# ANALYSIS OF SILICONE POLYMERS AT TRACE LEVELS BY PYROLYSIS GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

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## 1.0 Abstract

Silicone polymer release liner surfaces on paper, for self stick stamps and labels, become contaminants in paper recycling. Low print adhesion is one major problem limiting the inclusion of silicone release liners in recycling feed stock. A very sensitive method of analysis of silicone polymer during and after recycling employs pyrolysis GC/MS. The analysis provides a measure of siloxanes, ignoring inorganic silicon compounds such as silicates. The method also distinguishes between linear and branched polysiloxanes by different pyrolysis products. High sensitivity, to ppb, may be possible using single ion monitoring or selected ion data collection of mass spectra.

## 2.0 Introduction

Silicone polymers are used widely as thin coatings on paper as release liners for self-stick postage stamps, labels, etc. They are essential to the self-stick concept because adhesive does not stick to the silicone layer but does adhere instantly to uncoated paper, such as envelopes, etc. The composition of the silicone polymer is selected to have an optimum low level of adhesion to adhesive on the stamp or label, so that it does not fall off the release liner, but can be peeled off readily. The silicone polymer, however, presents problems for the recycling of paper. Recycled pulp made into recycled paper may contain silicone polymer on the surface of the paper, causing problems such as low adhesion of print. Paper mills may be forced to limit the feed stock for recycling to paper without silicone polymer. A sensitive and specific test for silicone polymer that would distinguish between silicon in organosilicone polymer and other silicon-containing materials, such as silicates in inorganic compounds, would be useful as a quality control method for the selection of mill feed stock and to detect silicone polymer in recycled paper. In this paper, we report the use of pyrolysis gas chromatography/mass spectroscopy (GC/MS) for the analysis.

An aspect of silicone polymer composition is the use of branched polymer (controlled release modifier) together with linear polysiloxanes to achieve an optimum low adhesion to the release liner. Pyrolysis GC/MS was studied as a means of detecting both types of silicone polymer, while also discriminating against inorganic silicon compounds. Detectability to low ppm and possibly ppb levels was also investigated.

Several references to silicone analysis are given in reference [1]. Reference [2] is a comprehensive review of silicone analysis in environmental samples.

## 3.0 Samples Analyzed

The following were furnished by Dr. James Klein of STR, Enfield, Connecticut: (1) release liner with stamps attached, referred to as laminate, (2) release liner without stamps, from which silicone coating was removed for analysis by scraping, (3) washings from paper recycling taken to dryness. The following were supplied by Dr. John Engel, Wausau-Mosinee Paper Corporation, Rhinelander, Wisconsin: (1) neat silicone polymer without silicone release modifier, (2) neat silicone polymer containing silicone release modifier, (3) and (4) release liner coated with (1) and (2), resp. The interest and assistance of Drs. Klein and Engel with samples are acknowledged with thanks.

## 4.0 Experimental Methods

Pyrolysis GC/MS instrumentation has been described previously [3, 4, 5] and is available on the internet.[6] The device design for both thermal desorption and pyrolysis was invented by Gary Lavigne, University of Connecticut. Pyrolysis equipment of a different design is available commercially.[7] The UConn pyrolysis device utilizes small quartz tubes into which sample is placed. Using controlled gas pressure, the tube with sample is lowered automatically into a commercial constant temperature furnace (SGE Pyrojector). Volatiles are transferred via a syringe needle into the GC injection port, and thence into the GC column for analysis by temperature programming. The sample tube is removed after pyrolysis with gas pressure. The GC/MS is a Hewlett/Packard 6890 electron impact (EI) instrument. The GC column is a J&W carbowax 0.25 mm ID x 25 meter 0.25 micron film. The mass spectrometer has a mass range of 10-700 and can be operated by single ion monitoring, selected ion data collection, and the usual total ion monitoring spectroscopy. In single ion monitoring, an ion or ions are isolated from a total ion spectrum. In selected ion data collection, the spectrometer is programmed to record only a specific ion or ions selected, without a total ion spectrum. Both single ion monitoring and selected ion data collection are means by which resolution is improved and detectability of a compound can be enhanced. The selected ion method provides greater sensitivity of the two methods. In this study, both methods were used. For selected ion data collection, the ions are selected from single ion monitoring and the mass spectra of compounds to be identified and quantified. The pyrolysis temperature and time were 750°C and 1 minute.

