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1	Supplementary Information
2	Jet-Mixing for the Production of Monodisperse Silver Nanoparticles Using Reduced
3	Amounts of Capping Agent
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10 S1. Silver nanoparticle (Ag NP) synthesis procedure

11 S1.1. Preparation of standard reactant solutions

12 S1.1.1. Preparation of 0.2 mM AgNO₃ + 0.2 mM TSC solution

A stock solution of 0.034 g silver nitrate (AgNO₃) in 20 g distilled water is prepared, wrapped in aluminum foil to prevent Ag⁺ photoreduction, and stored at room temperature. The solution is used up to a maximum of 6 days after preparation. Separately, a stock of 0.02 g trisodium citrate (TSC) in 5 g distilled water is prepared and stored in a refrigerator at $4 - 6^{\circ}$ C, to prevent TSC degradation. For a standard synthesis, 1 mL of the AgNO₃ stock is mixed with 735 µL of TSC stock and diluted using 48 mL of distilled water. The solution is thoroughly mixed to eliminate any concentration gradients in the solution.

20 S1.1.2. Preparation of 0.6 mM NaBH₄ solution

Distilled water (50 mL) is chilled in an ice bath for ~1 minute. The 12 wt.% sodium borohydride (NaBH₄) in NaOH solution ($6.9 \,\mu$ L) is added to the water and the mixture is thoroughly mixed. It is left in the ice-bath for 20 minutes before being used for Ag NP synthesis.

24 **S1.2. Standard batch synthesis of Ag NPs**

The 250 mL round bottom flask used for synthesis is wrapped in aluminum foil up to the neck. Artificial lighting is turned off to reduce chances of photoreduction by stray light. A 7/8"coated hexagonal stir bar is rotated in the flask at 200 RPM in a circular fashion. The impeller Reynolds' number for this geometry and RPM is calculated as:

$$N_{Re} = \frac{ND^2\rho}{\mu} \approx 278$$

30 Where N = rotational speed of the stir-bar (20.9 s⁻¹), D = diameter of stir-bar = 7/8", ρ = density of 31 water at 25°C = 1000 kg/m³, μ = viscosity of water at 25°C = 8.9 * 10⁻⁴ Pa.s.

The prepared NaBH₄ solution is poured into the flask. The AgNO₃ + TSC solution is poured into the round-bottom flask directly from the beaker in which it is prepared in a single motion within 1-2 seconds, while the NaBH₄ solution is being continuously stirred. The stirring is continued for ~2 minutes. The solution is plugged with a rubber septum and immediately stored in the refrigerator in the dark. All batch syntheses are consistently performed by a single operator to minimize variability.

38 **S1.3. Standard jet-mixing synthesis of Ag NPs**

The two reactant solutions are prepared in the same way as described in 1.1. They are 39 immediately filled into 60 mL BD Leur-Lok[™] syringes (cleaned before use with distilled water). 40 Any residual air bubbles are removed from the syringes to prevent two-phase flow in the system. 41 Two 22 gauge stainless steel needles are rinsed from the inside and outside with DI water and 42 43 connected to the syringes. The syringes are fixed to two separate KD Scientific KDS 100 Legacy single-syringe infusion pumps. After identifying the optimum flowrate that results in monodisperse 44 Ag NP formation (details in Section 2), the flow rate on each syringe pump is set to 48 mL/h (Q_i = 45 46 Q_r = 48 mL/h). The syringe type is selected as 'BD 60 mL'. The volume is set to 50 mL to ensure 47 delivery of the entire reactant solution. The jet-mixing assembly consists of an in-house manufactured PEEK reactor¹ with a 0.04" ID main line and two 0.02" ID jet lines. The fluidic lines 48 consist of PTFE tubing with 0.03" ID and connected using hand-tight HPLC PEEK fittings sourced 49 50 from IDEX. The entire assembly is rinsed with 5-10 mL of distilled water before the run to prevent 51 any contamination.

The Ag NP solution is collected in an aluminum foil-covered beaker in an ice bath downstream of the reactor. Artificial lighting is turned off around the synthesis assembly to avoid stray light and prevent the photolytic reduction of AgNO₃ from affecting the synthesis. The initial 2-3 mL of solution is not collected to prevent variations from unsteady state flow and to eliminate any remaining air bubbles. After collection is complete, the solution is immediately placed in the refrigerator and is analyzed after 15 minutes.

