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Rapid Analysis of Liquid Polyester Resins using Trimethylsulfonium Hydroxide (TMSH) and Gas Chromatography (GC)

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Abstract

Past efforts to achieve quantitative analysis of liquid polyester resins have relied on either a multi-step ASTM FAME-type method coupled to a GC based separation and analysis or by using Nuclear Magnetic Resonance (NMR) spectroscopy. The multi-step ASTM FAME method is based on first performing a caustic digestion and then an esterification on the sample. This methodology while effective, is time consuming, labor intensive, needs a large amount of glassware and suffers from a low sample throughput. The NMR methodology has the significant drawback of being cost prohibitive for most laboratories in addition to having severe limitations when analyzing multiple glycols and halogenated species among others.

Presented here is a single step, *in situ*, GC based methodology that can prepare a liquid polyester resin sample for qualitative and/or quantitative analysis in 30 minutes. This single step methodology has the advantages of simplicity, speed, small sample size, minimal labor and glassware requirements and an extremely high sample through-put. This paper will demonstrate this improved methodology with the analysis of several classes of liquid polyester resins, with samples containing a variety of glycols and acids.

Introduction

The ability to quickly, accurately and cost effectively analyze liquid polyester resins is vital to companies in the resin business for a variety of reasons. First and foremost is the ability to evaluate resin quality. A company must be able to evaluate the contents of a resin produced, be it from a small lab cook during R&D up to a large scale production batch. In addition a large component of a company's reputation is based on its ability to deliver resin to a customer in specification. If a suspect or off specification resin batch is produced in the plant then the ability to look for a possible formula mischarge or contamination before it reaches the customer is invaluable to a company's bottom line. Also, the ability to defend oneself from potential erroneous claims and litigation by providing evidence that the resin supplied to the customer was in specification and made according to formula.

A good analytical methodology can be called upon to do several different things by an analyst. First, the method can be called upon to perform a qualitative analysis. A qualitative analysis can quickly tell the analyst if all of the right components are there, if something is missing or if a contamination is present. Second, an analyst may require a semi-quantitative analysis. This type of analysis allows an analyst to compare a control sample, be it a lab cook or known good plant batch to a suspect or problematic sample. Third, a methodology may need to perform an absolute quantitative analysis on some or all components present in a sample. This type of analysis is useful when no reference sample is available for semi-quantitative analysis or if a contamination needs to be characterized.

Initial attempts to analyze polyester resins have relied first on multi-step ASTM based methodologies that were coupled to a GC. Problems with these methodologies include the amount of time it takes to perform, the man hours involved, the large amount of glassware that needs to be cleaned, prepared and used, along with the low sample through-put. (1-5)

Other well characterized methods have included the use of NMR spectroscopy. NMR methods are very effective in garnering the molar ratios of acids and glycols in liquid polyester resins with minimal sample preparation and quick turn around time under ideal conditions. Unfortunately, because of the extreme costs involved in their procurement, operation and maintenance, these instruments are cost-prohibitive for most companies. NMR spectroscopy has the further drawback of not easily being able to identify and quantify components that contain multiple glycols and halogenated species among others.

We describe here a much simplified sample preparation solution for rapid qualitative, semi-quantitative or quantitative analysis of polyester resins. This methodology can be performed in a single step and is based on an *in situ* saponification using TMSH as the reagent. This methodology has the advantages of simplicity, speed, small sample size, minimal glassware requirements and an extremely high sample through-put when compared to the existing ASTM based methodologies (1-5).

Experimental

Materials. Acetonitrile (ACN), stabilized tetrahydrofuran (THF), and benzene (EMD Chemicals). TMSH was purchased in a 0.2M solution in methanol (TCI America) and pentadecane (Sigma-Aldrich, Inc.). All reagents are HPLC grade or equivalent. 1.0mL Gastight syringe (SGE). 10mL and 100mL Class A volumetric flasks (VWR Scientific). 100mL graduated cylinder (VWR Scientific).

Solution Preparation. In a 500 mL glass bottle place 300mL of Acetonitrile (ACN), 100mL Stabilized Tetrahydrofuran (THF) and 100mL Benzene to make the extraction solution (ES). In a 100mL volumetric flask place 10mL of the TMSH solution and bring to volume with the ES solution to make the reaction solution (RS). Weigh 100mg of pentadecane into a 10mL volumetric flask and bring to volume with ES to make the internal standard solution (ISTD).

