Residual Monomers in Polymers by Multiple Headspace Extraction using the Agilent 7697A Headspace Sampler

Application Note

Petrochemicals

Abstract

Residual monomers are determined in a series of polymers including poly methyl methacrylate, poly acrylic, styrene co-methyl methacrylate, and styrene co-butadiene. Minimal sample preparation is required by using the well established technique of Multiple Headspace Extraction (MHE). The instrumental configuration consists of the Agilent 7697A Headspace Sampler interfaced to an Agilent 7890 Series GC with split/splitless inlet. An Agilent 5975C MSD was used for detection and confirmation.

Introduction

Residual monomer determination in polymers is an essential measurement in polymer production and quality control. From a sample preparation point of view, headspace is the method of choice. Sample dissolution is not required. Simply weigh the sample and place it in a 10 or 20 mL vial. In MHE a series of multiple extractions, each with decreasing analyte concentration, is used to determine the amount of analyte present in a complex matrix where calibration standards in that given matrix is not feasible. An external standard of the analyte is prepared for comparison to the real sample and for determination of a response factor. Cryo milling may be advantageous to produce a small homogeneous particle size. Cryo milling was not used in this work, and, as a result, longer headspace equilibration times were employed. Multiple Headspace Extraction has been used for the determination of leachable compounds in packaging materials in previously reported work [1].

Agilent Technologies
Experimental

The system configuration is shown in Figure 1. The headspace sampler is interfaced through the inlet septum using 0.45 mm ID deactivated fused silica. Headspace sampling vial pressure is controlled by a PCM module on-board the 7697A. Helium carrier is controlled by a 7890 s/s inlet EPC interfaced to the headspace sampler. The column used was a HP-FFAP, 30 m × 0.25 mm, 0.25 µm, part number 19091F-433.

In Tables 1 and 2, headspace sampling and GC/MSD parameters, respectively are shown. Typically, 0.02 to 0.09 grams of polymer was placed in 10-mL vials for analysis. PTFE lined septa with aluminum caps were used to seal the vials. Before sealing, the vials were purged with nitrogen. Pure monomers were purchased from Sigma-Aldrich. These were analyzed by full evaporation in 10-mL headspace vials as external standards. Typically, 0.1 µL of the pure monomer was injected directly into a sealed headspace vial. A regression analysis of the pure monomers using MHE is required as part of the calculations used to determine residual monomer amounts in the polymers or resins.

![Figure 1. System diagram for MHE experiments.](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Poly acrylic</th>
<th>Poly methyl methacrylate</th>
<th>Styrene co-butadiene</th>
<th>Styrene co-methyl methacrylate</th>
</tr>
</thead>
<tbody>
<tr>
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<td>200</td>
<td>75</td>
<td>120</td>
<td>120</td>
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<tr>
<td>Loop temp., °C</td>
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<td>130</td>
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<td>60</td>
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<tr>
<td>Vial size, mL</td>
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<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Vial shaking</td>
<td>Level 1</td>
<td>Level 1</td>
<td>Level 1</td>
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<tr>
<td>Fill mode</td>
<td>To pressure</td>
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</tr>
<tr>
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<tr>
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<td>0.1 min</td>
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<td>20 psi/min</td>
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<td>0.05 min</td>
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<td>MHE</td>
<td>MHE</td>
<td>MHE</td>
</tr>
<tr>
<td>Post Injection purge</td>
<td>100 mL/min, 5 min.</td>
<td>100 mL/min, 5 min.</td>
<td>100 mL/min, 5 min.</td>
<td>100 mL/min, 5 min.</td>
</tr>
<tr>
<td>Vent after last extract.</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Poly acrylic</th>
<th>Poly methyl methacrylate</th>
<th>Styrene co-butadiene</th>
<th>Styrene co-methyl methacrylate</th>
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</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>Split/splitless</td>
<td>Split/splitless</td>
<td>Split/splitless</td>
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<tr>
<td>HS interface</td>
<td>Fused silica through septum</td>
<td>Fused silica through septum</td>
<td>Fused silica through septum</td>
<td>Fused silica through septum</td>
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<td>Ultra Inert, single taper</td>
<td>Ultra Inert, single taper</td>
<td>Ultra Inert, single taper</td>
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<td>135 °C</td>
<td>135 °C</td>
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<td>100 to 1</td>
<td>100 to 1</td>
<td>100 to 1</td>
<td>100 to 1</td>
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<tr>
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<td>1 mL</td>
<td>1 mL</td>
<td>1 mL</td>
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<tr>
<td>5975C scan</td>
<td>19–250 amu</td>
<td>19–250 amu</td>
<td>19–250 amu</td>
<td>19–250 amu</td>
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<tr>
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<td>320 °C</td>
<td>320 °C</td>
<td>320 °C</td>
</tr>
<tr>
<td>MS quad</td>
<td>200 °C</td>
<td>200 °C</td>
<td>200 °C</td>
<td>200 °C</td>
</tr>
<tr>
<td>Agilent 7890 column</td>
<td>30 m × 0.25 mm, 0.25 µm HP-FFAP</td>
<td>30 m × 0.25 mm, 0.25 µm HP-FFAP</td>
<td>30 m × 0.25 mm, 0.25 µm HP-FFAP</td>
<td>30 m × 0.25 mm, 0.25 µm HP-FFAP</td>
</tr>
</tbody>
</table>
Discussion

