

NUCLEAR MAGNETIC RESONANCE METHOD FOR THE QUANTITATIVE DETERMINATION OF PLASTICIZERS IN CELLULOSE ACETATE FILTER RODS

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A rapid quantitative nuclear magnetic resonance (NMR) method was developed for the analysis of plasticizer mixtures in cellulose acetate filter rods. Five 20-mm rods were extracted into 25-ml CCl_4 with 0.4% trifluoroacetic acid containing benzene as internal standard. The NMR spectrum of the extract was obtained and the amounts of plasticizer components were determined from integrations of the spectrum. The method is applicable for filter rods containing poly(ethylene glycol) (PEG) and triacetin, triethylene glycol diacetate (TEGDA) and PEG, or TEGDA and triacetin. At the 95% confidence level, the standard deviation of rods containing 3.2% PEG and 6% triacetin is 0.44% PEG and 0.47% triacetin.

INTRODUCTION

Mixtures of triacetin, poly(ethylene glycol) (PEG), and triethylene glycol diacetate (TEGDA) are used as bonding plasticizers for cellulose acetate filter rods. After the plasticizer is extracted from the rods, the triacetin content may be determined by infrared spectrophotometry (1), titrimetry (2), colorimetry (3), or gas chromatography (3). However, none of these methods is applicable for the direct determination of mixtures of these plasticizers. The purpose of this study was to develop a rapid quantitative method for the simultaneous determination of a mixture of triacetin and PEG or a mixture of TEGDA and PEG on cellulose acetate filter rods or tips.

EXPERIMENTAL

Nuclear magnetic resonance (NMR) spectroscopy was used to determine the amounts of plasticizers present on filter rods. Carbon tetrachloride was the most suitable solvent for use with NMR; 0.4% trifluoroacetic acid was added to the solvent to swell the filter rods so that the plasticizer could be completely and rapidly extracted. This solvent system also had 22.5×10^{-3} mole (0.2% v/v) of benzene added as an internal standard.

The paper wraps were removed from five 20-mm cellulose acetate filter segments. The filters were weighed and placed in a 50-ml flask to which a 25-ml aliquot of the carbon tetrachloride-trifluoroacetic acid solution was added. The flask was stoppered and agitated for 15 min on a mechanical shaker. The liquid was decanted and analyzed by NMR.

A 0 to 10.8 ppm sweep width spectrum was recorded on a Jeol MH-100 NMR spectrometer. The following areas were integrated: area 1, the acetyl methyls of triacetin (or TEGDA) (singlet at 2.2 ppm); area 2, the ethylene protons of PEG (or TEGDA) (multiplets, 3.4–4.2 ppm); area 3, the aromatic protons of benzene (singlet at 7.37 ppm) (Figure 1). In the case of a mixture of triacetin and PEG 600, the moles of each are calculated from the following equations:

$$\text{moles of triacetin} = \frac{6(\text{area 1})}{9(\text{area 3})} \times \text{moles of benzene} \quad (1)$$

$$\text{moles of PEG 600} = \frac{6(\text{area 2})}{53(\text{area 3})} \times \text{moles of benzene} \quad (2)$$

In the case of TEGDA and PEG 600, the number of moles are calculated from the following equations:

$$\text{moles of TEGDA} = \frac{6(\text{area 1})}{6(\text{area 3})} \times \text{moles of benzene} \quad (3)$$

$$\text{moles of PEG 600} = \frac{\{6[(\text{area 2}) - 12(\text{area 1}/6)]\}}{53(\text{area 3})} \times \text{moles of benzene} \quad (4)$$

Any molecular weight PEG can be determined by substitution of the correct number of protons in equa-

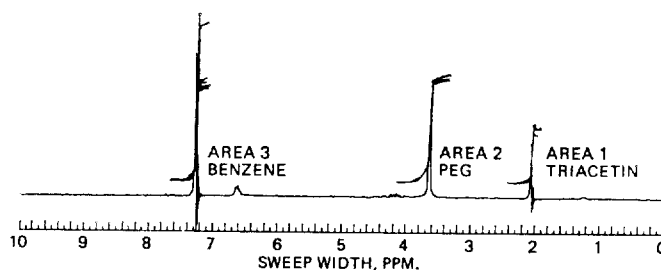


Figure 1. NMR Spectrum of Triacetin and PEG with Benzene as an Internal Standard.