Standard Preparation. In a 10mL volumetric flask weigh 100mg of the standard of interest then bring to volume with RS. Place volumetric flask onto a 60°C hot plate for 30 minutes. This will produce a 10mg/mL standard. In another 10mL volumetric flask place 1.0mL of each 10mg/mL standard of interest. This will make a 1.0mg/mL stock solution (SS) that all further dilutions will be made from. An example curve point preparation using the SS and a 10mL volumetric flask: using the equation $\mathbf{C_1 \times V_1 = C_2 \times V_2}$ a 10µg/mL curve point is desired. **1.0mg/mL x XµL = 10µg/mL x 10mL** where **X= 100µL.** Place the calculated amount of SS into a volumetric flask along with 10uL of ISTD and bring to volume with ES. Repeat calculation for each curve point desired.

Sample Preparation. In a 10mL volumetric flask weigh 100mg of the liquid polyester resin of interest. Add 10µL of the ISTD to the same volumetric flask and bring to volume with RS. Place volumetric flask onto a 60°C hot plate for 30 minutes. This will produce a 10mg/mL sample.

Instrumentation. All GC samples were analyzed using a 6890 Plus Gas Chromatograph coupled to an Agilent 5973N quadrupole Mass Spectrometer (Agilent, Palo Alto, CA), upgraded with an inert ion source and enhanced electronics package. Chromatographic separations were achieved with a BPX-50 Phenyl polysilphenylene-siloxane GC capillary column 30 m × 0.25 mm × 0.25 µm (SGE, Australia). The helium carrier gas was set to 1.1 mL per min. One microliter of sample was injected into the instrument in splitless mode. The injection port was set at 280 °C with an initial oven temperature of 50 °C. A 20 °C per minute ramp was applied until the oven temperature reached 320 °C where it was held for 5 min. The mass spectrometer was set in scan mode from 30 amu to 550 amu. Data were gathered using Agilent's Chemstation software

All NMR samples were analyzed using a Bruker Avance III 400MHz NMR. Samples were dissolved in deuterated chloroform and a deuterated water exchange was performed if necessary. Samples were analyzed using both 1D and 2D ^{1}H and ^{13}C techniques where necessary. Data were gathered using Bruker's Topspin 2.1 software package.

Results and Discussion

Analysis on a liquid polyester resin using a GC based analysis is impossible without some sort of chemical digestion to break down the polymer chain to its monomeric components. This is mainly caused by the fact that large molecules are not volatile or thermally stable enough to be put into the GC system, get through the analytical column and then get to the detector. The methodology presented here uses an *in situ* saponification and subsequent methylation in order to accomplish this break down. A saponification is the hydrolysis of an ester under basic conditions to form an alcohol and the salt of a carboxylic acid. (6) The acids then undergo methylation by having our saponification reagent (TMSH) in the presence of an excess of methanol. This method results in our getting the polyester's glycols in original form and getting the acids in the form of a methyl ester derivative. Please note that maleic anhydride will be seen mostly as fumaric acid dimethyl ester along with a small amount of maleic acid dimethyl ester because of isomerization. Partially etherified by-products of the glycols are also produced if there is too much excess TMSH; this phenomenon is demonstrated in **Figure 1** where the same resin is analyzed using increasing amounts of TMSH. This phenomenon can affect the quantitative outcome of the analysis unless these by-products are taken into account in an additional standard curve. Most, if not all of these byproducts have commercially available standards. **Table 1** shows a breakdown of a resin analysis and what some of these partially etherified by-products are that need to be accounted for when performing a formula comparison. The calculated amounts of each partially etherified by-product are added back to the total of their corresponding glycol on a per mole basis.

Figure 2 shows the chromatogram of a resin that has undergone the *in situ* saponification and methylation process. Present in the chromatogram are all of the glycols and partially etherified glycols along with the acids of interest. Other peaks found in the chromatogram are other monomers and additives not of interest for this analysis (i.e. styrene, etc.). This chromatogram generated by the GC instrument can now be used either for qualitative analysis, semi-quantitative analysis or if coupled to a standard curve can now be used for quantitative analysis.

Solving a resin performance issue or customer complaint through a qualitative analysis is trouble-shooting in its most basic form. **Figure 3** shows a chromatogram of a problematic resin batch produced in the lab. The analyst was told that the resin was a PG-Maleic-Ortho based resin that was off-specification. After saponification and a GC based analysis a dicylcopentadiene alcohol (DCPD-OH) peak was found that was determined to be the cause of the issues.