The popularity of static headspace analysis is due in large part to the simple and fast sample preparation that is adequate for most materials. MHE is somewhat more involved compared to standard headspace analysis in that a standard of the analyte that requires quantitative analysis in a given matrix must be analyzed in pure form using a full evaporation technique. MHE should be used when a complex matrix is encountered and a standard in that given matrix cannot be reliably made or purchased. The MHE technique is matrix independent and therefore the standard and analyte are not required to be in the same matrix.

In this work, six extractions each of standard and polymer sample were made. The vial remains in the oven between extractions. Venting of the vial between extractions was not performed; vial venting occurred only after the last extraction. With each extraction, the peak area should show an exponential decrease. Because a cryo mill was not used, particle sizes were larger than ideal. As a result, peak area of the first headspace extraction from the polymeric material was typically low by a few percent from examination of an initial exponential plot of area versus the extraction number. Longer headspace oven sample equilibration times help, to some extent, minimize the effect of a higher than ideal surface area to volume ratio of the particles. When this is seen, a modification of the equation for total peak area (Appendix) can be used as given below.

\[
\text{Total peak area} = A_1 + \frac{A_2}{1 - e^{-k}}
\]

The second part of this equation calculates the total peak area for the second through last extraction (6th in this work). In the semi-logarithmic plots presented in this work, the first extraction point was corrected so that it fell onto the regression line calculated from the 2nd to 6th extractions.

All polymers in this study were equilibrated above their glass transition temperature regions with the exception of poly acrylic acid (\(T_g = 102^\circ\text{C}\)) and poly methyl methacrylate (approximately \(T_g = 105^\circ\text{C}\)).

MHE calculations are made using an Excel spreadsheet. Inputs for the user consists of the following:

1. Areas from each extraction of the pure monomer
2. Areas of each extraction of the identified monomer peak in the polymer sample
3. Amount of the pure monomer in the headspace vial
4. Weight of the polymer sample in the vial

A total of six extractions from each vial were made. In this spreadsheet, the LOGEST array command is used to calculate the regression statistics. This command calculates an exponential curve from the MHE data. A semi-logarithmic plot of area versus the extraction number is made to visually check the results. Regression statistics from the exponential curve fit is shown on the right side of the Excel spreadsheet for both standard and sample (see Tables 4 to 7).

![Figure 2. TIC for the analysis of Styrene cobutadiene.](image-url)
Table 3 maps the four polymers studied in this work to their respective residual monomer calculations and semi log plots of peak area versus the extraction number. The TIC for styrene co-butadiene polymer is shown in Figure 2. 1, 3 Butadiene elutes at approximately 1.15 minutes. Extracted ion confirmation for 1, 3 butadiene is seen in Figure 3. For the sample, only calculations for styrene residual monomer is shown in Table 6.

