Specac

Application Note

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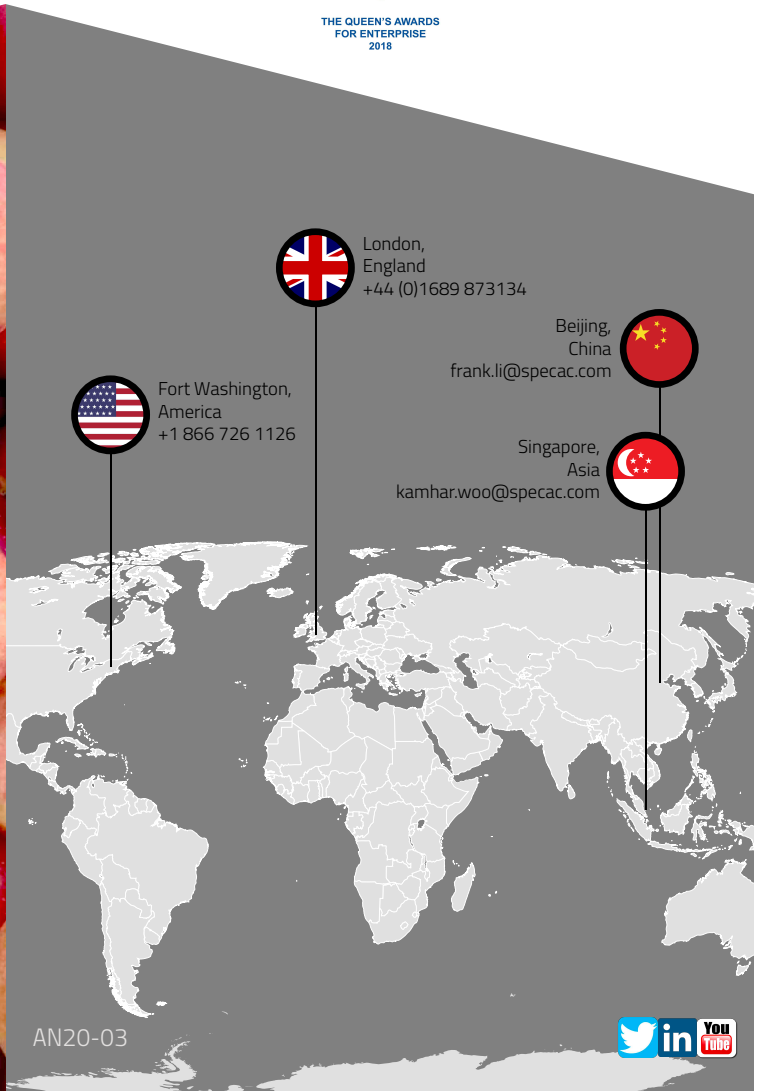
Liquid Film FTIR Analysis of Esterification Reaction Products in the Omni-Cell™

THE QUEEN'S AWARDS FOR ENTERPRISE 2018



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Inside: Learn how to qualitatively interpret spectra recorded in a simple transmission cell – the Omni-Cell™

Introduction

Esters are one of the most commonly occurring functional groups in nature. Low molecular weight esters are commonly used in fragrances owing to their sweet scent. They are formed by the equilibrium reaction of a carboxylic acid with an alcohol in the presence of an acid catalyst. n-butyl acetate is found in nature in Red Delicious apples and is also used as an alarm pheromone by some species of honeybees. Industrially, it is commonly produced for use as a flavouring in a variety of foods [1].

FTIR can be used to monitor the progress of reactions and to check the products. For rapid qualitative analysis of liquid samples, a liquid film can be formed by simply squeezing the sample between two windows without the need for a spacer. This technique is useful for the analysis of pure compounds where a very low pathlength is desired to prevent oversaturation of product peaks.

The Omni-Cell™ is a modular system for transmission analysis of liquids and mulls.

- Quick and simple for many analyses
- Convenient modular construction
- Pathlengths from 6-1000 µm
- Extensive range of window options
- 3x2 slide mounts to any spectrometer

Specac's Omni-Cell™

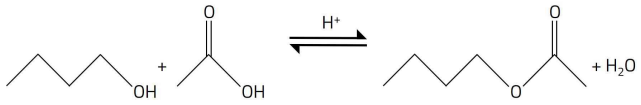

Figure 1: Reaction Scheme

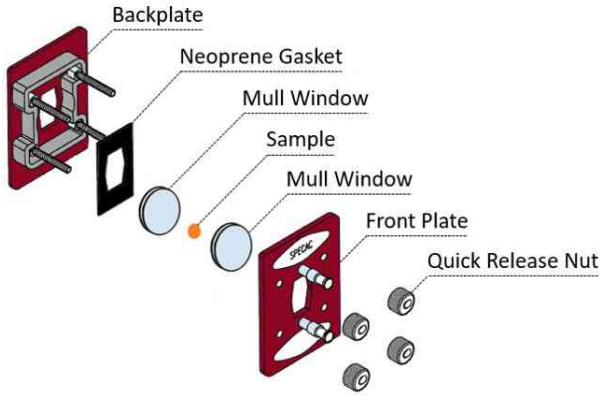

Figure 2: Schematic diagram showing the assembly of a liquid film cell.