Calibration for silicone polymer content was done using silicone polymer scraped from release liner. This was sufficient for the purpose of this study, which was mainly to have a method which would discriminate between organic silicone polymer and inorganic silicon, such as in silicates. Paper products may contain a high content of silicates to make paper opaque and dense. For accurate determination of silicone at low ppm to ppb range, an appropriate method of calibration at low concentrations is needed. That went beyond the objective of this study, but it should be capable of being accomplished.

Thermal desorption GC/MS was also done, using a temperature (225°C) which is low enough that little or no decomposition occurs; the volatiles detected provide information on composition of silicone and non-silicone components of the formulation.

## 5.0 Experimental Results

### 5.1 Silicone Content by Pyrolysis

Figure 1 is a total ion pyrolysis chromatogram of a laminate, i.e., stamp and release liner backing together, split 100/1, using 0.99 mg sample weight. Split 100/1 means only 1% of the volatiles goes through the GC column. Otherwise, it would be overloaded. There are so many peaks that it is not obvious which are the silicone polymer pyrolysis products. The latter compounds are cyclic silicones with 3, 4, 5 and 6 silicon atoms in the ring. The most prominent is the hexamethyl cyclotrisiloxane (fig. 2). In single ion monitoring, a prominent ion peak is used as a measure of a particular compound. The ion peak used should be unique to that compound and not be prominent or exist at all for other compounds present, such as cyclotetrasiloxane, etc. Figure 3 is the chromatogram for the 207 mass ion for cyclotrisiloxane. The appropriate ions for cyclotetrasiloxane, cyclopentasiloxane and cyclohexasiloxane are 281, 355 and 429, resp.

Figure 4 is a splitless selected ion data collection chromatogram for 0.037 mg of laminate, same as in figure 1, using ions 207, 281, 355 and 429. In this way, peaks are obtained specific for the 3, 4, 5 and 6 cyclic silicone compounds formed by pyrolysis. The ratio of the cyclic silicones most likely depends on the pyrolysis temperature and time. An advantage of an isothermal pyrolysis temperature oven, over a ramped heating cycle, may be better reproducibility of the pyrolysis products and relative amounts. The quantitative analysis of silicones depends on a reproducible content of pyrolysis products; in this case, the prominent trisiloxane peak is used for calibration and measurement. For a typical silicone polymer formulation, the cyclotrisiloxane content, under reproducible pyrolysis and chromatography conditions, is believed to be a practical marker for silicone analysis.

Figure 5 is the splitless selected ion data collection chromatogram for 0.443 mg of a paper recycling washing supernatant taken to dryness. The four cyclosiloxanes are seen in the same way as those for the laminate (fig. 4) which has much higher silicone content. The calculated siloxane content for figure 5 is 88 ppm, using the trisiloxane peak for calibration and measurement. The method is believed to be capable of measuring lower ppm levels, and possibly medium to high ppb levels.

### 5.2 Pyrolytic Analysis for Branched Silicone Release Modifier in the Presence of Linear Polysiloxane

Figure 6 is the total ion pyrolysis chromatogram, split 100/1, for silicone polymer which contains no added branched release modifier. Figure 7 is that for the release modifier polymer. The silicone modifier pyrolyzate contains about 50 times as much trimethylsilanol as linear polysiloxanes. It also has linear dodecamethylpentasiloxane not seen in the linear polymer. Figure 8 is the single ion monitoring chromatogram of release liner backing paper of silicone without release modifier. Ion 73 provides a measure of linear siloxane, and ion 75 for trimethylsilanol, a pyrolysis product of the modifier. Figure 9 is for the release liner backing paper with added release modifier. The method is certainly a qualitative means of detecting release modifier and could be quantitative using suitable calibration. The 75 mass ion is very prominent in the spectrum of trimethylsilanol.

### 5.3 Thermal Desorption GC/MS for Volatile Components of Silicone Formulation

Figure 10 is the splitless thermal desorption chromatogram using 225°C for desorption, 2 minutes, and 1.39 mg of silicone polymer scraped from release liner on paper. It shows a substantial content of hydrocarbons as a broad peak (10-24 minutes). Two silicone polymer related compounds detected are trimethylsilanol and cyclotetrasiloxane 2, 4, 6, 8 tetramethyl (fig. 11). The latter compound is believed to be a crosslinking agent via the SiH bonds. Figure 12 is the splitless selected ion data collection chromatogram of thermal desorption of silicone scrapings (225°C/1 minute) using ions 207, 281, 355 and 429. These four ions are the same ones used in pyrolysis chromatograms for Si-3, Si-4, Si-5 and Si-6 cyclic siloxanes. While present at low levels, the method readily detects the oligomeric cyclic siloxanes present as part of the overall compositional distribution of silicone polymer. Of the four, the pentasiloxane appears to be most prominent.

