) found that appreciable amounts of inorganic constituents remain behind in the insoluble residue after the soluble fraction of the ash of plant material has been leached out with dilute hydrochloric acid. To overcome this difficulty he resorted to volatilization of the silica with hydrofluoric and sulphuric acids prior to leaching out with dilute HCl. The majority of pasture samples coming in from the veld are, however, more or less contaminated with sand, and while every effort is being made to remove as much of this sand as possible, it is impossible in many cases to remove the finely-divided particles of dust adhering to the plant material. If silica is volatilized from the ash of such specimens the results for soluble ash and consequently for some of the individual constituents will be too high, because of the soluble bases derived from the decomposition of the sand dust contaminating the samples.

On the other hand, it is freely admitted that some of the inorganic constituents will be too high when the extract has been prepared from plant material contaminated with sand dust. Woodman *et al* (1926) introduced a correction for soil included in their pasture cuts by analysing a sample of such soil, calculating the soil content of the grass from a knowledge of the silica content of the grass as cut and the soil-free grass and then making the necessary corrections for the figures for individual constituents.

DETERMINATION OF SOLUBLE ASH IN PLANT MATERIAL.

Such a procedure is obviously impracticable where thousands of pasture samples from all over the country have to be dealt with at one central station. At the same time, if the figures for individual inorganic constituents as obtained by Woodman for worm casts can be taken as a criterion, and if, prior to grinding, pasture samples are handled in such a way as to reduce adhering soil particles to a minimum (3 per cent. and less), the effect of soil contamination on the analytical results will be insignificant.

Without volatilizing silica hydrochloric acid extracts of insoluble residues after they had been ignited have, however, been prepared and some of the constituents determined. In Table 3 below the soluble ash figures from first and second extractions together with values for some individual constituents in first and second extracts are tabulated. Values for silica are included and all figures are given as percentages of the original dry plant material.

TABLE 3.

	Extraction.	Soluble Ash.	P ₂ O ₅ .	CaO.	K ₂ O.	Na ₂ O.	Silica.
1	1st.....	14.43	0.1179	5.552	—	2.220	1.44
	2nd.....	0.08	0.0006	0.032	—	0.034	
2	1st.....	6.20	0.20	1.02	2.51	0.33	5.57
	2nd.....	0.094	0.002	0.007	0.014	0.002	
3	1st.....	6.89	0.41	0.76	3.56	0.17	4.30
	2nd.....	0.059	0.003	0.005	0.002	0.001	
4	1st.....	4.56	0.970	1.00	0.71	1.08	4.25
	2nd.....	0.047	0.003	0.005	0.0158	0.026	
5	1st.....	6.40	0.972	1.60	1.98	0.028	3.56
	2nd.....	0.072	0.005	0.007	0.0036	trace	

A consideration of the figures in Table 3 proves conclusively that for routine purposes the method for preparing the extracts for the determination of inorganic constituents in plant ash as described in this paper is highly satisfactory. The error introduced by ignoring the additional quantities of individual constituents yielded by a second extraction of the insoluble residue is negligible.

D. CONCLUDING REMARKS.

The nature and quantity of ground plant material incinerated for the preparation of the extract and the determination of the soluble ash largely determine the efficiency with which the acid-soluble fraction of the ash is recovered by filtering and washing to 100 c.c. A small quantity of material means less salts to be washed from the filter and this in turn will ensure a more thorough washing with the limited volume of wash water. (See Treadwell and Hall.)

An additional advantage in using about 6 gm. instead of approximately 10 gm. of material as directed by Malan and van der Lingen (1931) is that larger aliquots of the extract may be used for the determination of sodium, calcium and magnesium. It was pointed out by Louw (1933) that the concentration of potassium in a plant extract limits the aliquot allowable for the direct determination of sodium. In some cases aliquots as low as 0.2 c.c. had to be used. Although the actual amount of sodium present in a larger aliquot from the extract prepared by incinerating about 6 gm. material will be the same, the possible error through pipetting very small volumes is eliminated. With regard to the micro-determination of calcium and magnesium the actual concentration of these constituents in the extract limits the volume of the aliquot permissible. When about 10 gm. of plant material is used for the preparation of the extract it will often be necessary to dilute the extract before a suitable aliquot can be taken, whereas with the smaller quantity (6 gm.) of herbage preliminary dilutions of the extract will seldom, if ever, be necessary.

E. SUMMARY.

(1) A routine method for the determination of soluble ash in plant material is described in detail.

(2) Evidence is presented to show that the results obtained by this rapid method compare very favourably with those obtained by following the standard procedure.

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* It is stated in the 1930 edition of "Methods of Analysis" (p. 102), which came to hand after the completion of this work, that the alkali soluble silica of plants is rendered insoluble by heating the ash for one hour on the steam-bath after it has been treated with concentrated hydrochloric acid, a procedure similar to that described in this paper.