

# Method for the determination of the glyoxal content in cellulose ethers



## Abstract

In the field of cellulose ether chemistry the treatment with glyoxal is a common way to confer a delayed solubility to cellulose ethers.

The treatment includes a reaction of glyoxal with the hydroxyl groups of the cellulose ether polymer to establish hemi-acetal crosslinks which provide a retardation effect in water.

Due to the equilibrium process of the reaction of a dialdehyde with the hydroxyl groups of the polymer backbone, small amounts of glyoxal, which have not reacted, may still be present.

In consequence of the new regulation 1999/45/EC for preparations in Europe which will be implemented as of 30 July 2002 all products containing more than 0.1 % of glyoxal are subjected to the labelling requirements of sensitizers. Therefore a method for an exact quantification of the glyoxal concentration in cellulose ethers was required.

Several tests showed that an extraction method using tetrahydrofuran (THF) followed by a photometrical test with 3-methyl-2-benzothiazoline hydrazone hydrochloride (MBTH) is the most suitable. The sample is used as delivered.

The development of the test procedure involved the following steps of optimization:

From several tested solvents THF has been chosen as extracting agent being a good solvent for glyoxal and a non-solvent for most cellulose ethers.

The extraction process is carried out by shaking the sample in THF instead of stirring it or making use of a soxhlet apparatus. It has been shown that the values determined by applying the different procedures were very close. The shaking procedure proved to be the most practical and the least time consuming.

Further tests with the shaking procedure revealed that shaking the sample once for 4 hours compared to shaking it four times during 1 hour showed no significant differences of the values detected, especially in the critical region of the 0.1 % limit.

3-Methyl-2-benzothiazoline hydrazone hydrochloride (MBTH), which is already known from the glyoxal method given in the hydroxyethylcellulose (HEC) monograph of the European Pharmacopoeia, is used as dye. It shows to be a highly sensitive and highly selective reagent and forms the respective colour with 1,2-dicarbonyl compounds such as glyoxal.

Two hours of reaction time with MBTH with glyoxal proved to be long enough for forming the colour.

# Determination of the Glyoxal Content in Cellulose Ethers

## 1. Purpose

Determination of glyoxal content in cellulose ethers with delayed solubility by partial crosslinkage with glyoxal.

## 2. Principle

The sample of cellulose ether is extracted at room temperature for 4 hours with tetrahydrofuran and the glyoxal content of the extract is measured using the photometrical test with MBTH (3-methyl-2-benzothiazolinone hydrazone hydrochloride).

## 3. Chemicals

3.1 Tetrahydrofuran anhydrous (max. 0.01 % H<sub>2</sub>O), e.g. Merck cat. no. 1.08107  
Alternatively reagent grade tetrahydrofuran (e.g. Merck cat. no. 1.09731) generally can be used without prior drying, if the water content is at maximum 0.01 %.  
In case reagent grade tetrahydrofuran is used, prior to usage the water content of each lot of THF has to be checked e. g. by Karl Fischer method.

3.2 MBTH reagent solution  
Dissolve 0.200 g of 3-methyl-2-benzothiazolinone hydrazone hydrochloride (e. g. Merck cat. no. 1.04527) in 40.0 g glacial acetic acid (e. g. Merck cat. no. 1.00063) and 10.0 g deionized water; the solution has to be freshly prepared daily, and stored in a fridge when not in use.

3.3 Glyoxal 40% aqueous solution, e. g. Merck cat. no. 8.20610  
Use a fresh solution free of polymerized solids (filtrate if necessary!) and determine the exact content by titrimetric procedure (e. g. as described in DIN 54603 : 1981-09 Section 10.1.1).

3.4 Glyoxal standard solution  
approx. 5 mg/l  
Weigh about 1.25 g of glyoxal 40% to the nearest of 1 mg into a 1 l volumetric flask and make up to volume with deionized water; pipette exactly 10.00 ml of this solution into a second 1 l volumetric flask and make up to volume with deionized water.  
Calculate the exact concentration of the resulting standard solution using the previously determined glyoxal content and weight of the portion of glyoxal 40%. The standard solution has to be prepared freshly before use.

## 4. Apparatus

4.1 UV/Visible spectrophotometer.

4.2 Extraction vessels 100 ml, e. g. bottles or flasks with screw cap or ground stopper.

4.3 Overhead mixer (e. g. REAX 2, Heidolph), roller mixer (e. g. SRT 2, Stuart Scientific) or similar apparatus.

4.4 Membrane filter 0.45 µm (suitable for organic media) and filtration unit, e. g. ready-to-use syringe filter unit SPARTAN 30/0.45 RC (Schleicher & Schuell) together with disposable syringe made of polypropylene.