## 6.0 Discussion

The pyrolytic chromatograms above clearly show that the method, with GC/MS, provides high resolution, sensitive detection of the main linear silicone polymer as well as release modifier. Levels down to low ppm are certainly possible and possibly even in the ppb range. Some of the potential difficulties are that solid silicone polymer or silicone oil are present in so many materials that every solvent tried for the preparation of low levels of silicones as standards for calibration had more silicone present than the low levels we wanted to prepare. Silicone GC septa may cause blanks to contain low levels of silicone. The SGE Pyrojector furnace has a short space between the furnace and the GC injection port, where volatiles can condense and tend to bleed off in a sequence of runs. These considerations are not a significant factor in qualitative or semi-quantitative analysis of moderate to high levels of silicone polymer. For quantitative analysis at the low ppm level, they may affect accuracy. Nevertheless, with attention to all the factors that can contribute silicone in a chromatogram, it should be possible to provide useful data for silicone content of such things as recycled paper.

One of the major objectives of the study was to demonstrate that pyrolysis GC/MS can measure silicone content without interference from inorganic silicon compounds, such as silicates. Clearly, that is the case. There is no reason to believe that an inorganic silicon compound without carbon will pyrolyze to an organic cyclic siloxane compound.

The method provides a measure of release modifier based on trimethylsilanol content in the pyrolyzate. Thermal desorption gives compositional information on non-silicone components, such as hydrocarbon oil, as well as silicone oligomers and unreacted crosslinking agent (SiH compound), and trimethylsilanol.

The silicone pyrolysis products, for the samples studied, appear to give a reproducible composition in which cyclotrisiloxane predominates. It provides a convenient means of calibration and measurement. If the Si-3 composition is a variable between different silicones, accuracy may be affected. Further studies could determine how variable the Si-3 composition in pyrograms is between different silicone polymers and systems. In any case, pyrolysis GC/MS is a promising method of analysis of silicone polymer down to trace levels in paper and other materials.

## References

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7. CDS Analytical, Inc., Oxford, PA 19363-0277, website <www.cdsanalytical.com>.

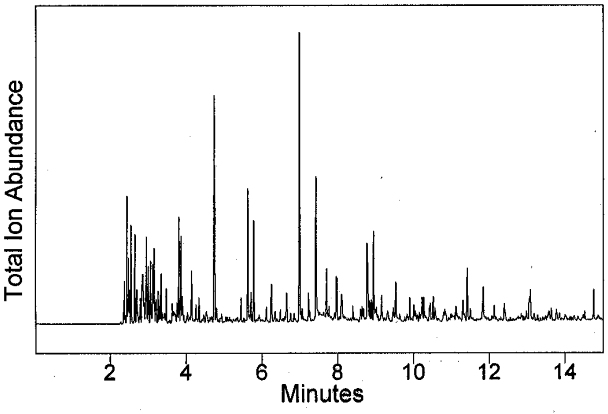

Figure 1 – Total ion pyrolysis chromatogram of 0.99 mg of laminate (stamp and release liner backing).

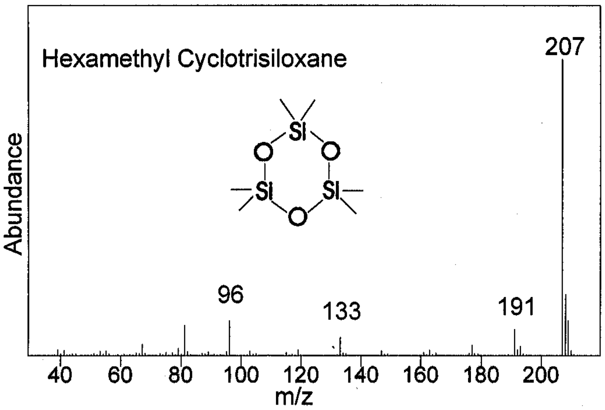

Figure 2 – Mass spectrum and formula of cyclotrisiloxane.

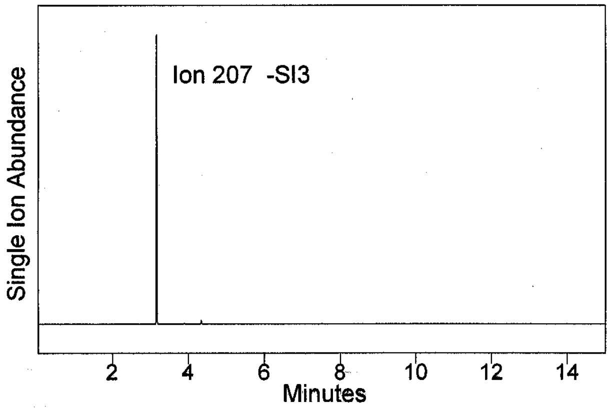

Figure 3 – Single ion monitoring chromatogram of 207 mass ion in figure 1.

