The production of methyl chlorosilanes

Benefits at a glance
- Chemically reactive environment
- Optimization of reaction conditions for product formation
- Replaces slower on-line chromatography method

Introduction

Methyl chlorosilanes are important raw materials for the production of polyalkylsiloxanes, the basic ingredient of silicone oils and silicone rubbers. One of the main methods for the commercial production of methyl chlorosilanes, known as the direct process, involves a reaction between elemental silicon and methyl chloride. This reaction generates a mixture containing a potpourri of compounds that includes simple methyl chlorosilane compounds, some Si–H– containing compounds, such as $MeHSiCl_2$, Me_2HSiCl and $HSiCl_3$, and simple chlorinated compounds ($MeCl_4$ and $SiCl_4$). The principal product is dimethylchlorosilane, which is used to form the polydimethylsiloxanes.

Although the other methyl chlorosilanes have practical uses as raw materials, the reaction conditions are normally optimized to maximize the yield of the dimethylchlorosilane. This compound is separated from the reaction mixture by distillation - all the materials are liquids boiling in the range 26–71 °C, with the exception of methyl chloride, which is a gas. It is necessary to monitor the reaction products during the reaction and throughout the distillation to ensure optimum formation of the dimethylchlorosilane. The traditional approach is to use gas chromatography as the monitoring tool. However, this method has drawbacks. It is too slow for optimum control, taking 20 to 60 minutes per analysis, and the instrumentation requires a high level of maintenance. Material corrosivity is the primary maintenance issue.

Raman spectroscopy is a practical solution providing feedback within as little as five minutes. The technique provides spectral differentiation of the key ingredients. It offers a wide dynamic range, and delivers the required sensitivity, down to 100 ppm for key components.

Reaction summary

$$\text{Si (solid)} + \text{Me}_2\text{SiCl}_2 + \Delta H \xrightarrow{\text{catalyst}} + \text{MeCl (gas)} + \text{MeSiCl}_3 + \text{Me}_3\text{SiCl (liquids)}$$

Other products: (liquids) $MeHSiCl_2$, Me_2HSiCl, $HSiCl_3$ $MeCl_4$ and $SiCl_4$

Experimental

A major benefit of using Raman spectroscopy for chemical process reaction monitoring is that fiber optics may be used to separate the spectrometer from the point of measurement. The spectrometer may be located in a non-classified area, such as in a purged analyzer house or within the control room. In the example presented, the spectrometer was placed in a standard NEMA-4 enclosure, rated for operation in a NFPA Class 1, Division 2 environment. The Raman analyzer operated with a frequency doubled 532 nm Nd:YAG laser. Response factors for the selected Raman bands were calculated from gas chromatography (GC) data. In cases where the total number of components is known, the band

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

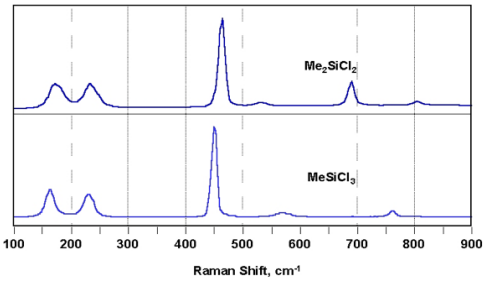

Figure 1: Example spectra of chlorosilanes

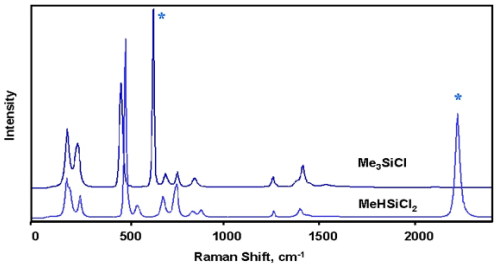

Figure 2: Comparison of chlorosilanes with and without Si-H

intensities are normalized and the composition calculated from the sum of the components, assuming a constant response.

Results

Example spectra for some of the key reaction components are shown in Figures 1 and 2. The spectra of the chlorosilanes, although similar in general appearance, are sufficiently well differentiated to permit measurement of each component without the need for multivariate modeling (chemometrics). These compounds provide an extremely strong Raman signal, and the spectra presented were obtained within a few seconds. The Si–H–containing compounds are characterized by the hydride band close to 2200 cm^{-1}.

The use of fiber optic probe coupling makes it practical to switch monitoring locations within the process. Three of the streams studied in this example exhibited some form of abnormal behavior, reflected in the measured composition of either major and/or minor components. A five-minute data sampling rate was selected, and this provided information on relatively short-term fluctuations occurring in all three streams. These perturbations are related to instability in the distillation column at start-up, or some other event occurring during the reaction or the distillation. The longer measurement time of the GC method does not provide the temporal resolution required to monitor these changes. An example of a monitored variation is presented in Figure 3.

Figure 3 shows a stream containing essentially two components: Me_3SiCl and $MeHSiCl_2$. These exhibit a cyclic change in relative composition during a seven-hour period. This occurred during a recycle phase of the process while material from the column overhead and bottom

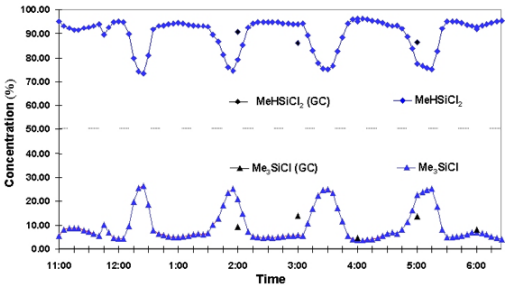

Figure 3: Process anomalies monitored by Raman

streams was returned to the distillation column. This is a real phenomenon of the process as indicated by the exact mirroring of concentration profiles. Note that the chromatographic method of measurement is too slow to pinpoint these events.

Conclusions

The advantages of Raman reaction monitoring are clearly demonstrated with this application, where the key issues are remote monitoring of a chemically reactive and corrosive environment, the ability to take rapid measurements, and the opportunity to monitor different streams in the process.[1] In the latter case, the ability of the Raman analyzer to provide convienent multiplexing is a significant advantage. Raman monitoring provides information on changes in the reaction and/or distillation process as they occur, with sensitivities in the 100–1000-ppm range.

Reference

1. Lipp, E.D. and Grosse, R.L, "On-line Monitoring of Chlorosilane Streams by Raman Spectroscopy," *Applied Spectroscopy,* Vol. 52, No. 1, **January 1998**.