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# A New Purge Tool for Use with Automated Headspace Analysis

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## Abstract

Static (equilibrium) headspace injection is commonly used for GC determination of volatiles in solid and liquid samples. Quantitative analysis can be performed using standard techniques, such as external or internal standard methods and/or methods of standard addition.

If matrix effects adversely influence quantitation, a multiple headspace extraction (MHE) approach can be utilized to prove that equilibrium has been reached. The total amount of an analyte or standard in a sample can then be determined mathematically by extrapolating the peak areas from subsequent extractions of the same vial to calculate the total peak area. A key step to this technique is venting of the headspace between injections, followed by re-equilibration of the sample. Traditionally, pressure balanced and pressure loop type headspace samplers have offered automated MHE. For conventional syringe based systems this has not been possible, because they are limited in the amount of headspace which can be removed from the vial in each extraction step, usually equal to the volume injected. A 1.0 to 2.0 mL injection from a 20 mL headspace vial usually does not displace enough analyte to accurately extrapolate and calculate the total analyte amount.

A novel purge tool for the GERSTEL MultiPurpose Sampler (MPS 2) under MAESTRO software control allows the headspace of a sample vial to be purged with inert gas between injections. This new feature enables the syringe based MPS 2 to perform MHE quantitation. The tool also allows automated purging of headspace samples prior to extraction. A brief explanation of MHE methodology along with specific examples will be given.

## Introduction

Multiple headspace extraction for static headspace analysis is an excellent choice for quantitation of analytes in difficult matrices as well as for headspace method validation. The technique allows the analyst to determine whether or not equilibrium has been established and to mathematically extrapolate the total peak area for an analyte in a sample. If the obtained semi-logarithmic MHE curve is linear, it is proof that equilibrium has been reached. MHE has been difficult, if not impossible to perform using syringe based headspace samplers due to their inability to purge the headspace of a sample/standard between injections. A novel purge tool in combination with a GERSTEL purge station and MAESTRO software control now enables the syringe based GERSTEL MultiPurpose Sampler (MPS 2) to perform MHE. In an MHE experiment, a sample or standard is placed in a sealed vial. The vial is thermostated for a pre-determined period of time to establish equilibrium for the analyte between the sample and headspace in the vial. A portion of the headspace is then injected into the GC. The headspace of the vial is purged, and the sample re-equilibrated before the next injection. The process is repeated and the analyte peak area decays in an exponential fashion. If equilibrium is reached for each step, a plot of ln peak area versus n-1, where n is the extraction number, yields a straight line. The total peak area can then be derived from the equation:

$$\text{TotalArea} = \frac{e^{\text{Intercept}}}{1 - e^{\text{Slope}}}$$

A more formal derivation of this equation can be found in [1]. To illustrate the use of the purge tool for MHE quantitation, two examples, the analysis of residual toluene in duct tape and the analysis of α-pinene in toothpaste are presented.

## Experimental

*Instrumentation.* GERSTEL MPS 2 robotic sampler with Headspace option, GERSTEL Purge Station and Purge Tool, GERSTEL CIS 4 Cooled Inlet System with LN2 option, GERSTEL MACH Modular Accelerated Column Heater, Agilent 7890 GC/MSD

*Analysis conditions.*

| | |
|---|---|
| Headspace: | 60°C (10 min); tape |
| | 50°C (30 min); toothpaste |
| | 1 mL injection volume |
| | 60 mL/min purge flow |
| | 1 min purge time |
| PTV: | split (10 mL/min) |
| | 250°C |
| Column: | 30 m Rtx-1 (Restek); MACH format |
| | $d_i$ = 0.25 mm  $d_f$ = 0.25 µm |
| Pneumatics: | He, ramped pressure |
| | 7.1 psi (1 min); 1.14 psi/min; 12.8 psi (tape) |
| | 7.1 psi (1 min); 0.57 psi/min; 15.7 psi (toothpaste) |
| Oven: | 40° C (1 min), 20° C/min, 140° C (tape) |
| | 50° C (1 min), 10° C/min, 190° C (toothpaste) |

*Sample Preparation.* The toothpaste, approximately 0.25 g, was placed directly into a 20 mL headspace vial. The tape was placed on a Kimwipe and a 0.40 g sample cut and placed into a 20 mL headspace vial.