![Figure 3](image)

**Figure 3.** Extracted ion chromatograms for 1,3 butadiene at a retention time 1.15 minutes.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>MHE calculations</th>
<th>Plot - standard</th>
<th>Plot - residual monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly acrylic</td>
<td>Table 4</td>
<td>Figure 4a</td>
<td>Figure 4b</td>
</tr>
<tr>
<td>Poly methyl methacrylate</td>
<td>Table 5</td>
<td>Figure 5a</td>
<td>Figure 5b</td>
</tr>
<tr>
<td>Styrene co-butadiene</td>
<td>Table 6</td>
<td>Figure 6a</td>
<td>Figure 6b</td>
</tr>
<tr>
<td>Styrene co-methyl methacrylate</td>
<td>Table 7</td>
<td>Figures 7a, 7c</td>
<td>Figures 7b, 7d</td>
</tr>
</tbody>
</table>
Table 4. **MHE Calculations for Poly Acrylic Acid**

<table>
<thead>
<tr>
<th>Extraction no.</th>
<th>Sample poly acrylic</th>
<th>Standard acrylic acid</th>
<th>Standard</th>
<th>Stats</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17900000</td>
<td>73398095</td>
<td>0.505705</td>
<td>1.46E+08</td>
</tr>
<tr>
<td>2</td>
<td>13356229</td>
<td>37321132</td>
<td>0.004488</td>
<td>0.014884</td>
</tr>
<tr>
<td>3</td>
<td>9537816</td>
<td>19097365</td>
<td>0.99987</td>
<td>0.014191</td>
</tr>
<tr>
<td>4</td>
<td>6887156</td>
<td>9701384</td>
<td>23082.55</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>4913843</td>
<td>4761376</td>
<td>4.648531</td>
<td>0.000604</td>
</tr>
<tr>
<td>6</td>
<td>3380211</td>
<td>2400283</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Regression correlation:
- Sample: 0.99987
- Standard: 0.999404

Slope (k) = ln(E2 or E9)
- Sample: -0.324781
- Standard: -0.681801

Total area = (A(1)/(1-e(-k))
- Sample: 64547619
- Standard: 148490529

Analyte in vial (mg)
- Sample: 0.003764
- Standard: 0.00866

Sample amt (mg) in vial
- Sample: 345

Concentration (ppm) in wt/wt
- Sample: 10.91

Concentration (wt-%)=ppm * (10 ^ -4)
- Sample: 0.00109

---

**Figure 4. Regression plots for Acrylic acid standard and residual monomer.**

4a. Acrylic acid

y = 1E+08e^{-0.684x}
R² = 0.9999

4b. Acrylic acid in polymer

y = 3E+07e^{-0.333x}
R² = 0.9888

Acrylic acid in polymer
Table 5.  MHE Calculations for Poly Methyl Methacrylate

<table>
<thead>
<tr>
<th>Extraction no.</th>
<th>Sample (PMMA)</th>
<th>Standard (methyl methacrylate)</th>
<th>Standard</th>
<th>Stats</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12206500</td>
<td>120157970</td>
<td>0.571287</td>
<td>2.11E+08</td>
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<tr>
<td>2</td>
<td>11028812</td>
<td>69114398</td>
<td>0.000996</td>
<td>0.003878</td>
</tr>
<tr>
<td>3</td>
<td>9990828</td>
<td>39474218</td>
<td>0.999987</td>
<td>0.004166</td>
</tr>
<tr>
<td>4</td>
<td>8718874</td>
<td>22364001</td>
<td>316068.5</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>7634967</td>
<td>12808405</td>
<td>5.485311</td>
<td>6.94E-05</td>
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<tr>
<td>6</td>
<td>6642230</td>
<td>7350760</td>
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<td></td>
</tr>
</tbody>
</table>

