RECENT PROGRESS IN THE ANALYSIS OF CATTLE FOODS.[1]

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OUR methods of analysis of cattle foods are essentially the Weende methods, published nearly thirty years ago in *Landw. Versuchs Stationen*, **6**, (*1864*,) 496, by Henneberg. An outline of the methods as given in the place cited, will at once show this to be true.

Henneberg gives the following directions for the determination of the various components of fodders.

1. *Water.*—A few grams of the finely powdered, air-dry sample are heated at 100–110° C., and the results calculated on the original substance.

2. *Mineral Matters* (ash excluding carbon dioxide).—100 to 200 grams are ignited in a muffle oven at as low temperature as possible, and the crude ash weighed, carbon dioxide and char are then determined in a portion of the crude ash, and corrections made accordingly.

3. *Protein.*—Determination of nitrogen and using the factor 6.25.

4. *Crude Fiber.*—A quantity corresponding to three grams water-free substance is taken, and heated for one-half hour in a flat porcelain dish with 200 cc. of a 1¼ per cent. sulphuric acid solution, adding water as it boils away; the solution is then left to settle and the clear liquid pipetted off into a beaker; the sample is again boiled for one-half hour with water, the clear liquid pipetted off into the same beaker as before, and the operations of boiling with 200 cc. of water and pipetting off repeated a second time. 200 cc. of a 1¼ per cent. potassium hydroxide solution are then added and boiled for half an hour, the clear liquid pipetted off into a second beaker, the residue boiled twice with 200 cc. of water, each time uniting the liquid with that already in the second beaker. The residue is then brought on a filter and also that which has settled in the beaker containing the alkaline fluid; the filter is washed until neutral reaction, when the residue in the other beaker is added and the washing repeated and finished by

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successive washings with alcohol and ether, drying, weighing, and incineration, which gives the crude fiber by difference.

5. *Ether Extract* (fat).—Complete extraction with boiling anhydrous ether, distillation of the united filtered distillates, and drying the residue at 100–110° C.

Since these methods were first published, our knowledge of the composition of plants and feeding stuffs has been greatly widened; we understand far better than did the writers thirty years ago, what the various groups separated out by the Weende experimenters include, and the conditions which must be observed in each case in order to obtain correct results. But on the purely analytical side we have made but very little progress; the problems have grown more complex every year, and the difficulties of the problems have increased much faster than has our ability to meet them.

In giving a short account of the progress made during recent years in the analysis of cattle foods, I shall take up the various components in the order adopted by Henneberg and still followed by agricultural chemists in general, and shall show the changes which the methods have undergone and suggest the reason for these changes.

As shown by Wilm, Bahring, Baessler, and others, *moisture* cannot be determined in many of our food stuffs by a simple drying in the air, as the fat contained in them will oxidize and the sample thus increase in weight, which means a too low percentage of moisture. Desiccation must, therefore, be conducted in the medium of an indifferent gas; the gas now generally adopted for drying is hydrogen or carbon dioxide, preferably the former. Märcker has further shown that drying above 100° C. may cause formation of resinous substances, and Jenkins found that a volatile oily matter passed off when fodders were heated at 110° in the air or in other gases; the same was observed by Baessler, Wiley, and Cutter. The temperature ought, therefore, never to exceed 100° C. The time necessary for drying will depend on the kind of apparatus used and will vary from four to ten hours; in case of a dry current of hydrogen being passed through the samples, four to six hours will as a rule be found necessary, the velocity of the current being the deciding factor

as to the time required; 90 to 100 bubbles of hydrogen per minute is a maximum velocity (Anderson). The loss of volatile substances will be increased when a very rapid current is passed through the sample. Where the fodders are heated on watch glasses or in open disks in an atmosphere of hydrogen, longer time will be necessary than otherwise, sometimes as much as ten hours, the temperature of drying being all the time that of boiling water.

Ether Extract.—The determination of ether extract has been greatly facilitated by the adoption of the Soxhlet continuous extraction apparatus; the form of extraction tube generally used in the United States is the Johnson extractor, the most recent modification of this being the Caldwell extractor.

The ether extract is determined in the water-free sample, as the air-dry sample extracted with ether will give too high results, for obvious reasons. The ether to be used for extraction must be anhydrous and alcohol-free, as too high results will otherwise be obtained. Numerous comparisons of extraction with ether of different kinds and under varying conditions of drying previous to extraction, have been made by Atwater, Babcock, Wilm, Bahring, Wagner, Märcker and scores of others, and the above points have been fully settled.