## Results and Discussion

Figure 1 shows a picture of the purge tool. The sequence of events for purging a vial consists of transporting the vial to the purge vial position, picking up the purge tool, and purging the vial. The purge gas is supplied through the headspace needle. A regulator at the rear of the MPS rail controls the flow. The purge gas exits to atmosphere through a second needle in the purge tool. Figure 2 shows a picture of the MPS 2 purging a vial.


**Figure 1.** Purge tool and purge tool holder.


**Figure 2.** A vial is being purged in the MPS.

The Purge Vial function is activated in the GERSTEL MAESTRO PrepSequence, details can be seen in the screen shot in figure 3.

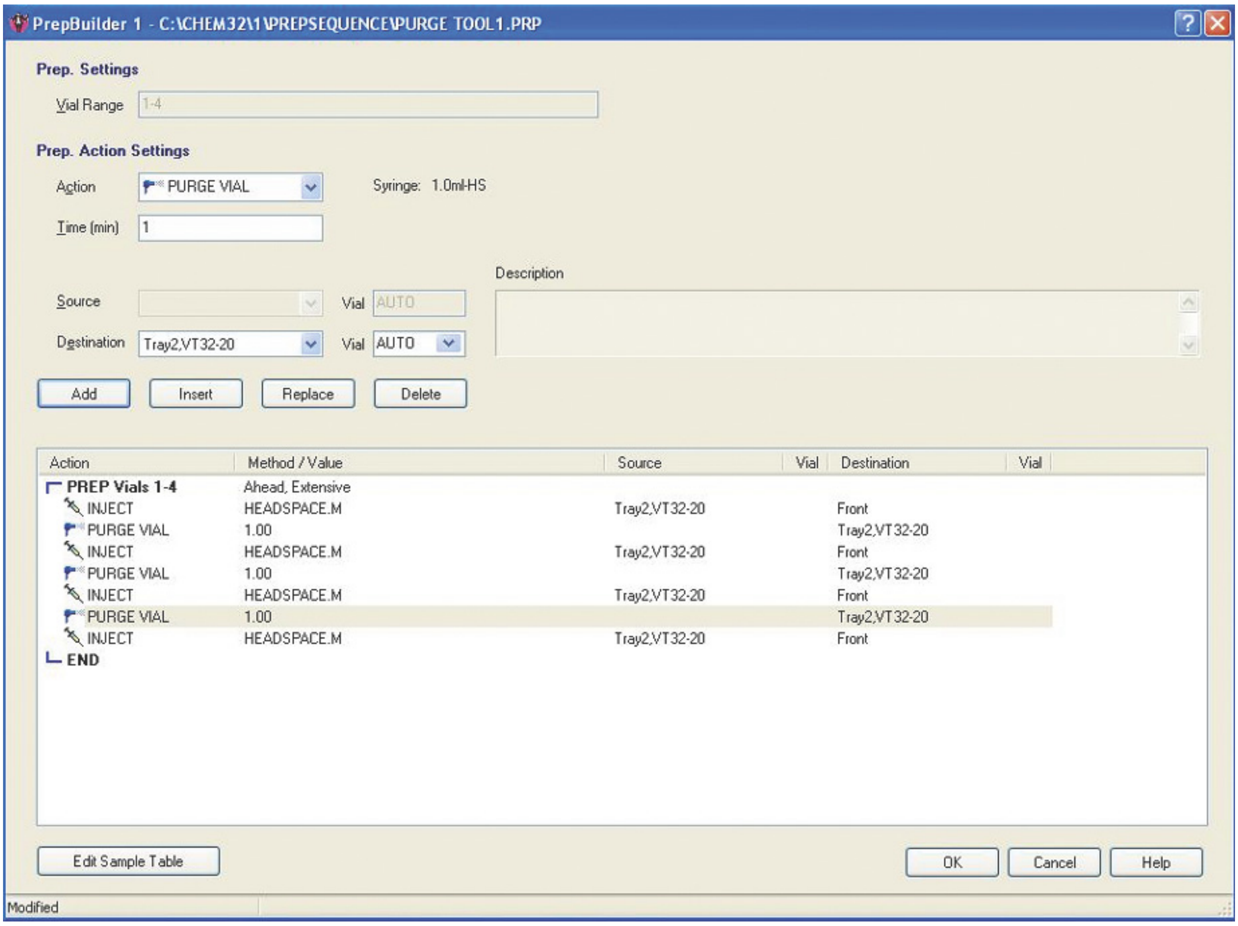


**Figure 3.** MAESTRO control software, the purge vial function is activated in the PrepSequence.

The first example shows the quantitation of residual toluene in duct tape. A toluene standard was prepared in methanol resulting in a concentration of 1355 µg/mL. The standard was pipetted into separate headspace vials (0, 1, 3, 5, and 8 µL) to prepare a calibration curve. The vials were extracted