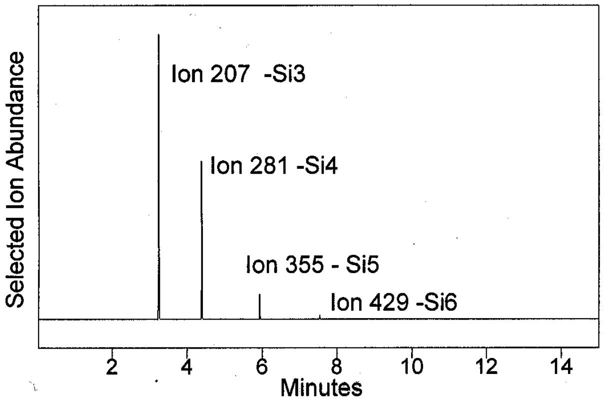

Figure 4 – Splitless selected ion data collection chromatogram of 0.037 mg of laminate (same as used in figure 1), using ions 207, 281, 355 and 429.

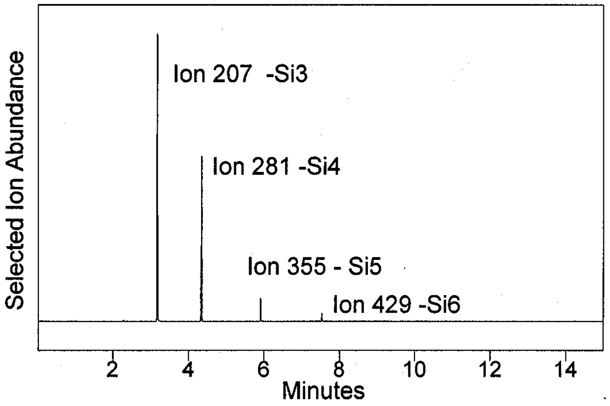

Figure 5 – Splitless selected ion data collection chromatogram for 0.443 mg of a paper recycling washing supernatant taken to dryness.

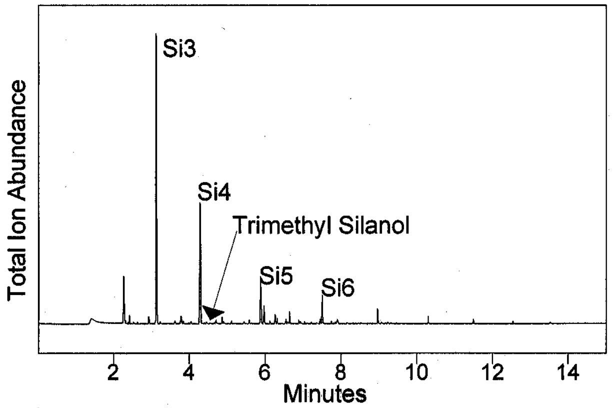

Figure 6 – Total ion chromatogram split 100/1 of linear polysiloxane polymer containing no added branched release modifier.

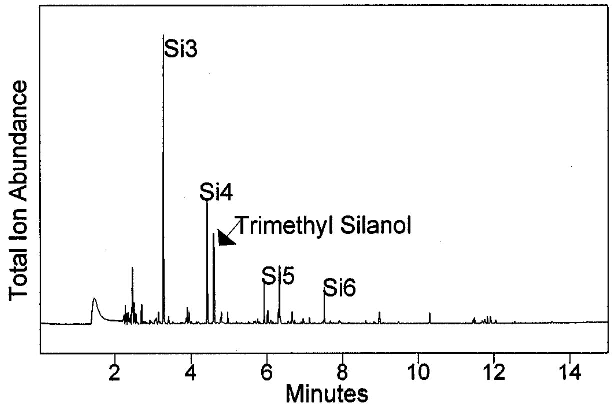

Figure 7 – Total ion chromatogram split 100/1 of branched silicone release modifier polymer.

