ELSEVIER

Journal of Chromatography A, 977 (2002) 247–250

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Determination of acid substituents and unesterified hydroxyl groups in cellulose esters

G. William Tindall[a,*], Brendan W. Boyd[b], Randall L. Perry[b]

[a]*Analytical Science Solutions, 888 Christian Bend Road, Church Hill, TN 37642, USA*

[b]*Eastman Company, Division of Physical and Analytical Chemistry, P.O. Box 1972, Kingsport, TN 37662, USA*

Received 26 February 2002; received in revised form 6 May 2002; accepted 23 August 2002

Abstract

The properties of mixed cellulose esters are strongly affected by the nature and ratio of acid substituents. Fast reliable methods are needed to determine the acid substituents of these products. For some applications it is necessary to also determine the unesterified hydroxyl content. A generally applicable method has been developed to determine acid substituents of mixed cellulose esters. The cellulose ester sample is rapidly hydrolyzed with a reagent consisting of a polar, aprotic solvent, for example dimethyl sulfoxide, with sodium hydroxide and methanol. The hydrolyzed acids are determined by reversed-phase liquid chromatography with UV detection. The results are sufficiently precise so that unesterified hydroxyl content can be calculated by difference.

Keywords: Degrees of substitution; Cellulose esters

1. Introduction

Mixed esters of cellulose are used for molding plastics, films, coatings, and many other applications. The nature of the acid substituents, as well as their ratios, strongly affects the mechanical properties and solvent solubility of the mixed ester products. For example, increasing the size of the acid substituent lowers the glass transition temperature and modulus. A butyrate–acetate ester with a low degree of substitution is alcohol soluble and useful in ink formulations, while a highly substituted butyrate–acetate ester is soluble in ketones and suitable for use in lacquers. It is, therefore, essential to be able to determine both the amount and ratio of ester substituents. In some applications where the unesterified hydroxyl is used for crosslinking, such as coatings, the amount of unesterified hydroxyl must be determined.

There are numerous references for the determination of single acid substituents. Saponification and titration has been used extensively for the analysis of single component esters [1]. A review of chromatographic approaches that could be used for mixed esters was published in this journal [2]. This review considered gas chromatography, ion chromatography, ion-exclusion chromatography and capillary electrophoresis (CE). It was concluded that CE was the most widely applicable technique. Since the time of the review, CE has not become widely practiced

*Corresponding author.

E-mail address: bjtindall@mindspring.com (G. William Tindall).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)01353-5

and many laboratories do not have this capability. In addition, CE is more limited in dynamic range and precision when compared to other techniques. Liquid chromatography was not considered a possibility at the time of this earlier publication. At that time reversed-phase columns that would retain hydrophilic compounds such as acetic acid were not available.

In the past few years several companies have introduced liquid chromatography columns that are compatible with 100% aqueous mobile phases. The ES Industries Aquasep, the Keystone Aquasil and YMC ODS-AQ are some examples. These columns are particularly suited for the determination of aliphatic and aromatic acids [3]. All acids commonly used to prepare commercial cellulose esters are readily separated on any of these columns. In addition, liquid chromatography typically provides better precision than other chromatographic techniques and exceptional dynamic range. The objective of this work was to investigate liquid chromatography for the determination of cellulose ester substituents hydrolyzed from mixed cellulose esters.

The amount of underivatized hydroxyl can be calculated indirectly from the acid substituent results, if the assumption is made that each monomer unit has three hydroxyl groups available for esterification. Essential to the success of this approach is a precise acid determination, especially when the amount of hydroxyl remaining after esterification is small. There are methods for the direct determination of unesterified hydroxyl groups [4,5]. The most widely used method involves the derivatization of the unesterified hydroxyl with phenyl isocyanate [4]. While this method is capable of producing precise results, the procedure is lengthy and requires considerable care to achieve high precision.

The preferred hydrolysis procedure uses a mixture of methanol, sodium hydroxide and a polar aprotic solvent, for example dimethyl sulfoxide (DMSO) [6]. This procedure provides near instantaneous hydrolysis of cellulose esters, which enables rapid and convenient sample preparation [2]. The challenge of using liquid chromatography, or any other chromatographic procedure, with this reagent is to be able to separate the large amount of hydrolysis solvents from the smaller amounts of liberated acids. As will be shown, favorable conditions were found to achieve this separation by liquid chromatography.