three times each using the conditions outlined above. The ln Peak Area was plotted versus n-1 for each standard. The linear regression data was used to calculate the total area for each standard. Table 1 shows the regression data for the standards. The total area was found using equation 1. Figure 4 shows the resulting calibration curve. The calibration curve shows excellent linearity.

**Table 1.** Regression data for toluene standards.

| Std Amount [µg] | $r^2$ | m | b | Total Area |
|---|---|---|---|---|
| 0 | -- | -- | -- | 0 |
| 1.36 | 0.9881 | -0.974 | 13.2 | 892859 |
| 4.07 | 0.9997 | -1.31 | 14.5 | 2578443 |
| 6.78 | 0.9994 | -1.25 | 14.9 | 3947447 |
| 10.8 | 0.9996 | -1.12 | 15.3 | 6883849 |

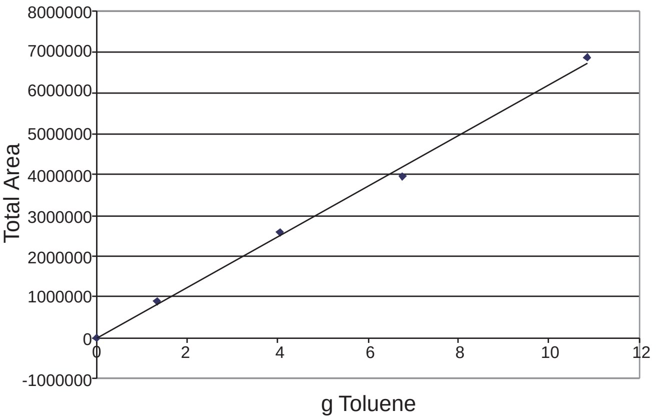

**Figure 4.** Calibration curve for toluene.

Three samples of the duct tape were run under the same extraction conditions as the standards. Figure 5 shows a plot of ln Area versus n-1 for a sample and standard. Table 2 shows the regression data and calculations for the samples. The average level of toluene in the tape was found to be 30.1 ppm with a % RSD of 3.55 for n=3 samples.