Figure 4 shows an overlay of two chromatograms of two separate batches of the same resin product. It is

easily seen that one chromatogram shows a significant difference in the levels of adipic acid along with orthophthalic acid. One of the resins is considered a control and therefore using raw area counts a semi-quantitative determination of differences can be obtained. In this case adipic acid and orthophthalic acid was found to be 15% and 14% less respectively when compared to the control.

It was shown that the molar ratio data generated with the new methodology closely matched the formula and NMR data and was a marked improvement over the old style ASTM based methodology. **Table 2** shows a table comparing the techniques of interest to the formula of the supplied resin. It can be seen that the new methodology gives comparable results to the NMR data generated but at a fraction of the cost. The new methodology also was able to improve on the accuracy of the old ASTM-based methodology while minimizing the time required to perform. The new methodology also was able to limit the glassware used to one volumetric flask per sample.

The average reproducibility of the GC/MS instrument using all glycols and acids in the example resin was 3.0% with 8 replicates. The RSD of the methodology was found to be 3.4% also with 8 replicates. The limit of detection (LOD) for some of the most common glycols was found to be as low as 100ppm and acids were found to be 1ppm or better. The coefficient of determination (R^2) for standard curves using the most common glycols and acids was found to be consistently 0.995 or better. Data not shown.

Conclusion

We have presented here a single step, *in situ*, GC based methodology that can prepare a liquid polyester resin sample for analysis in as little as 30 minutes. This methodology is a marked improvement over past ASTM and GC based methodologies and also an improvement over NMR based techniques. This single step methodology has the advantages of simplicity, speed, small sample size, minimal labor and glassware requirements and an extremely high sample through-put.

This methodology was found to be reproducible, with an RSD of 3.4% along with being sensitive enough to detect many common acids and glycols in the low ppm range. Furthermore, it was demonstrated that this methodology can be used for qualitative, semi-quantitative and quantitative analysis.

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Figures

Table 1. Shows some of the partially etherified by-products generated by this methodology and how they are accounted for in the formula comparison.

Compounds Quantified	Formula**	Resin 1 Liquid**
Ethylene Glycol	81	88.1
Ethylene Glycol Half-Ether	*	*3.8
Propylene Glycol	12.9	15.1
Propylene Glycol Half-Ether	*	*1.1
Diethylene Glycol	15.9	19.9
Diethylene Glycol Half-Ether	*	*1.1
Fumaric Acid, Dimethyl Ester	*	*24.7
Maleic Acid, Dimethyl Ester	23.6	25
Isophthalic Acid, Dimethyl Ester	*	*0.2
Orthophthalic Acid, Dimethyl Ester	76.4	75

*Compounds not found in formula, but present in sample due to impurities, partial methylation from TMSH reaction or isomerization. Totals for these compounds have been added back to their corresponding glycols on a per Mole basis

