Evaluating Raman spectroscopy to replace GC for quantitative analysis of methyltin chlorides

Benefits at a glance
- Process analytics using Raman spectroscopy: an alternative to GC
- Improved safety and QA/QC using *in situ* sampling
- Robust in-line sampling coupled with simple univariate calibration

Introduction

Methyltin chlorides, including methyltin trichloride (CH_3SnCl_3) and dimethyltin dichloride ($(CH_3)_2SnCl_2$), are commonly used as precursors for the synthesis of heat stabilizers for the commercially important polymer polyvinyl chloride (PVC). Determining the fractions of these two species in the product is an important QA/QC task. At-line gas chromatography (GC) has traditionally been used for this application, but because organotin compounds are highly toxic, a tedious, complicated sampling method must be used in order to avoid human contact with the sample.

Raman spectroscopy offers a convenient alternative to GC for analyzing organotin compounds. It can be performed in-line using a remotely operated system with an insertion probe, which minimizes human exposure, thus improving safety and quality control. Whereas GC requires grab samples to be obtained from the process stream and analyzed off-line, Raman spectroscopy enables real-time in-line analysis that can be used to support process control. Moreover, whereas GC provides a single band for a single analyte, the Raman spectrum can be used to provide information on both molecular structure and functional groups.

Experimental

Raman spectra was acquired using a Raman analyzer with excitation radiation provided by a 785 nm NIR laser. The samples in this study were mixtures of methyltin trichloride and dimethyltin dichloride that were analyzed in the liquid phase after melting in an oven. The immersion probe used for sampling had wetted parts constructed of sapphire and alloy C-276, making it capable of withstanding the corrosive effects of methyltin chlorides.

Before the spectra were used for quantitative analysis, they were truncated using the GRAMS® software package to include only the analytically useful range, 300–650 cm^{-1}. In each spectrum, the curved fluorescence baseline was fit to a fifth-order polynomial that was then subtracted and the new corrected baseline was re-zeroed.

Results

Spectra of both solid and liquid dimethyltin dichloride were acquired. Specific spectral features are identified in Figure 1. The liquid sample, heated above its melting point of 105 °C, shows a broad fluorescence background. The solid sample at room temperature was exposed to the laser for a period of time before data were acquired, eliminating the fluorescence background. That this “photobleaching”

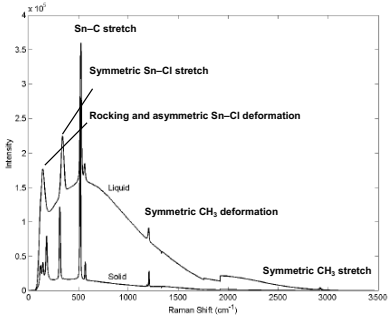

Figure 1: Raman spectrum of dimethyltin dichloride with important bands labeled. The Raman bands are visible atop the fluorescence background. *(Adapted with permission from Ref. 1. Copyright © 2001 InfoScience Services.)*

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

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eliminated the fluorescence but not the methyltin chloride Raman signal indicates that the fluorescence arose from an impurity that was destroyed by the prolonged exposure to the laser. In order to eliminate variation due to background noise, spectra of different samples were compared only after the baselines were subtracted and re-zeroed as described above.

Methyltin trichloride and dimethyltin dichloride can be distinguished by unique Raman bands: methyltin trichloride has a band at 548 cm^{-1} and dimethyltin dichloride has bands at 524 cm^{-1} and 564 cm^{-1}. The relative concentrations of these species in a sample can be determined quantitatively using the heights of characteristic Raman peaks. Figure 2a contains Raman spectra of heated liquid samples in vials with high dimethyltin dichloride content and varying fractions of methyltin trichloride. The spectral intensities were normalized to the intensity of the 524 cm^{-1} peak. The

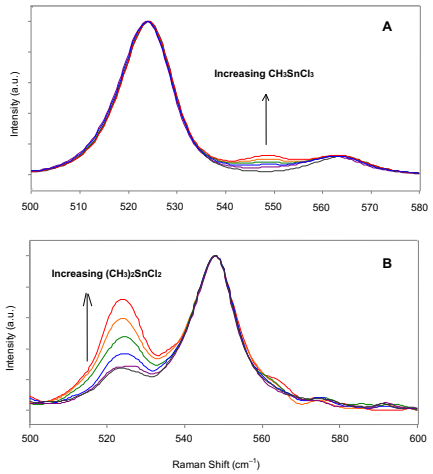

Figure 2: Normalized Raman spectra of methyltin chloride mixtures of various compositions. *(Adapted with permission from Ref. 1. Copyright © 2001 InfoScience Services.)*

known fraction of methyltin trichloride was correlated to the normalized intensity of the peak at 548 cm^{-1}.

Similarly, Figure 2b contains Raman spectra of heated liquid samples with high content of methyltin trichloride and varying fractions of dimethyltin dichloride. These spectra were normalized to the intensity of the 548 cm^{-1} peak and the known fraction of dimethyltin dichloride was correlated to the normalized intensity of the peak at 524 cm^{-1}.

These results were used to construct a calibration curve for methyltin chloride mixtures with over 80% methyltin trichloride shown in Figure 3. On-line Raman analysis of a process sample using this calibration data was found to correlate well to results from at-line GC analysis. The standard deviations of the band ratios from the process sample and the prepared samples fell in the range 0.02-0.04. The uncertainty in the fraction of methyltin trichloride was approximately 1%.

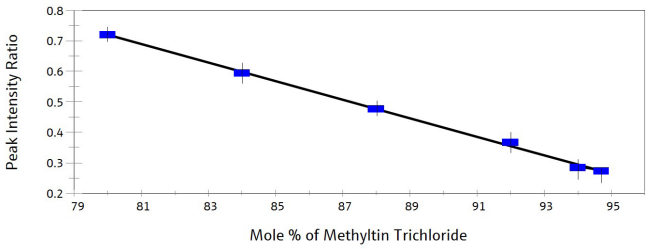

Figure 3: Calibration curve for methyltin trichloride

Conclusion

In-line Raman spectroscopy significantly streamlines QA/QC of methyltin chloride production. Whereas GC requires grab samples to be obtained from the process stream and analyzed off-line, introducing a significant time delay, Raman spectroscopy can be used to acquire data in real time from within the process line with no sacrifice in the quality of the data. By eliminating the difficult sampling procedure required for GC analysis and enabling remote operation, Raman provides increased safety over GC and protection of the product from contamination while enabling real-time process control that would be unfeasible with at-line GC.

Reference

1. Lee, D.; and Chabot, P. "Raman Spectroscopy of Methyltins." *Journal of Process Analytical Chemistry*, Vol. 6, No. 1, **2001**, 31.