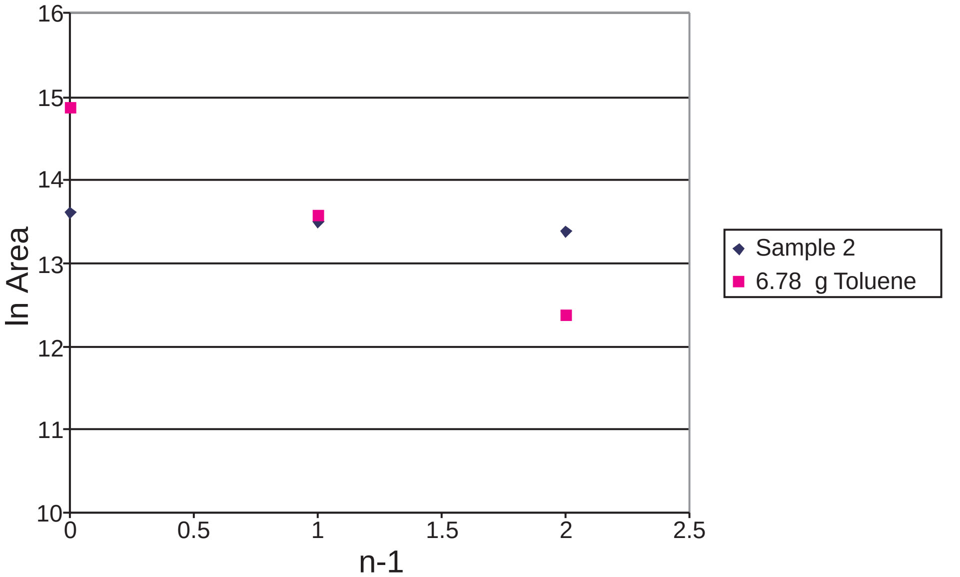

**Figure 5.** MHE curves for toluene in sample and standard.

**Table 2.** Regression data and analysis results for duct tape samples.

| Sample No. | Sample Weight | m | b | $r^2$ | Total Amount | Toluene [µg] | Toluene [ppm] |
|---|---|---|---|---|---|---|---|
| 1 | 0.3940 | -0.0971 | 13.4 | 0.9996 | 7371790 | 11.8 | 30.1 |
| 2 | 0.3933 | -0.1127 | 13.6 | 0.9991 | 7639530 | 12.3 | 31.2 |
| 3 | 0.3878 | -0.0988 | 13.4 | 0.9974 | 7015629 | 11.3 | 29.1 |
| | | | | | | Average | 30.1 |
| | | | | | | % RSD | 3.55 |

The second example shows the analysis of α-pinene, a flavor ingredient, in toothpaste. Figure 6 shows a typical chromatogram obtained from the static headspace analysis of toothpaste. This chromatogram represents the first extraction of a sample. The α-pinene elutes at retention time 4.317 minutes. Table 3 shows the regression data and total area calculated for the standards. The resulting calibration curve is shown in Figure 7. The standard curve shows excellent linearity with a correlation coefficient of 0.9991.

