

saccharina von ca. 4 % im Spätsommer bis zu 14 % im Winter. Nach Haas⁴ tritt das von ihm aus der Rotalge *Griffithsia flosculosa* isolierte Peptid nur im Winter und Frühling auf. Man kann deshalb annehmen, dass auch die Aminosäurezusammensetzung bei Meeresalgen mit der Jahreszeit variiert. Die Abweichungen unserer Resultate von denen anderer Verfasser können möglicherweise auf solchen jahreszeitlichen Schwankungen beruhen.

Die Aminosäuren der Braunalgen scheinen mit den gewöhnlich in Landpflanzen gefundenen übereinzustimmen. Von den essentiellen Aminosäuren konnte Tryptophan von uns nicht nachgewiesen werden.

Die Verfasser sind Herrn Dr. Mats Waern, Växtbiologiska Institutionen, Uppsala, herzlichen Dank schuldig für die Hilfe bei der Einsammlung der Algen und deren botanischer Klassifizierung, sowie Herrn Ing. Lars Ljungdahl, A.B. Stockholms Bryggerier, für die Kontrolle der Chromatogramme.

Professor Dr. Harry Lundin, Vorstand des Instituts, zeigte förderndes Interesse an vorliegender Arbeit und gab uns Gelegenheit zu fruchtbaren Diskussionen.

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Eingegangen am 26. April 1952.

Determination of Ethylenediamine in Cupriethylenediamine Solutions

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During the last ten years the cupriethylenediamine (CED) reagent has found extended use as a solvent for cellulose, especially in connection with measurements of its degree of polymerisation. It is therefore not surprising that many attempts have been made to work out methods for the analysis of this reagent. All the procedures described in the literature¹⁻⁷ are based on the same principle. Copper is first determined by an iodometric titration, and the CED solution is then titrated with acid to an end point at about pH 3.0–3.5. The ethylenediamine content is then related to the difference in the number of equivalents of the titrants used in the two titrations. However, it appears that no published method is free from more or less serious objections.

If the cupric ions are precipitated with hydrogen sulfide prior to the acid titration the equivalence point will be much more easily indicated, and as one equivalent of hydroxyl ions is used up for each equivalent of copper present in the original solution the acid consumption will be a direct measure of the amount of ethylenediamine present. When analytically pure cupric hydroxide is used in the preparation of the reagent this new method appears to be much superior to the previous ones. However, the commercial cupric hydroxide now sometimes employed often contains appreciable amounts of anions of strong

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Table 1. Results of distillation experiments for the determination of ethylenediamine in CED-solution. The receiver was charged with 50 ml of 1 N HCl.

Treatment	Ml of 0.946 N NaOH consumed	Difference from blank
1. Blank (50 ml of acid)	50.50	
2. 25 ml of ethylenediamine solution added to 50 ml of acid	16.00	34.50
3a. 25 ml of ethylenediamine solution made alkaline with NaOH and distilled without xylene	33.00	} 34.55
3b. Residue from 3a. distilled with xylene	33.45	
4. 25 ml of ethylenediamine solution made alkaline with NaOH and distilled with xylene	16.02	34.48
5. 25 ml of ethylenediamine solution + equivalent amount of CuCl_2 solution precipitated with H_2S , filtered, and distilled with xylene	15.90	34.60
	16.02	34.48

acids which cause erroneous results, and due to the presence of alkali metal ions the method can not be much improved with the aid of anionexchangers (generally somewhat low results were obtained).

To overcome these difficulties the present authors have precipitated the cupric ions with hydrogen sulfide and recovered the ethylenediamine by distillation of the alkalinized solution, xylene being added to facilitate the process. In this way the ethylenediamine passes over quantitatively in a reasonably short time — 30–60 minutes. Some data demonstrating the accuracy of the new process are shown in Table 1.

Recommended procedure. Twentyfive ml of CED reagent (1 M in $\text{CuEn}_2(\text{OH})_2$) is pipetted into a 250 ml Erlenmeyer flask. Hydrochloric or sulfuric acid is added in slight excess as judged from the colour, and hydrogen sulfide is passed into the solution for 5–10 minutes. The precipitate is filtered off and washed with water, the filtrate and washings being collected in a 250 ml volumetric flask. The flask is filled to the mark with distilled water,

and the contents are thoroughly mixed by shaking. One hundred ml of the mixture is pipetted into a Kjeldahl distillation apparatus, the receiver of which is charged with 50 ml of 1 N hydrochloric or sulfuric acid. An excess of strong soda lye is added to the test solution and most of it is distilled into the receiver. Then about 100 ml of pure, redistilled xylene is added to the residue in the distillation flask, and most of the xylene is distilled over. The contents of the receiver are then back-titrated either potentiometrically or using bromophenol blue as indicator.

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Received April 25, 1952.