2. Experimental

2.1. Sample preparation

Solvents were obtained from Burdick and Jackson. Aliphatic acid standards were obtained from Aldrich and 85% *o*-phosphoric acid was obtained from Mallinckrodt. All aqueous solutions were prepared using water obtained from a Millipore deionization system.

The moisture content of cellulose ester samples can vary from 0 to 10% depending on substituents, which affect the hydrophobicity of the material, humidity, and sample history. Typically, samples may need to be dried in a vacuum oven at 60 °C overnight.

A 15-ml culture tube is convenient for sample preparation. A 0.1-g amount of cellulose ester is dissolved in 4 ml of DMSO or *N*-methylpyrrolidone (NMP). While stirring the dissolved sample on a vortex mixer, add 1 ml of 5 *M* NaOH prepared in methanol and mix for 1 min. Next, add 5 ml of water and briefly mix. Quantitatively transfer contents to a 25-ml volumetric flask. Add 0.7 ml of concentrated phosphoric acid to the flask, dilute to volume with water and mix thoroughly. Filter a portion of the sample through a Gelman 0.45-μm PTFE filter into an autosampler vial.

2.2. Liquid chromatography

Liquid chromatography was performed on a HP 1090 chromatograph using an external ultraviolet absorbance detector (DraChrom) set at 210 nm. A 150×4.6 mm Keystone Aquasil C_{18} column with 5-μm particles and 100-Å pore size was used in this work (P/N 155–775). A 5-μl volume was injected onto the column.

A gradient separation was used to separate the aliphatic acids from the hydrolysis reagent. Mobile phase (A) was an aqueous solution of phosphoric acid at a concentration 0.02% (w/w) and the organic component (B) was 100% acetonitrile. A flow-rate of 1.5 ml/min was selected for the separation. After injection, the mobile phase composition was held at 100% A for 1 min. Then the organic component was increased linearly from 0% B to 50% B over 10 min. This mobile phase composition (50% B) was held for 5 min to elute strongly retained components of

the hydrolysate. The mobile phase composition was returned to 100% A and held for 6 min to re-equilibrate the column prior to the next injection.

Data from the detector were collected and digitized at 2 Hz using a Perkin-Elmer 900 series interface. Chromatograms were analyzed using Perkin-Elmer TURBOCHROM.

3. Results and discussion

Fig. 1A shows the separation of acetic and butyric acids hydrolyzed from a cellulose acetate butyrate ester using DMSO in the hydrolysis reagent. The acids are well separated from the hydrolysis solvents which enables precise integration of their respective areas. If it was present, propionic acid would elute under the DMSO peak. Fig. 1B shows a chromatogram of acetic and propionic acids hydrolyzed from a sample of cellulose acetate propionate. In this case, NMP was used instead of DMSO in the hydrolysis mixture. Acetate and propionate are well separated from the hydrolysis solvents. But, in this case butyric acid would elute under the NMP peak, if it was present. Fortunately, cellulose ester products seldom contain both butyrate and propionate and it is normally known whether a sample is a propionate or butyrate ester. Therefore, the need to use a different solvent for propionate and butyrate esters is not a significant limitation of the method.

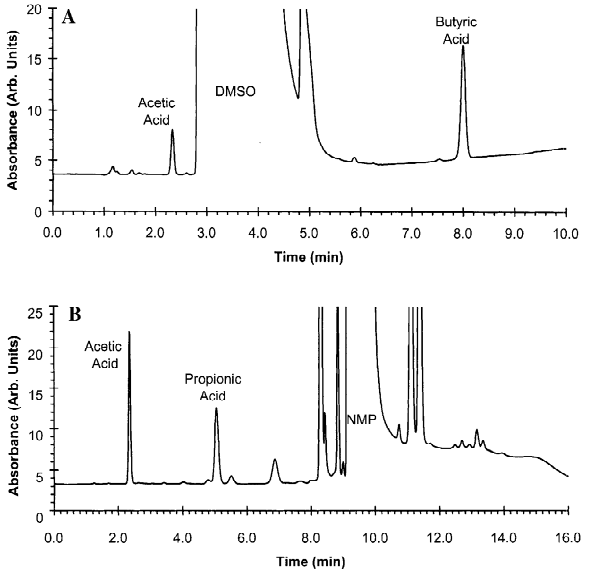

Fig. 1. (A) Chromatogram of hydrolysate of cellulose acetate butyrate using dimethyl sulfoxide (DMSO). (B) Chromatogram of hydrolysate of cellulose acetate propionate using *N*-methylpyrrolidone (NMP).