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tions 2 and 4. The number of protons is determined by the following:

$$\text{number of protons} = \left[\frac{\text{molecular weight of PEG} - 18}{\text{repeat unit (44)}} \right] \times \left[\text{number of protons per repeat unit (4)} \right] \quad (5)$$

For PEG 600, the number of protons is:

$$\left[\frac{600 - 18}{44} \right] \times 4 = 53$$

For PEG 400, 34.7 is used instead of 53.

RESULTS AND DISCUSSION

Filter rods containing PEG 600 and triacetin, PEG 600 and TEGDA, and PEG 400 and triacetin were analyzed by the NMR method described; the results are shown in **Table 1** and **Table 2**. The amounts of triacetin present were checked by a gas chromatographic method (3).

This NMR method can be used to determine combinations of triacetin and PEG, combinations of TEGDA and PEG, or combinations of TEGDA and triacetin. Filter rods containing a mixture of PEG 400 and PEG 600 may be analyzed by this method if the ratio of the two is known. The NMR spectrum of TEGDA overlaps the spectra of both PEG and triacetin. If TEGDA, PEG and triacetin are present, the ratio of TEGDA to either triacetin or PEG in the bonding plasticizer formulation must be known to determine all three plasticizers by this method.

Filter rods containing triacetin and PEG 600 were analyzed; the average amounts of triacetin and PEG were 9.1×10^{-3} moles and 2.1×10^{-3} moles, respectively. Similar rods were spiked with a solution containing 5.0×10^{-3} moles triacetin and 2.0×10^{-3} moles PEG. The average amounts of triacetin and PEG present in the spiked samples were 14.3×10^{-3} moles and 4.0×10^{-3} moles, respectively. The recovery of the spiked samples was 101% for triacetin and 98% for PEG.

The standard deviation of the analyses of filter rods containing approximately 3% PEG 400 and 6% tri-

Table 1. NMR Analysis of filter rods containing plasticizer mixtures

Filter Rod	Amount of Component ^a %		Gas Chromatographic Determination, %
Sample 1			
PEG 600	5.8	2.7×10^{-3}	7.2 ± 0.5
Triacetin	6.6	8.4×10^{-3}	
Sample 2			
PEG 600	2.5	1.2×10^{-3}	
TEGDA	6.4	7.1×10^{-3}	

^a Average of multiple determinations.

Table 2. NMR Analysis of PEG 400 and Triacetin in Filter Rods

Filter Rods, g	PEG, %	PEG, Moles	Triacetin, %	Triacetin, Moles
0.6237	3.5	2.2×10^{-3}	6.1	7.0×10^{-3}
0.6282	3.2	2.0×10^{-3}	6.2	7.1×10^{-3}
0.6187	3.2	2.0×10^{-3}	5.7	6.5×10^{-3}
0.6296	3.0	1.9×10^{-3}	5.6	6.5×10^{-3}
0.6276	3.2	2.0×10^{-3}	5.8	6.7×10^{-3}
0.6180	3.2	2.0×10^{-3}	5.8	6.6×10^{-3}
0.6278	3.7	2.3×10^{-3}	6.2	7.2×10^{-3}
0.6184	3.1	1.9×10^{-3}	6.1	6.9×10^{-3}
0.6211	3.2	2.0×10^{-3}	5.7	6.5×10^{-3}
Average	3.2 ± 0.44	2.0×10^{-3}	5.9 ± 0.47	6.8×10^{-3}

acetin was calculated from the series of determinations shown in **Table 2**. At the 95% confidence level, the values were 0.44% for PEG 400 and 0.47% for triacetin.

Previously, the extraction of total plasticizers and lubricants required at least 2½ hr; the gas chromatographic analysis of triacetin required 1½ hr; and the PEG was determined indirectly. With this NMR method, a direct simultaneous quantitative determination of both plasticizers requires ¾ hr.

LITERATURE CITED

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