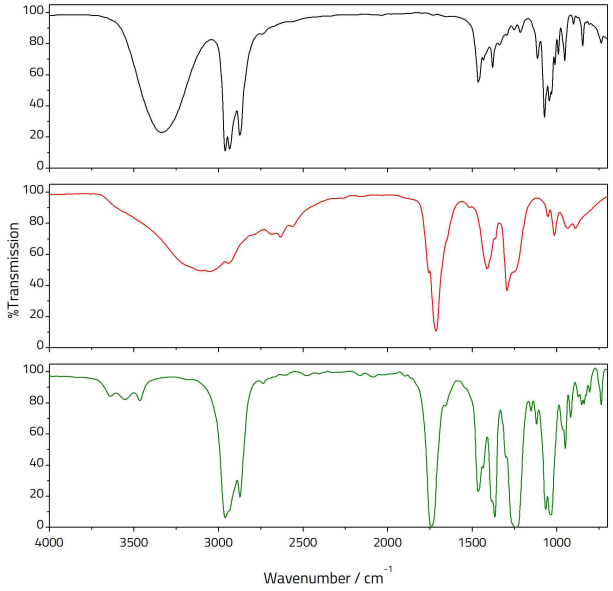

Figure 3: FTIR spectra showing n-butanol (top), acetic acid (middle) and the distilled product spectrum of n-butyl acetate (bottom)

Experimental

n-butanol (12.3 g) was mixed with excess acetic acid (24 g) and then concentrated sulfuric acid (4 ml) catalyst was added dropwise over 90 s. The solution was gently refluxed for 1 hour. The reaction scheme is shown in Figure 1. The reaction was allowed to cool and then the organic phase containing the ester product was washed with 60 ml water. Unreacted acetic acid was removed by extraction into the aqueous phase using sodium hydrogen carbonate to deprotonate the acid. The crude ester product was then dried with magnesium sulfate which was subsequently removed by filtration. A crude yield of 70% (13.1 g) was obtained and then the colorless oily product was further purified by distillation at atmospheric pressure with a yield of 66% (12.6 g). The boiling point of the product was 129°C.

FTIR spectra of the reagents and pure product were recorded using a thin liquid film sandwiched between two mull windows in a Specac Omni-Cell™. A small drop of sample is placed onto a window and then the cell assembled as shown in Figure 2. The quick release nuts were finger tightened to compress the liquid sample into a thin film. Spectra were recorded in a commercially available spectrometer.

Results and Discussion

n-butyl acetate has 54 vibrational degrees of freedom (3N-6). Group theory [2] can be used to determine how many of these will be IR and Raman active. The molecule is assigned to the Cs point group, with an irreproducible representation of $\Gamma_{3N-6} = 32A' + 22A''$ all of which are IR and Raman active. Therefore 54 bands are expected to be observed in the IR spectrum, however many of these bands overlap and are indistinguishable as separate peaks.

The spectra of the reagents and products are shown in Figure 3, whilst the major functional groups for the products and reagents are assigned in Table 1. As can be seen from the spectra, the absence of a very broad, intense peak around 3400 cm^{-1} in the product spectrum confirms the absence of an OH functional group as expected.

The peak shift in the carbonyl region (from 1703 in the acid to 1740 cm^{-1} in the product) is also indicative of the formation of an ester which is typically observed between 1735-1750 cm^{-1} [3].

	n-Butanol / cm^{-1}	Acetic Acid / cm^{-1}	n-Butyl Acetate / cm^{-1}
O-H Stretch	3334	~3250*	-
C-H Stretch	2960, 2934, 2874	3010, 2935	2961, 2875
C=H Stretch	-	1703	1740
C-H Bend	1462	~1450*	1466
O-H Bend	1378	1408	N/A
O-C(=O) Stretch	-	1288	1366
O-C(OH)	1380	-	N/A
O-C(H_2nPr) Stretch	-	-	1065

*Table 1: Tentative peak assignments for the major functional groups in the reagents and product. * indicates the peak appears a shoulder on another peak so exact position is uncertain.*

Conclusion

Liquid film FTIR analysis in the Omni-Cell™ of the product confirms the successful formation of an ester. The procedure is simple to perform and provides rapid qualitative data to the chemist about the success or failure of their reaction.

References

[1] Filatova, A.G., Volkov, I.O., Krikunova, N.I., *Russ. Chem. Bull., 49*, (2000), 314–316

[2] Vincent, A., Molecular Symmetry and Group Theory, Wiley, ISBN: 0-471-48939-5

[3] Socrates, G., Infrared and Raman Characteristic Group Frequencies, Wiley, ISBN: 0-470-09307-2