

## THE DETERMINATION OF TANNIN BY METALLIC OXIDES.<sup>1</sup>

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THE following experiments were suggested by a method proposed for the estimation of tannin by Mr. Kerr, associate reporter on tannin, during the progress of the official work for the Association of Official Agricultural Chemists. This method consisted of the percolation of the tannin-bearing liquor through a column of asbestos with which a certain amount of yellow mercuric oxide had been intimately mixed. After making a number of attempts to obtain concordant results, I found it too difficult to secure uniform conditions such as rate of percolation, extent of contact and uniformity in the asbestos layer, and therefore turned to find some other way of using the oxide. It then occurred to me to substitute it for the hide-powder in the ordinary shaker method. During the work I extended the investigation to three other oxides, *viz.*, magnesium, zinc, and lead oxides.

At the beginning it was evident that much more time would be consumed in absorbing the tannin in this manner and a number of preliminary experiments were made to determine this time limit if possible. In all cases when, upon filtration after shaking a certain length of time, it was found that combination was incomplete, the solution was allowed to stand until this was accomplished. It was thus found, that with magnesium and mercuric oxides, it was best to shake about four hours and then let the mixture stand over night, when it would be ready for filtration.

With lead oxide the process required two days, after being shaken four hours, and the mixtures with zinc oxide stood a week before the tannin was totally absorbed. These two oxides were, therefore, rejected as requiring too much time, though the analyses made with them, are given below for comparison.

The extract used contained 42.35 per cent. soluble solids, and the diluted liquor used in the analyses, contained two grams of this extract per 100 cc. This diluted extract gave in twenty-

<sup>1</sup> Read at the Annual Meeting of the Association of Official Agricultural Chemists, Sept. 5, 1895.



Experiments with magnesium oxide.

| Method.                               | Grams MgO used. | cc. diluted extract used. | cc. filtrate evaporated. | Weight of residue. | Per cent. tannin in extract. | Weight ash in residue. | Weight MgO in ash. |
|---------------------------------------|-----------------|---------------------------|--------------------------|--------------------|------------------------------|------------------------|--------------------|
| Shaken 2½ hours, stood over night...  | 2.0             | 75                        | 25                       | 0.1134             | 19.67                        | 0.0209                 | 0.0055             |
| " 2½ " " " " " ...                    | 2.0             | 75                        | 25                       | 0.1028             | 21.79                        | 0.0195                 | 0.0042             |
| " 2½ " " " " " " ...                  | 2.0             | 75                        | 25                       | 0.1230             | 17.75                        | 0.0232                 | 0.0052             |
| " 2½ " " " " " " ...                  | 2.0             | 75                        | 25                       | 0.1246             | 17.43                        | 0.0247                 | 0.0058             |
| Stood 24 hours with occasional sh'k'g | 2.0             | 75                        | 50                       | 0.2063             | 21.72                        | 0.0252                 | 0.0074             |
| " 24 " " " " " " ...                  | 2.0             | 75                        | 50                       | 0.2061             | 21.74                        | 0.0244                 | 0.0076             |
| " 24 " " " " " " ...                  | 2.0             | 75                        | 25                       | 0.1157             | 19.21                        | 0.0213                 | 0.0044             |
| " 24 " " " " " " ...                  | 2.0             | 75                        | 25                       | 0.1114             | 20.07                        | 0.0205                 | 0.0038             |
| " 48 " " " " " " ...                  | 2.0             | 75                        | 50                       | 0.1941             | 22.94                        | 0.0326                 | 0.0064             |
| " 48 " " " " " " ...                  | 2.0             | 75                        | 50                       | 0.1959             | 22.76                        | 0.0339                 | 0.0070             |
| Shaken 3½ hours, stood over night...  | 2.0             | 75                        | 50                       | 0.2165             | 20.70                        | 0.0349                 | 0.0102             |
| " 3½ " " " " " " ...                  | 2.0             | 75                        | 50                       | 0.2191             | 20.44                        | 0.0355                 | 0.0111             |
| " 3½ " " " " " " ...                  | 2.0             | 75                        | 50                       | 0.2179             | 20.56                        | 0.0359                 | 0.0115             |

This table shows that a considerable amount of the oxide is dissolved, and passes into the filtrate, increasing the weight of the residue, and correspondingly lowering the tannin. That this error may be quite considerable is shown by the fact that in almost every estimation, the ash is almost double that found in the original diluted extract. Furthermore, this error does not seem to be constant, so that no correction can be made for it.