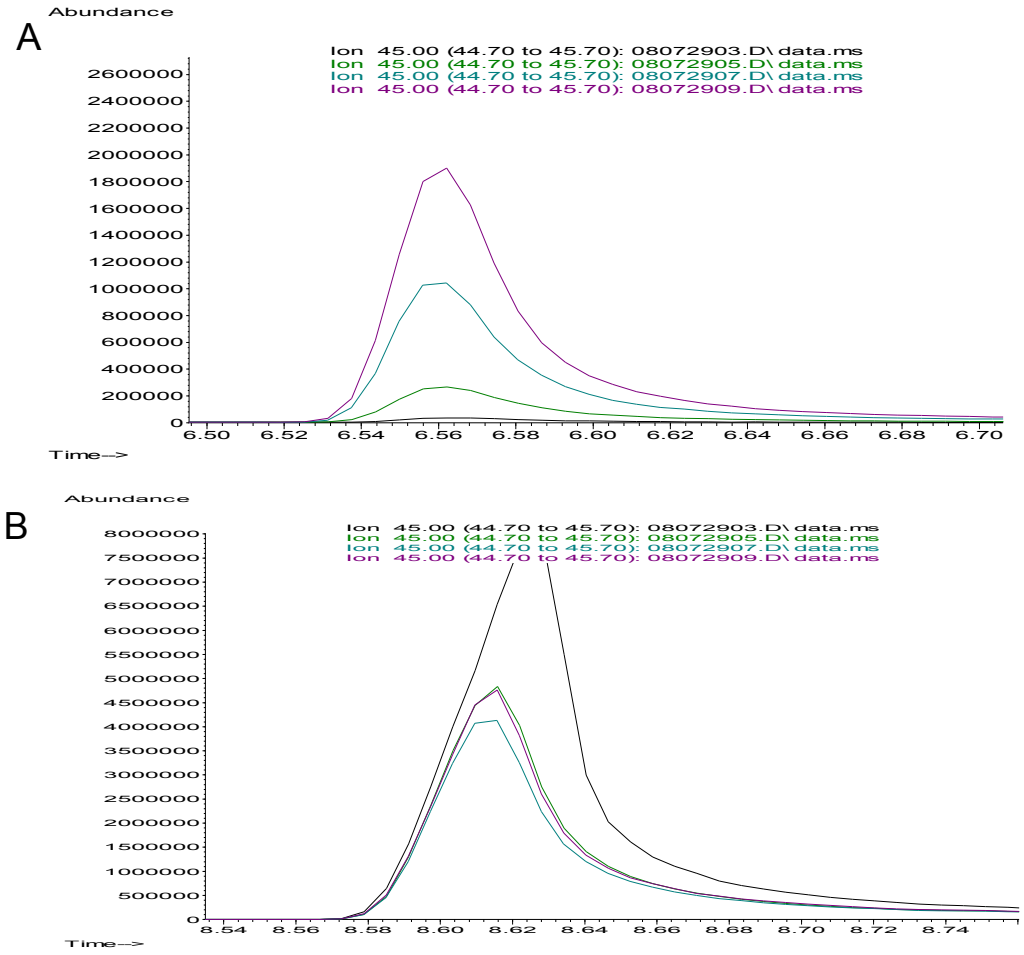
**Total moles of acids are set equal to 100, with amount of glycols adjusted accordingly

Table 2. Resin 1 technique comparisons to formula.

Compound	Formula*	NMR*	Old Method Resin 1 Liquid*	TMSH Method Resin 1 Liquid*
Ethylene Glycol	81	61.2	112.4	88.1
Diethylene Glycol	15.9	27.1	35.1	19.9
Propylene Glycol	12.9	12.9	16.3	15.1
Orthophthalic Acid	76.4	77.8	73.9	75
Maleic Acid	23.6	22.2	26.1	25

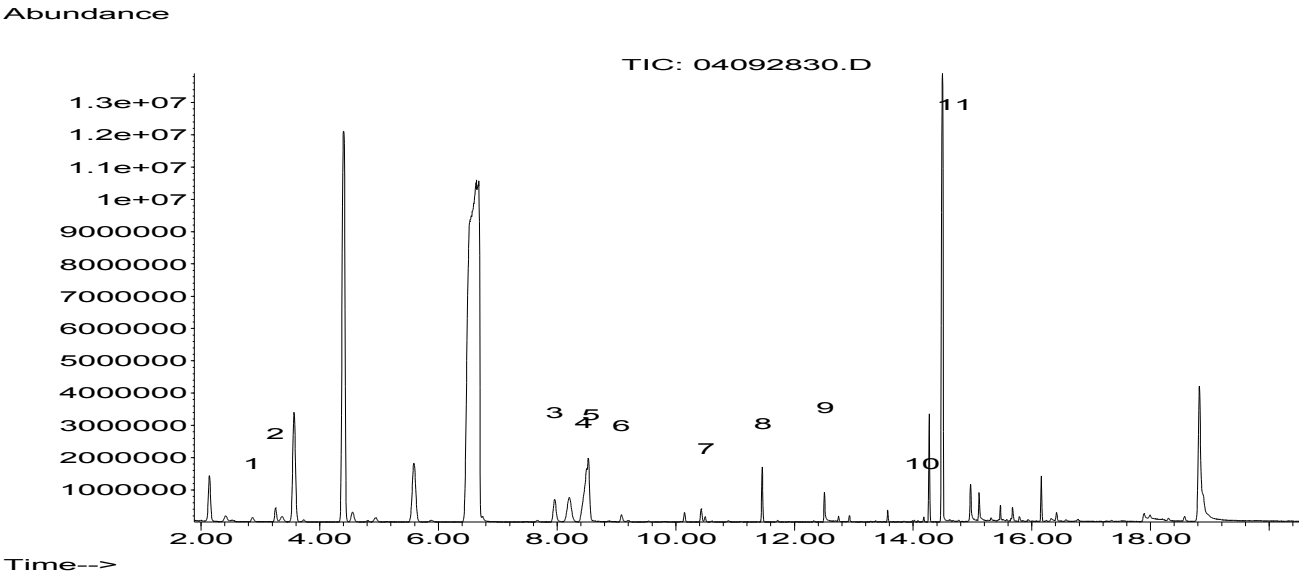
*Total moles of acids are set equal to 100, with amount of glycols adjusted accordingly

