Titration of Amides in Acetic Anhydride with Perchloric Acid
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Wimer has demonstrated that a representative number of amides can be titrated with perchloric acid using acetic anhydride containing less than 10% of acetic acid as a solvent. The titration was carried out potentiometrically using a modified calomel-glass electrode couple. The method is now adopted in Handbook of Analytical Chemistry.

In titrating several primary amides according to Wimer we found that the results were not accurate. The procedure was reproducible but it was impossible to obtain a purity of about 100% even if highly purified samples were analysed.

It is now proved that there is a systematic error in the titration; this is most probably due to a slight acetylation of the primary amide. If the potentiometric titration is carried out within a period of 4–5 min about 2–3% of the amide is acetylated. The secondary amide formed is too weak a base to be titrated. With a titration time of about 11 min as much as 5–10% of acetylation takes place.

The following data can be reported:

Purity (%) found with a titration time of ca. 5 min ca. 11 min
Acetamide 97.2 94.9
Propionamide 96.9 91.7
Isobutryramide 94.1 88.8

In order to make sure that the time dependence was not due to an apparatus factor the purity of potassium hydrogen phthalate was determined by the same method and it was found that the result was independent of the titration time. We therefore conclude that Wimer’s procedure cannot be used safely for the determination of unsubstituted amides. The method has not been checked with other types of amides.

All attempts to modify the procedure so as to avoid the acetylation have failed.

The Behaviour of Lignin in Alkaline Pulping
I. Model Experiments with Phenylcoumarans
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Some years ago a study of the behaviour of lignin in the alkaline pulping processes was initiated in this laboratory. Our main interest was to elucidate the reactions of lignin in the “kraft” or “sulphate” process, in which a cooking liquor containing sodium sulphide in addition to sodium hydroxide is used. Extensive studies on the reactions of lignin model compounds and of isolated lignin on heating with aqueous sodium hydroxide (“soda cooking” conditions) were recently reported by Gierer et al. and work on the sulphate cooking process is being published by the same group. In the present paper and two following communications we wish to give a brief account of some of our own results.

The comparatively high content of phenolic hydroxyl groups found in lignin isolated from soda or sulphate “black liquors” indicates that cleavage of aryl alkyl ether linkages is a characteristic feature of alkaline lignin dissolution processes. Two types of such ether linkages have been shown to occur in lignin, viz., the benzyl aryl ether linkage and the arylglycerol-β-aryl ether linkage. The present communication deals with the behaviour of the cyclic benzyl aryl ether I, dihydro-dehydrodiconiferyl alcohol, a model of the dimeric units of phenylcoumaran type which make up about 18% of the average lignin molecule.

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*** For preliminary data see Falkkehag, I. Paper and Timber (Finland) 43 (1961) 655.

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