

High Temperature Headspace Assay of Polymers with Teledyne Tekmar HT3™ Static Headspace Instrument

Introduction

Since the early 1990's air quality in enclosed spaces such as office buildings, homes and automobiles has become a major environmental concern. The concern is that man made materials used in these environments release volatile (VOC) and semi-volatile organic compound (SVOC) reducing air quality in these environments.

Manufactures of materials used in these environments have quickly responded to minimize or remove VOC's and SVOC's from their processes to reduce or eliminate these compounds concentration in enclosed areas, thus improving the quality of the indoor air. One type of polymer that is used in these areas is high temperature polymers.

The VOC's and SVOC's from high temperature (HT) polymers is typically determined with thermal desorption methods instead of headspace. These HT polymers have glass transition and melt temperatures well above 200°C, which is typically the upper limit of most commercially available headspace instruments.

The Teledyne Tekmar HT3™ Headspace instrument however has an upper sample heating temperature of 300°C.

Also, thermal desorption instruments limit the sample size to the internal diameter of the thermal desorption tube, 4 mm. Large solid samples must be reduced in size by mechanical methods, which can heat the sample releasing VOC's and SVOC's prior to the analysis. This could create a false negative result.

A sample assayed with a headspace instrument can be up to 11 mm wide, the size of the vial opening and 60mm long, the depth of the vial, thus allowing minimal to no mechanical resizing of the sample.

This paper documents the assay of a HT polymer with Teledyne Tekmar's HT3™ Static headspace instrument at 280°C. This temperature is above the glass transition temperature of the HT polymer at about 200°C and is below its melt temperature of 300°C. The HT polymer was tested to compare the VOC's and SVOC's released during headspace analysis to the current thermal desorption method.

Instrument Parameters

The HT3™ Static Headspace instrument was connected to an Agilent 6890 GC with an FID. The static headspace instrument conditions for the HT3™ are presented in Table 1.

Variable	Static Value	Variable	Static Value
Platen/Sample Temp	280°C	Pressurize	12psig
Valve Oven Temp	280°C	Pressurize Time	2.00 min
Transfer Line Temp	280°C	Pressure Equil. Time	0.20 min
Standby Flow Rate	50mL/min	Loop Fill Pressure	9psig
Sample Equil. Time	30 min	Loop Fill Time	2.00 min
		Inject Time	1.00 min

Table 1: Static (Loop) HT3 Parameters

Column	Rtx-200, 30m x 0.32µm, 1.5µm film, column flow of 2.0 mL/min
Inlet	Split ratio 30:1, inlet temperature of 150°C, 1 mm IP-deact liner
Oven	40°C, 1 minute, 15°C/min to 120°C, 30°C/min to 260°C, 2 minute final hold
FID	320°C, Hydrogen flow - 35mL/min, Air flow - 400mL/min, Constant column and make up flow - 30mL/min

Table 2: Agilent 6890 Conditions

Sample Preparation

A HT polymer was obtained as raw pellets. Four sample weights, 1g, 2g, 4g, and 8g, were weighed into 22mL headspace vials. These were capped and sealed with Teflon lined septa. The sample weight range will provide data to determine the linearity of the VOC and SVOC peaks observed in the sample. Figure 1 is a photo of the four sample size concentrations, indicating their volume in the 22mL headspace vial.



Figure 1: Comparison of 1g, 2g, 4g, and 8g of a HT Polymer Sample in 22mL High Temperature Headspace Vials.

A standard was prepared by dissolving 100mg of one of the expected VOC's in 5mL of methanol and placing 50µL into a 22mL headspace vial. The vial was immediately capped and sealed with a Teflon lined septa. The samples and standard were assayed with the HT3™ headspace conditions and the GC conditions listed in Tables 1 and 2.

Results

Low level VOC's and SVOC's were readily detectable with this static headspace method. Ten compounds were detected and their peak area used to calculate their linearity versus the HT polymer sample weight. Figure 2 is the overlay of the chromatograms for the four HT polymer sample weights.

Compound 5 was present at approximately 500 times greater than the other compounds. These remaining compounds are displayed on scale as inserts in Figure 2 prior to and after compound 5, because of their lower concentration.

The peak areas for these compounds are listed in Table 3 along with the correlation coefficient for each compound. The peak area for the standard and the calculated ppm of the sample VOC and SVOC peaks is also included in Table 3. The VOC and SVOC compounds were detected from 0.02 to 20ppm of the HT polymer.

Compound 9 was not well resolved from a system peak and its integration from the system peak introduces some error.