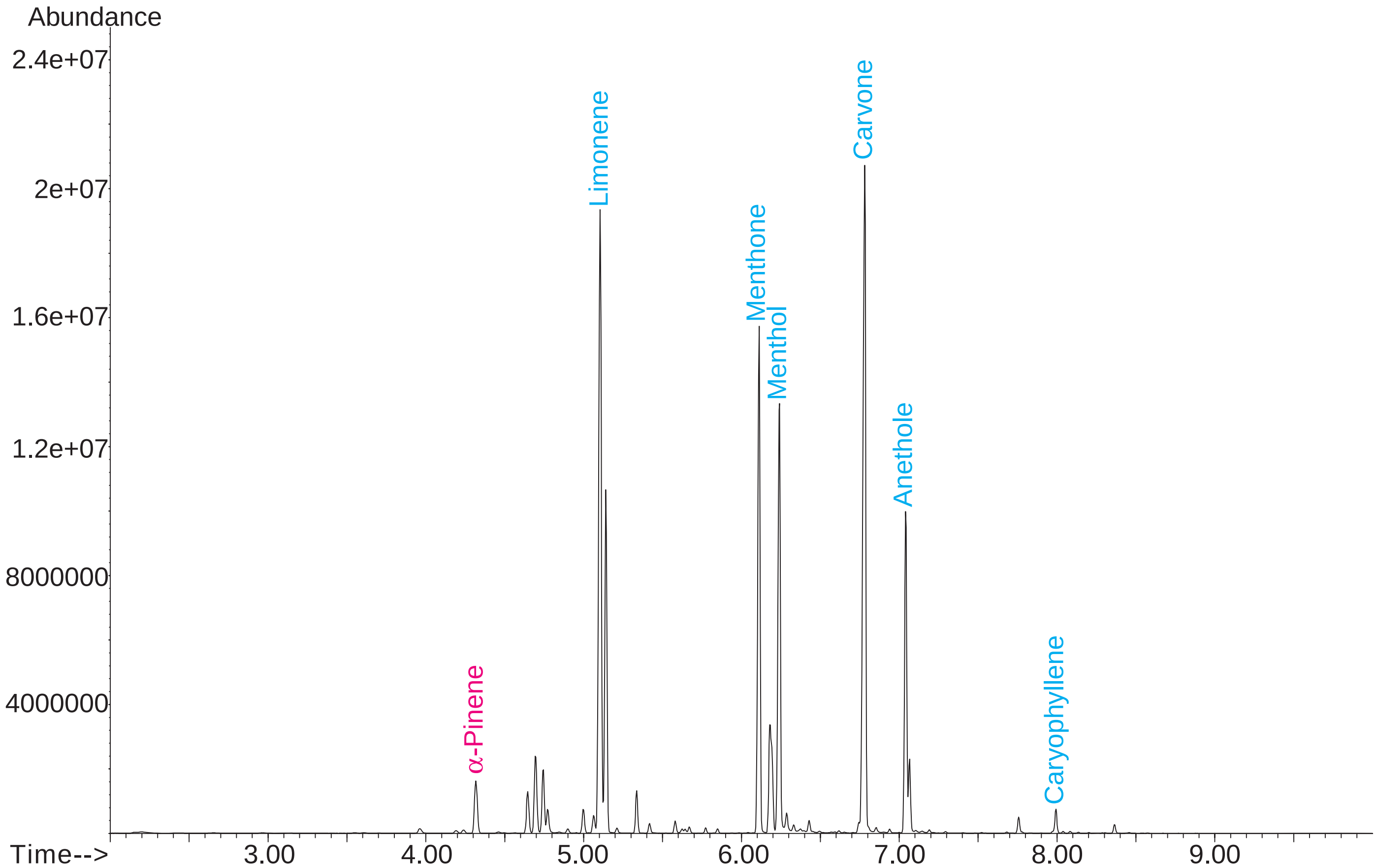


**Figure 6.** Chromatogram for static headspace extraction of toothpaste sample.

**Table 3.** Regression data for α-pinene standards.

| Std Amount [µg] | r2 | m | b | Total Area |
|---|---|---|---|---|
| 0 | -- | -- | -- | 0 |
| 0.7 | 0.9952 | -2.52 | 12.7 | 363626 |
| 2.1 | 0.9979 | -2.17 | 13.9 | 1232683 |
| 3.5 | 0.9700 | -1.48 | 14.2 | 1889237 |
| 7.0 | 0.9926 | -2.17 | 15.1 | 3932561 |

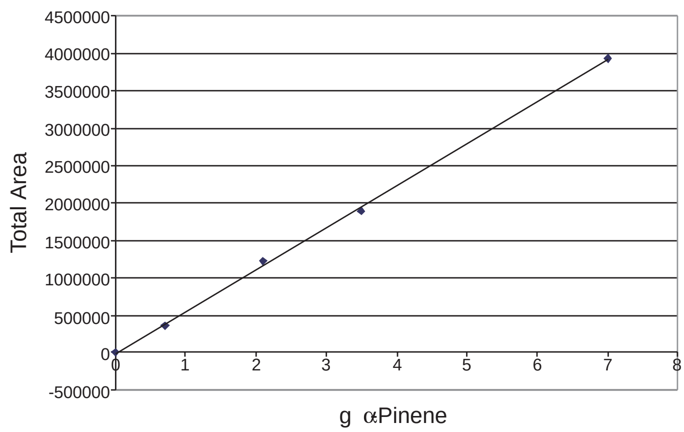


**Figure 7.** Calibration curve for α-pinene.

Three samples of the toothpaste were run under the same extraction conditions as the standards. Table 4 shows the regression data and calculations for the samples. The average level of $\alpha$-Pinene in the toothpaste was found to be 5.05 ppm with a % RSD of 8.91 for n=3 samples