Figure 1. A resin saponified using increasing levels of the TMSH reagent. A. Shows the partially etherified byproduct of DEG (DEG monomethyl ether) increasing with TMSH concentration. B. Shows the amount of DEG found in the sample decreasing with increasing levels of TMSH.



Legend:
Black line = 10%TMSH
Green line = 20%TMSH
Blue line = 30%TMSH
Purple line = 40%TMSH

Figure 2. Chromatogram of an example Polyester Resin



Legend:
1.Propylene Glycol Half-Ether
2.Ethylene Glycol Half-Ether
3.Propylene Glycol
4.Ethylene Glycol
5.Fumaric Acid, Dimethyl Ester
6.Diethylene Glycol Half Ether
7.Maleic Acid, Dimethyl Ester
8.Butanedioic acid, Methoxy-, Dimethyl Ester
9.Diethylene Glycol
10.Isophthalic Acid, Dimethyl Ester
11.Orthophthalic Acid, Dimethyl Ester

Figure 3. Chromatogram demonstrating qualitative analysis leading to the discovery of a contaminant.

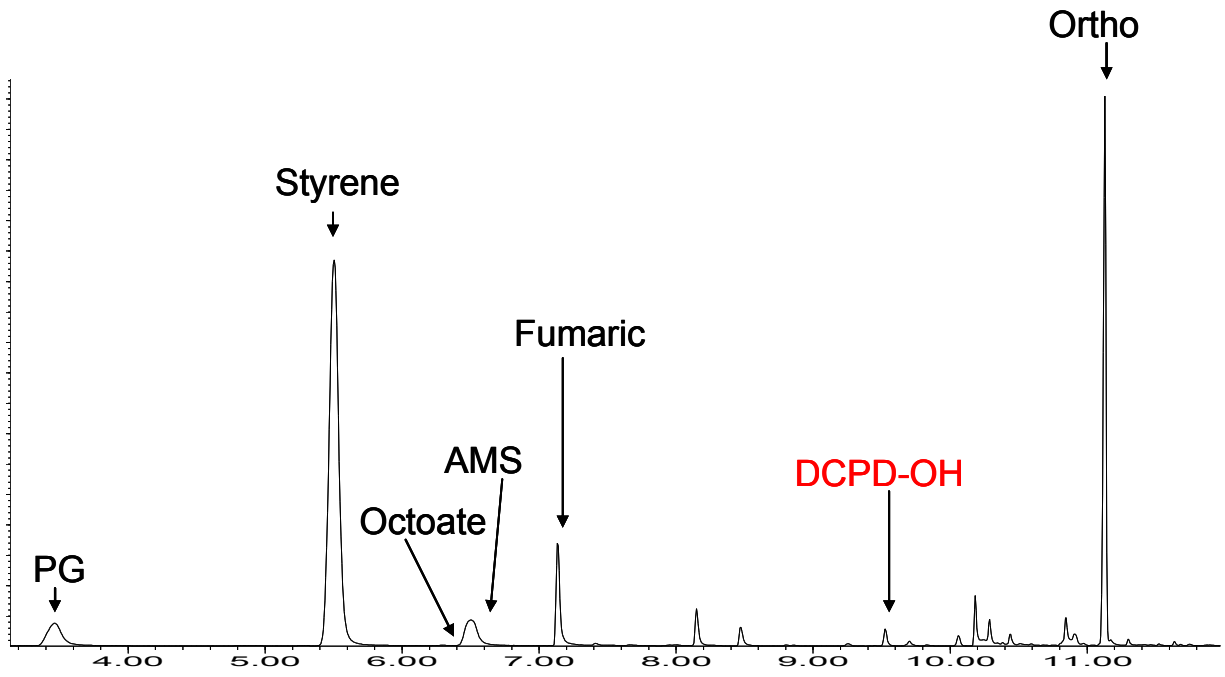


Figure 4. Overlay and zoom-in of the chromatograms of two separate batches of the same product to demonstrate semi-quantitative analysis.