4.5 Reaction vessels, e. g. 20 ml screw cap vials or test tubes with rubber serum cap.

4.6 Standard laboratory equipment such as analytical balance, pipettes, volumetric flasks etc.

## 5. Instrument parameters

Carry out absorbance measurements with settings given below:

Wavelength: 405 nm

Slit width: 2.0 nm (or instruments default setting for quantitative analysis)

Cell light path: 10 mm (standard cells or sipper with flow-through cell may be used)

## 6. Procedure

6.1 *Sample extraction* (Remark 9.1)

6.1.1 Weigh 1.0 g of cellulose ether to the nearest of 0.1 mg into a suitable 100 ml bottle or flask with screw cap or ground stopper, add exactly 50.0 ml of anhydrous tetrahydrofuran and seal the vessel tightly.

6.1.2 Mix continuously for 4 hours at room temperature and low speed on an overhead mixer, roller mixer or similar apparatus.

6.1.3 Allow the solid to settle, filter a fraction of the supernatant liquid by a 0.45 µm membrane filter (preferably use a disposable syringe with ready-to-use syringe filter unit) and store the clear extract in a tightly sealed vessel.

## 6.2 Photometric determination

6.2.1 Pipette exactly 0.200 ml of the filtered THF-extract into a reaction vessel (preferably use a positive displacement pipette) and add deionized water to make a total volume of 2.00 ml (remark 9.2); prepare a blank with 2.00 ml of deionized water.

6.2.2 Add 5.00 ml of MBTH reagent solution to test mixture and blank, mix and allow the solutions to stand at room temperature for two hours in the sealed vessel.

6.2.3 Measure the absorbance of the test mixture against the blank at 405 nm.

6.2.4 If the absorbance reading exceeds the range of calibration curve, repeat steps 6.2.1 to 6.2.3 with a smaller volume THF-extract (e. g. 0.1 ml).

## 6.3 Preparation of calibration curve.

6.3.1 Pipette different volumes of glyoxal standard solution 5 mg/l - e. g. 0 ml (blank), 0.100 ml, 0.200 ml, 0.500 ml, 1.000 ml and 2.000 ml - into a reaction vessel each, add deionized water to make a total volume of exactly 2.00 ml and carry out color reaction and absorbance measurement in analogy to sections 6.2.1 to 6.2.3; using the proposed volumes of standard solution, the masses of glyoxal are approx. 0.5 µg, 1 µg, 2.5 µg, 5 µg and 10 µg (calculate the precise values regarding to exact concentration of the standard solution).

6.3.2 Prepare a calibration curve by plotting the absorbance readings versus the masses of glyoxal used (see section 6.3.1); the result is a straight line running approximately through the origin.

9.2 Alternatively pipette 10.00 ml THF-extract into an 100 ml volumetric flask, make up to volume with deionized water and use 2.00 ml of the diluted extract for photometric determination of glyoxal.

## 7. Evaluation

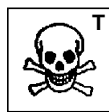
$$w(\text{C}_2\text{H}_2\text{O}_2) = \frac{m}{1000} \times V \times 100 \\ \frac{V_A \times m_{\text{CE}}}{}$$

## 10. Jointly applicable documents / literature

Omitted

$w(\text{C}_2\text{H}_2\text{O}_2)$	mass fraction of glyoxal in the cellulose ether	[%]
m	mass of glyoxal corresponding with the absorbance reading (determined from a calibration curve according to section 6.3)	[µg]
V	total volume of sample extract (usually 50 ml)	[ml]
$V_A$	volume of sample solution applied in photometrical test (usually 0.2 ml)	[ml]
$m_{\text{CE}}$	mass of cellulose ether used for extraction	[mg]

## 8. Safety notes



3-methyl-2-benzothiazolinone hydrazone hydrochloride is toxic if swallowed; observe workplace specific safety instructions.

## 11. Changes to preceding version

Not applicable

## 12. Annex

Omitted

## 9. Remarks

9.1 The sample extraction (section 6.1) can be scaled down, e.g. by factor 5 (extraction of 0.2 g cellulose ether with 10 ml tetrahydrofuran in a 20 ml vessel). This may be useful in case of simultaneous analysis of a larger number of samples.

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**Cefic**  
**Avenue E. van Nieuwenhuysse 4**  
**B - 1160 Brussels**  
**tel +32 2 676 72 11**  
**Fax +32 2 676 73 00**  
**mail@cefic.be**  
**www.cefic.org**