**Table 4.** Regression data and analysis results for toothpaste samples.

| Sample No. | Sample Weight | m | b | $r^2$ | Total Amount | Toluene [µg] | Toluene [ppm] |
|---|---|---|---|---|---|---|---|
| 1 | 0.2373 | -1.33 | 13.2 | 0.9781 | 711940 | 1.28 | 5.41 |
| 2 | 0.234 | -1.53 | 13.0 | 0.9521 | 588731 | 1.06 | 4.55 |
| 3 | 0.2434 | -1.64 | 13.2 | 0.9865 | 701590 | 1.27 | 5.20 |
| | | | | | | Average | 5.05 |
| | | | | | | % RSD | 8.91 |

A comparison was made with and without venting between injections for toothpaste samples. Figure 8 shows a comparison of the exponential decay for toothpaste samples with and without venting. The sample without venting is mainly flat while the vented sample shows a nice linear decay. This demonstrates the necessity for venting and the ability to accomplish this with the purge tool.

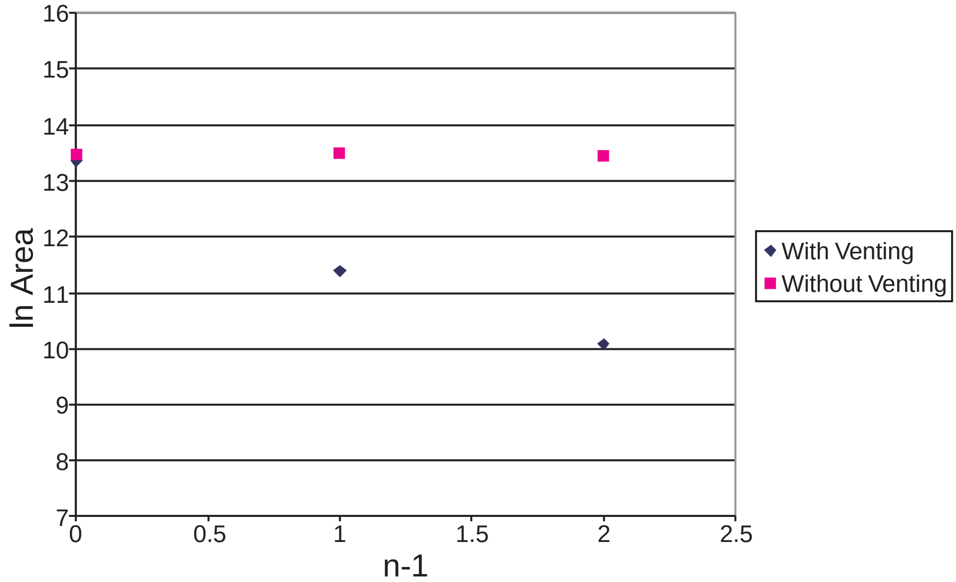


**Figure 8.** MHE curves for $\alpha$-pinene in toothpaste with and without venting.

## Conclusions

The purge tool, GERSTEL Purge holder, and MAESTRO software control enable the MPS 2 sampler to effectively perform multiple headspace extraction experiments by venting the headspace of a vial between injections. MHE is very useful for quantification of volatile analytes in difficult matrices.

## References


[1] Bruno Kolb and Leslie Ettre, „Static Headspace-Gas Chromatography: Theory and Practice“, Wiley-VCH, New York, 1997, pp. 40-43

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