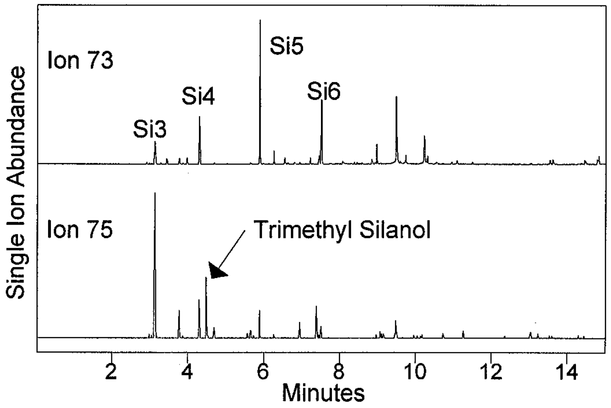

Figure 8 – Single ion monitoring chromatogram of release liner paper backing of linear polysiloxanes (fig. 6). Ion 73 is for linear polysiloxanes and ion 75 is for trimethylsilanol, a measure of release modifier.

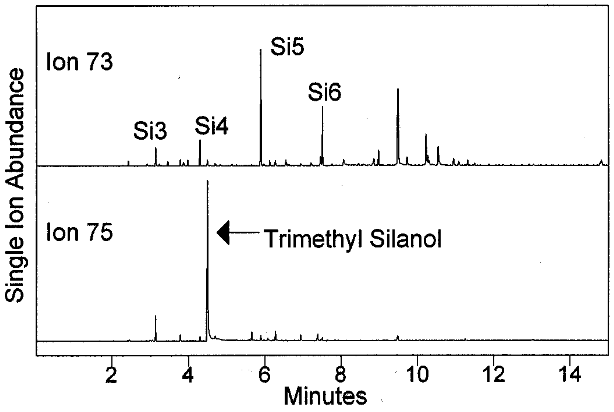

Figure 9 – Same as figure 8 for release liner backing paper with release modifier (fig. 7).

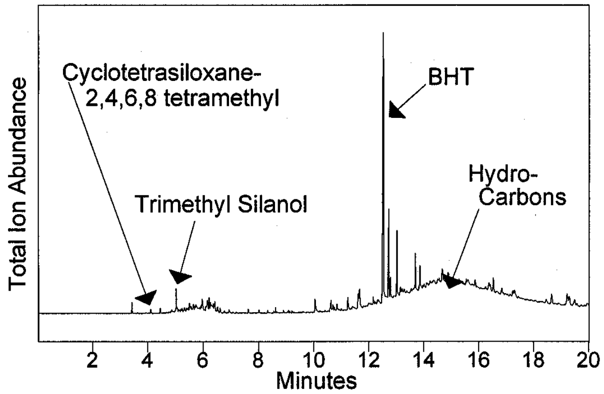

Figure 10 – Thermal desorption chromatogram (225°C) of 1.39 mg of silicone scrapings.

Keywords – silicone analysis, pyrolysis GC/MS, thermal desorption GC/MS, paper recycling

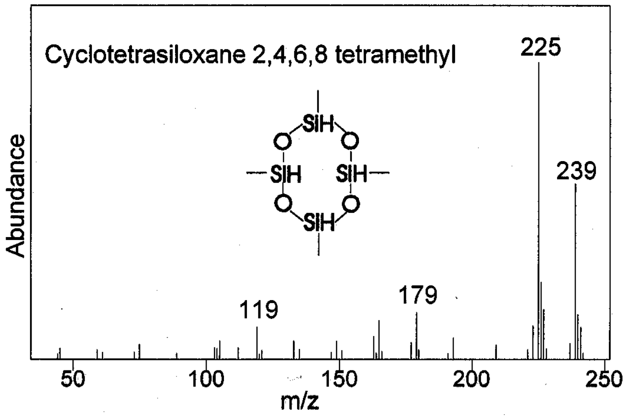

Figure 11 – Mass spectrum and formula of cyclotetrasiloxane 2, 4, 6, 8 tetramethyl.

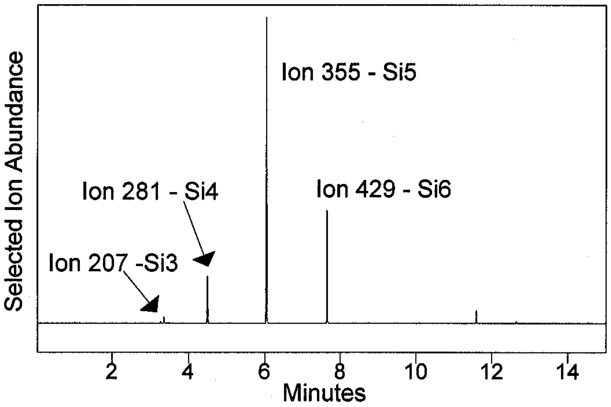

Figure 12 – Thermal desorption splitless selected ion data collection chromatogram of silicone scrapings for ions 207, 281, 355 and 429.