It was anticipated that liquid chromatography would provide superior precision compared to CE. To determine the practical precision of this approach, a sample of cellulose acetate butyrate was analyzed in triplicate each day for 7 days. Calibration was done each day. The average concentration of butyrate was 48.14 ± 0.67 wt.% with a relative standard deviation (RSD) of 1.4% and average concentration of acetate was 8.9 ± 0.30 wt.% with a RSD of 3.4%. There is nothing inherently less precise about determining acetate. The poorer precision in this example is simply the result of integration error for the smaller acetate peak. These results are at least a two-fold improvement in precision over CE [2].

The improved precision enables the determination of unesterified hydroxyl content by difference. Acid substituents are traditionally reported as wt.%. Hydroxyl content is often reported as degree of substitution, DS, and it is easier to visualize the method when DS is used to report results. Each cellulose monomer unit has three hydroxyls before esterification. A typical butyrate product has an unesterified hydroxyl DS of 0.25, which means that on the average there are 0.25 unesterified hydroxyl groups per monomer unit after esterification. To calculate unesterified hydroxyl DS from the acid percentages, the acid percentages are first converted to DS values. If, for example, an acid substituent DS of 2.75 is calculated from the wt.% acids found after hydrolysis, then the calculated DS for hydroxyl is $3-2.75$, or 0.25. Using the precision values reported above, an error analysis yields a standard deviation of 0.02 for hydroxyl DS calculated by difference. This precision is sufficient for determining the amount of hydroxyl available for crosslinking.

The sample preparation procedure has been validated [2]. In summary, it was found that hydrolysis was quantitative and near instantaneous. The slow steps in the overall procedure are drying, if necessary, and sample dissolution. Most cellulose esters are soluble in DMSO or NMP. However, cellulose esters can be very slow to dissolve even in good solvents. The dissolving particles form a gel at the surface that retards dissolution and enables particles

to stick together in intractable clumps. There are two approaches to address sample dissolution. In one case, the sample is weighed into a vial. The solvent is added, the vial capped and the contents are briefly shaken vigorously to suspend the sample. Multiple sample vials are then put into a larger cylindrical container and placed on a roller overnight to complete dissolution. This approach has the advantage of involving little personal effort. Alternatively, dissolution can be hastened under high shear conditions. Instead of the roller that gently tumbles the solvent, a vortex mixer can be used. With this approach, samples can be dissolved in a few minutes, but constant attention is required.

In spite of the small molar extinction coefficients of aliphatic acids (35 in the case of acetic acid in water with 0.02 wt.% phosphoric acid at 210 nm), this method is quite sensitive. With modern fixed wavelength detectors, it is possible to achieve detection limits less than 1 ppm acetic acid in standards with the conditions described. This sensitivity is more than adequate to determine less than 1% of an acid substituent on a cellulose ester, considering the dilutions in sample preparation.

4. Conclusions

Hydrolysis of cellulose esters is rapid and quantitative when a mixture of DMSO or NMP with sodium hydroxide and methanol is used for the hydrolysis reagent. The liberated acids can be precisely determined by reversed-phase liquid chromatography. The high precision of this method enables the amount of underivatized hydroxyl to be calculated from the acid results.

References

[1] American Society for Testing and Materials, Philadelphia, PA, 1983, Method D871.
[2] G.W. Tindall, R.L. Perry, J. Chromatogr. 633 (1993) 227.
[3] G.W. Tindall, R.L. Perry, A.T. Spaugh, J. Chromatogr. A 868 (2000) 41.
[4] C.J. Malm, L.J. Tanghe, B.C. Laird, G.D. Smith, Anal. Chem. 26 (1954) 189.
[5] R.I. Jackson, Tappi 51 (1968) 560.
[6] G.W. Tindall, R.L. Perry, J.L. Little, A.T. Spaugh, Anal. Chem. 63 (1991) 1251.