Regression correlation: 0.994725176
Slope (k): -0.17348098
Total area = (A(1)/(1-e(-k))) = 110242171
Analyte in vial (mg): 0.03650844
Sample amt (mg) in vial: 55

Concentration (ppm) in wt/wt: 670
Concentration (wt-%)=ppm * (10 ^ –4): 0.067

Figure 5. Regression plots for methy methacrylate standard and residual monomer.
Table 6. MHE Calculations for Styrene co-butadiene

<table>
<thead>
<tr>
<th>Extraction no.</th>
<th>Sample (styrene)</th>
<th>Standard (styrene)</th>
<th>Standard</th>
<th>Stats</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2890000</td>
<td>242387425</td>
<td>0.570668</td>
<td>4.19E+08</td>
</tr>
<tr>
<td>2</td>
<td>2660000</td>
<td>135439623</td>
<td>0.005277</td>
<td>0.017501</td>
</tr>
<tr>
<td>3</td>
<td>2443870</td>
<td>76792496</td>
<td>0.999735</td>
<td>0.016687</td>
</tr>
<tr>
<td>4</td>
<td>2236942</td>
<td>43866719</td>
<td>11307.31</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>2062892</td>
<td>25754414</td>
<td>3.148593</td>
<td>0.000835</td>
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<tr>
<td>6</td>
<td>1881711</td>
<td>15293635</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Regression correlation (E4 or E11) 0.998100414
Slope (k) = ln(E2 or E9) –0.088860895
Total area = (A1/(1-e(-k))) 34694797
Analyte in vial (mg) 0.005587439
Sample amt (mg) in vial 92
Concentration (ppm) in wt/wt 60.73
Concentration (wt-%) = ppm * (10 ^ -4) 0.00607

Figure 6. Regression plots for styrene standard and styrene monomer.
Table 7. MHE Calculations for Styrene co-methyl Methacrylate

<table>
<thead>
<tr>
<th>Extraction no.</th>
<th>Methyl methacrylate sample</th>
<th>Styrene sample</th>
<th>Methyl methacrylate STD</th>
<th>Styrene STD</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1809940</td>
<td>1604252</td>
<td>139277886</td>
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<tr>
<td>2</td>
<td>1544357</td>
<td>1341511</td>
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<td>3</td>
<td>1308275</td>
<td>1085316</td>
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<td>4</td>
<td>1120663</td>
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<td>27223930</td>
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</tr>
<tr>
<td>5</td>
<td>953713</td>
<td>778087</td>
<td>15802381</td>
<td>25754414</td>
</tr>
<tr>
<td>6</td>
<td>814080</td>
<td>676849</td>
<td>9227813</td>
<td>15293635</td>
</tr>
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</table>

Regression correlation (E4 or E11): 0.999947538
Slope (k) = ln(E2 or E9): –0.159878316
Total area = (A(1)/(1-e(-k))): 12249808.6
Analyte in vial (mg): 0.003524765
Sample amt (mg) in vial: 17
Concentration (ppm) in wt/wt: 207.34
Concentration (wt-%) = ppm * (10 ^ -4): 0.02073

<table>
<thead>
<tr>
<th>Regression correlation ()</th>
<th>Methyl methacrylate</th>
<th>Methyl methacrylate STD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.999947538</td>
<td>0.99996157</td>
</tr>
<tr>
<td>Slope (k) = ln()</td>
<td>–0.159878316</td>
<td>–0.543355164</td>
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<tr>
<td>Total area = (A(1)/(1-e(-k)))</td>
<td>12249808.6</td>
<td>332243943.1</td>
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<tr>
<td>Analyte in vial (mg)</td>
<td>0.003524765</td>
<td>0.0956</td>
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<tr>
<td>Sample amt (mg) in vial</td>
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<tr>
<td>Concentration (ppm) in wt/wt</td>
<td>207.34</td>
<td></td>
</tr>
<tr>
<td>Concentration (wt-%) = ppm * (10 ^ -4)</td>
<td>0.02073</td>
<td></td>
</tr>
</tbody>
</table>