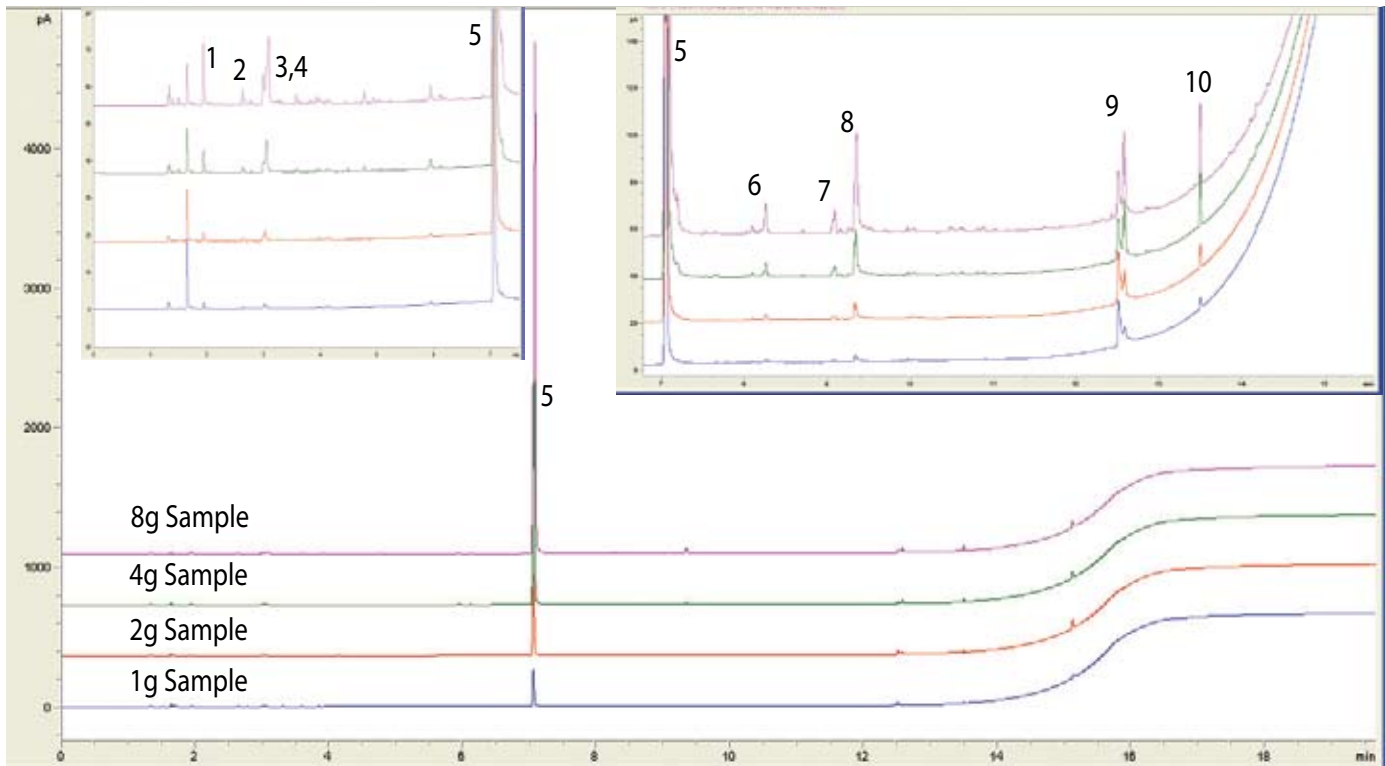


Figure 2: Overlay of the 1g, 2g, 4g, and 8g Sample Chromatograms with Static Headspace with the Major VOC on Scale. The Inset Chromatograms Display the Lower Concentration VOC's and SVOC's Prior to and After the Major VOC.

Peak Number	RT	1g	2g	4g	8g	Correlation Coefficient	ppm
1	1.93	2.5730	3.7051	9.0210	24.6508	0.9995	0.06
2	2.62	0.9212	1.1544	3.4051	8.4198	0.9961	0.02
3	2.99		1.9530	4.3111	14.3690	1.0000	0.04
4	3.09	4.2638	5.6731	21.4841	60.0200	0.9968	0.15
5	7.08	431.0443	932.9901	2903.8462	7663.9688	0.9991	19.55
6	8.26	2.1443	3.8398	9.8273	20.6628	0.9980	0.05
7	9.09	2.3791	3.6140	8.7752	20.7271	0.9987	0.05
8	9.35	5.0935	13.1178	40.1065	114.4496	0.9998	0.29
9	12.58	6.4461	14.0116	34.1594	51.7675	0.9953	0.13
10	13.50	5.6552	10.8397	26.2911	43.5544	0.9957	0.11

Standard 48994.1

Table 3: Peak Area and Correlation Coefficient Data of the VOC and SVOC Compound for the Four Concentrations of HT Polymer Samples. The parts per million (ppm) is Calculated with the Peak Areas of the Standard Listed at the Bottom of the Table and the 8g Sample.

Conclusion

Ten VOC's and SVOC's were detected by static headspace analysis. All of the compounds exhibited good linearity, indicating that the headspace method provides reproducible results. The ppm concentration of Peak 5 obtained with the HT3™ method is consistent with the result obtained by the thermal desorption method.

The sample preparation by the HT3™ method was minimal, with the sample pellets placed directly into the headspace vials instead of being mechanically reduced. The pellet size did not have to be reduced to fit into a 4 mm ID thermal desorption tube.