As there are several reasons for believing that prolonged drying of any food stuff even at 100° C. modifies the solubility of the fat and the amount of ether extract found, the writer has recently proposed the use of anhydrous copper sulphate in ether extraction. The sulphate will dehydrate both fodder and ether used, and no special precautions for dehydration of either are necessary. The sample of 2-3 grams weighed out may be mixed with about five grams of copper sulphate and the mixture placed in the extraction tube and extracted as usual.

Stellwaag's and Maxwell's investigations have shown the complexity of the bodies making up the ether extract of most feed stuffs. The former found from 0.5 to 34.6 per cent. of insaponifiable components in twenty-five common fodders; lecithin, cholesterin, and hydrocarbons have been shown to be present in many cases, as well as coloring matters. It is especially the ether extracts of coarse fodders and roots which contain large pro-

portions of non-glycerides; the extracts of seeds of all kinds are as a rule fairly pure. Various methods have been proposed for the purification of the crude fat, but none have been generally adopted. The purification by means of animal charcoal, proposed by G. Kühn, nearly twenty-five years ago, and proved inaccurate by König in 1871, and by Schulze in 1872, was brought forward again a few years ago by Patterson, who obtained correct results with it. By more recent, thorough investigations it has been shown, however, that animal charcoal will retain fat from ethereal solutions passing through it. There is considerable difference in this respect between different kinds of charcoal, making the method entirely unsatisfactory in quantitative analysis.

Crude Protein is determined by multiplying the per cent. of nitrogen found by the Kjeldahl method by 6.25. A great step in advance was made in the adoption of this method (pub. 1883) in agricultural laboratories, and also in the separation of crude protein into albuminoids and amides, according to Stutzer's copper hydrate method (pub. 1880). The Kjeldahl method has been modified by a large number of chemists, and also so as to include nitrate nitrogen; the latter modifications most adopted are those of Jodlbauer and Ulsch.

Crude Fiber.—The Weende method is still the one used by most agricultural chemists. Schulze's method (pub. 1866) and Hönig's (pub. 1891) have both been proved unreliable by several chemists; but on the other hand the investigations made have also proved conclusively that the Weende method gives too low results, contrary to the experience of Kühn and Kern. In comparative determinations the results by the Weende method have come lower in every case, being often only one-half or two-thirds of those found by the Schulze or Hönig method in case of our ordinary cattle foods. It cannot, therefore, be denied that we are still without a satisfactory method for the determination of cellulose or crude fiber in fodders, and use the Weende method only for want of something better.

Ash is determined in a small quantity of the fodder at the present time, not exceeding ten grams. The manner of procedure is otherwise as in the Weende method; or the sample is

carefully burned at a low red heat, the crude ash treated with water, filtered, the residue ignited to whiteness, united with the filtrate, which is then evaporated and the residue heated to low red heat. The reason for this method of proceeding is the easy volatilization of chlorides by direct heating of the ash above red heat, which is necessary to burn the carbon of the ash.

Nitrogen-free Extract is determined by difference, as directed by Henneberg. The errors of analysis incident to the determination of all other components, therefore, enter here and often make the results unsatisfactory. The heterogeneous character of the bodies coming in under this head makes it unfortunate to class all together. A great deal of study has been expended in separating and identifying the various constituents of the nitrogen-free extract of fodders. Pentosans, as galactose, arabinose, xylose were discovered in cattle foods some years ago by Tollens, Schulze and their assistants, and have been found in appreciable quantities in nearly all our common food stuffs. While no satisfactory quantitative method for their determination has yet been devised, the furfurol reaction, worked out by Stone, Allen, and Wheeler, gives a very sharp qualitative test for them.

If determinations of sugar, starch, and possibly also pentosans, could be made in our cattle foods, the rest of the nitrogen-free extract could be classed as *undetermined* and would then include many bodies present in all fodders, the properties of which we yet know very little about, and whose nutritive value is perhaps inferior.

From this short sketch we readily see that more progress has been made in our knowledge of the composition of food stuffs, and in the identification of these constituents than in their estimation. While brought to a certain perfection as far as working details go, the analytical side is yet far behind, and no fully satisfactory system of fodder analysis can be worked out until we are able to classify nutrients more according to their physiological importance than is done in our present methods.