Experiments with mercuric oxide (yellow).

| Method.                               | Grams HgO used. | cc. diluted extract used. | cc. filtrate evaporated. | Weight of residue. | Per cent. tannin in extract. | Weight ash in residue. | Weight HgO in ash. |
|---------------------------------------|-----------------|---------------------------|--------------------------|--------------------|------------------------------|------------------------|--------------------|
| Stood 48 hours with occasional sh'k'g | 4.0             | 75                        | 25                       | 0.0833             | 25.69                        | 0.0070                 | 0                  |
| " 48 " " " " " " ...                  | 4.0             | 75                        | 25                       | 0.0829             | 25.77                        | 0.0077                 | 0                  |
| " 48 " " " " " " ...                  | 4.0             | 75                        | 25                       | 0.0829             | 25.77                        | 0.0071                 | 0                  |
| Shaken 1½ hours, stood over night...  | 4.0             | 75                        | 25                       | 0.0842             | 25.51                        | .....                  | ..                 |
| " 2 " " " " " " ...                   | 4.0             | 75                        | 25                       | 0.0867             | 25.01                        | .....                  | ..                 |
| " 3½ " " " " " " ...                  | 4.0             | 75                        | 25                       | 0.0863             | 25.09                        | 0.0081                 | 0                  |
| " 3½ " " " " " " ...                  | 4.0             | 75                        | 25                       | 0.0860             | 25.15                        | 0.0080                 | 0                  |
| " 4 " " " " " " ...                   | 4.0             | 75                        | 25                       | 0.0839             | 25.57                        | 0.0084                 | 0                  |
| " 4 " " " " " " ...                   | 4.0             | 75                        | 25                       | 0.0849             | 25.37                        | 0.0065                 | 0                  |
| " 4 " " " " " " ...                   | 4.0             | 75                        | 20                       | 0.0638             | 26.41                        | 0.0065                 | 0                  |
| " 4 " " " " " " ...                   | 4.0             | 75                        | 20                       | 0.0629             | 25.05                        | 0.0103                 | 0                  |
| " 4 " " " " " " ...                   | 4.0             | 75                        | 20                       | 0.0682             | 25.29                        | 0.0094                 | 0                  |
| " 4 " " " " " " ...                   | 4.0             | 75                        | 25                       | 0.0863             | 25.09                        | 0.0083                 | 0                  |
| " 4 " " " " " " ...                   | 4.0             | 75                        | 25                       | 0.0849             | 25.37                        | 0.0097                 | 0                  |
| " 4 " " " " " " ...                   | 4.0             | 75                        | 25                       | 0.0842             | 25.51                        | 0.0084                 | 0                  |

The above analyses show that even though the conditions may be varied, fairly concordant results can be obtained with mercuric oxide as long as care is taken to ensure the complete absorption of the tannin before filtering. The end of the reaction may be easily observed, since, when it is reached, the yellow oxide

no longer sinks to the bottom, but the whole mass partially gelatinizes and becomes dirty brown. A clear filtrate free from tannin and mercury can then be readily obtained.

The results in the ash column show that a certain amount of the ash present in the extract is held back, but this error is quite constant and so small as to have little influence on the result. Although the time required for the analysis of a tannin-extract by this method is somewhat longer than with hide-powder, still the uniform results obtained more than compensate for this, and, at the most, an analysis will not take more than two days. A number of analyses can be made at a time by adapting a shaker so as to hold several 100 cc. sugar flasks, which are of a convenient size for this work.

### THE ESTIMATION OF SULPHUR IN REFINED COPPER.<sup>1</sup>

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SEVERAL general methods for the estimation of sulphur in copper have been published, most of which are defective, or not accurate for all classes of work.

It is the writer's purpose to call attention to these processes, and then to present the results of some experiments, and an improved method, devised especially for the determination of traces of sulphur.

R. Fresenius<sup>1</sup> proposed to treat twenty grams of copper with strong nitric acid, nearly neutralize with ammonia, add a few drops of barium nitrate and allow to stand for several hours. As stated by the same authority, very small quantities can not be separated in this way, since barium sulphate is somewhat soluble in copper nitrate.

For small amounts of sulphur, W. Hanpe's "chlorine" process has been recommended. This consists in heating thirty grams of the metal in a glass tube in a current of pure, dried chlorine gas. The sulphuric acid evolved, is absorbed by water saturated with chlorine.

From personal experience, the method is not judged to be a

<sup>1</sup> Read at the Springfield Meeting.

<sup>2</sup> *Ztschr. anal. Chem.*, 13, 223.