Styrene

Regression correlation (E4 or E11): 0.995564077
Slope (k) = ln(E2 or E9): –0.174916797
Total area = (A(1)/(1-e(-k))): 9997013.166
Analyte in vial (mg): 0.001592539
Sample amt (mg) in vial: 17
Concentration (ppm) in wt/wt: 93.68
Concentration (wt-%) = ppm * (10 ^ -4): 0.00937

<table>
<thead>
<tr>
<th>Regression correlation ()</th>
<th>Styrene</th>
<th>Styrene STD</th>
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<tbody>
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<tr>
<td>Slope (k) = ln()</td>
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<td>–0.553006115</td>
</tr>
<tr>
<td>Total area = (A(1)/(1-e(-k)))</td>
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<td>570616095.6</td>
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<tr>
<td>Analyte in vial (mg)</td>
<td>0.001592539</td>
<td>0.0909</td>
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<tr>
<td>Sample amt (mg) in vial</td>
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<td></td>
</tr>
<tr>
<td>Concentration (wt-%) = ppm * (10 ^ -4)</td>
<td>0.00937</td>
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Figure 7a and 7b. Regression plots for Methyl methacrylate standard and residual monomer.

Figure 7c and 7d. Regression plots for Styrene standard and residual monomer.
Conclusions

MHE is a relatively easy technique for the determination of residual monomer content. Reducing the levels of residual monomer is highly desirable among polymer producers. Pricing, commercial value, and material properties are affected by the level of monomers in the final product. Safety concerns are also relevant as long-term exposure in the manufacturing environment may need to be considered. The system described here should assist in the study of monomer reducing techniques to quickly check their effectiveness.

Appendix

In classical MHE, the sample is equilibrated at a given temperature for a specified time in the headspace oven prior to sampling. The cycle time should be equal to or shorter than the vial equilibration time so that each extraction experiences the same heating time. An exponential decrease in peak area should be observed. An infinite number of extractions to remove all of a given analyte from the matrix will yield the total amount of analyte present as shown in equation (1)

\[ \text{Total peak area} = \sum_{n=1}^\infty A_n = A_1 + A_2 + A_3 + \ldots + A_n \]  

Because a large number of extractions are impractical, first order kinetics is assumed and it follows that:

\[ -dc/dt = kc, \]  

which integrated becomes \( c = c_0 e^{-kt} \) \( (3) \)

If the gas extraction is carried out carefully and for equal times, and equal portions of the headspace are introduced into the GC, then the peak area of a given analyte will follow the same exponential rule since at equilibrium the distribution coefficient \( K_d \) is a constant, \( K_d = c_c/c_g \), where \( c_c \) and \( c_g \) are the concentrations of the analyte in the condensed and gas phase, respectively. For a discontinuous or stepwise gas extraction performed at equal time intervals, equation 3 becomes:

\[ A_n = A_1 e^{(1-n)k} \]  

\( A_n \) = peak area of nth injection,  

\( A_1 \) = peak area of 1st injection

For an infinitely large number of extractions, the total peak area for an analyte becomes

\[ \sum_{n=1}^{\infty} A_n = A_1/(1 - e^{-k}) \]  

This decreasing geometric progression in equation 5 converges to

\[ \sum_{n=1}^{\infty} A_n = A_1/(1 - e^{-k}) \]  

Therefore a complete gas extraction is not necessary to obtain the total peak area; only values for \( A_1 \) and \( K \) are needed. The \( A_1 \) value is the measured peak area of the analyte after the 1st extraction and \( K \) is the slope obtained from a regression analysis (equation 4).

\[ \ln A_n = \ln A_1 + (1 - n)K \]  

Once the total area of the analyte in the matrix sample is known, it follows that:

Calculations, \( T_{area} = \) total area, and \( Am = \) amount

\[ T_{area, analyte}/Am_{analyte} = T_{area, standard}/Am_{standard} \]

or

\[ Am_{analyte} = T_{Area, analyte}/T_{Area, standard} * Am_{standard} \]
Reference


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