THE MICRO-DETERMINATION OF COBALT IN PLANT MATERIAL

by W. B. DEIJS and J. H. FELDMEYER

Central Institute for Agricultural Research, Wageningen

1. Introduction. The diseases of cattle known as "Pining", "Enzootic Marasmus", "Morton Mains disease" and "Bush sickness" have occurred in countries as widely separated as Scotland and Australia and New Zealand. During the last ten years experiments have shown the relationship of these diseases to a deficiency of cobalt (See a.o. reviews of the literature by Russell1) and Stiles2). In the Netherlands3) and also in Denmark attention is being paid to cobalt deficiency as a possible cause of diseases.

In this connection several methods for the micro-determination of cobalt in fodder (grass, hay) and animal tissue (liver) were worked out. The methods previously used for estimation of cobalt in biological materials differed widely and were unsatisfactory in some cases; it was therefore decided to work out a method specially suited to the requirements of the present investigation. The first consideration was accuracy of the method which should also be as simple as possible in view of the large number of samples of material to be analysed.

As in the case of estimation of other inorganic constituents of plant material the method of digestion of the sample is important. Since some authors (Seekles, c.s.)4) have referred to losses of cobalt during ashing, digestion has been carried out using sulphuric and nitric acids. It should also be noted that other workers (Ellis and Thompson)5) are of the opinion that good results can also be obtained by dry ashing if certain precautions are taken. The possibility of dry ashing and simplification of the wet digestion method are to be studied separately (Hiscox6).

In the colorimetric estimation of cobalt most investigators have
used nitroso-\(R\)-salt (1-nitroso-2-hydroxy-3,6-naphthalene disodium sulphate) which forms an intensely red coloured complex with cobalt. Seekles (l.c.) and Claassen and Westerveld\(^\text{15}\) also used this method in recent investigations.

Ellis and Thompson\(^\text{8}\) determined cobalt as a ligroin soluble complex salt of o-nitroso-cresol (1-methyl-3-hydroxy-4-nitroso benzene). This method has a higher sensitivity than the \(R\)-salt method, but the procedure is more complicated. Using the method of Ellis and Thompson it is possible to determine very small traces of cobalt in milk (0.6–0.7 \(\gamma\) per litre). Such sensitivity is not required in the analysis of plant material as the content of cobalt frequently amounts to more than 100 \(\gamma\) per kg of dry matter.

2. The colorimetric estimation of traces of cobalt using nitroso-\(R\)-salt. 

a. The standard cobalt solution. For the preparation of a calibration curve and routine checking of the photoelectric colorimeter a solution containing 1 \(\gamma\) of cobalt per ml. was used. This was obtained by diluting a solution containing 100 mg of cobalt per litre immediately before use. In the preparation of the standard solution 2 g of cobalt carbonate p.a. were dissolved in a small excess of hydrochloric acid after which 1.2 ml of concentrated sulphuric acid were added. After evaporation on a steam bath the excess of sulphuric acid was gradually driven off by heating on a hot air bath and the residue finally heated at 250–300°C to constant weight. Of the dry cobalt sulphate thus obtained 263 mg (100 mg Co) were dissolved in one litre of distilled water containing 1 ml of concentrated sulphuric acid.

It is possible to start from pure cobalt acetate or cobalt nitrate as well as cobalt carbonate in the preparation of the standard cobalt solution.

b. Preparation of the calibration curve. At first the method of Bayliss and Pickering\(^\text{7}\) was used for the production of the cobalt nitroso-\(R\)-salt complex. In this method the excess of \(R\) salt is removed by boiling with bromine water; this treatment does not discolor the cobalt complex. A good calibration curve was obtained by the use of this method but the procedure is somewhat tedious and does not link up so well with the method ultimately used in the preparation of samples. As in the case of other methods the more laborious one of Bayliss and Pickering was retained for routine use.

Bayliss and Pickering showed that the excess of \(R\) salt can be removed by boiling with bromine water: the excess of bromine is removed by precipitation of thallous chloride; the precipitate is filtered and the filtrate is finally distilled. The method is laborious and the treatment of the thallous chloride precipitate is somewhat tedious.