58 S2. Determining optimal flowrates for jet-mixing synthesis

In the jet-mixing reactor, the flow rate of either the jet line (Q_i) or main line (Q_i) can be 59 varied to vary the mixing intensity. The effect of varying both the main and jet line flowrates is 60 investigated, while maintaining $Q_i = Q_r$. Standard concentrations of all reagents are used. The 61 flowrate of each line is varied between 2 mL/h to 100 mL/h. The concentration of each species at 62 the point of mixing is the same for each run as the main line and jet line flowrates are equal. 63 64 However, there is increase in mixing intensity for both the jet and main lines. The outlet Ag NP 65 product is analyzed via UV-vis 15 minutes after collection and the full width at half maximum (FWHM) is noted to understand the effect on Ag NP particle size distribution (PSD). The FWHM 66 as a function of jet line/main line flow rate has been shown in Figure S1 with the calculations for 67 68 finding FWHM given in Section 3.1. It is observed that the FWHM decreases sharply from 2 mL/h 69 to 48 mL/h, and stabilizes above 48 mL/h. Hence, a flow rate of 48 mL/h has been chosen for 70 further experiments.

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Figure S1. Plot of FWHM obtained from UV-vis spectra of Ag NPs synthesized via jet-mixing as

a function of the reactant flow rate. Each reactant flowrate is varied between 2 mL/h to 100 mL/h, while maintaining $Q_r = Q_j$. Other synthesis conditions are as follows: [NaBH₄] = 0.6 mM, [AgNO₃]

76 = 0.2 mM, [TSC] = 0.2 mM.

77 S3. Ag NP characterization

78 S3.1. Calculation of FWHM from UV-vis spectra

The UV-vis spectrum between wavelength of absorption 350 – 500 nm (the area corresponding to the SPR peak) is fit by a Gaussian curve using IGOR Pro 8. The width of the fitted peak is used to calculate the FWHM.

82
$$FWHM(nm) = 2 * \sqrt{\ln(2)} * Width of peak(nm)$$

83 S3.2. Calculation of PSD from TEM images

For PSD analysis, four different regions of the TEM grid are considered. ImageJ analysis software is used for particle size analysis.² The image is first calibrated using the scale bar on the image using the 'Set scale' function. The 'Measure' function is then used to record the diameter of around 300 randomly selected particles. Only particles with clear and distinct boundaries are selected for PSD analysis.

89 **S3.3. Calculation of standard deviation**

The % standard deviation for a given property (e.g. absorbance, FWHM, etc.) has been calculated by the following formula:

92 % standard deviation =
$$\frac{sample \ standard \ deviation}{mean} * 100$$

93 The sample standard deviation has been calculated for n observations as:

94 Sample standard deviation =
$$\sqrt{\frac{\sum_{i=1}^{n} (x_i - x)^2}{n-1}}$$

95 Where x_i is the *i*th observation and *x* the mean of all observations.

96 S4. Ag NP yield calculation

97 Using the Beer-Lambert law to find particle concentration is a common technique to 98 calculate the yield of nanomaterials exhibiting surface plasmon resonance.³ The yield for Ag NPs 99 synthesized in batch and via jet-mixing is calculated from the maximum absorbance of their UV-100 vis spectra on the basis of molar absorption coefficients (ϵ) obtained from previous literature.⁴ 101 Depending on the volume-weighted average size of the Ag NP samples, the process used for 102 calculation of ϵ is outlined below.

103 S4.1. Batch synthesis

104 For batch-synthesized Ag NPs, the volume-weighted average size is calculated to be 105 10.4 nm. Paramelle et. al. have found ε for citrate-capped Ag NPs in the range of 8 nm to 100 106 nm. The experimentally-determined ε increases non-linearly with the particle diameter. However, 107 for the range of 10 nm to 18 nm particles, ε can be assumed to increase linearly with diameter, 108 as Figure 5 in the reference shows.⁴ A linear fit of the ε in this range gives an R² value of 0.985, 109 supporting this assumption. The ε for the average size of particles in batch is then calculated from 100 the fitted line.

111 $\varepsilon_{batch \ standard} = 5.462 \ * \ 10^8 \ M^{-1} \ cm^{-1}$

112 From the average particle size, the average number of Ag⁰ atoms per particle can be 113 calculated:

- 114 Size of 1 NP (d_p) = 10.37 nm
- 115 Volume of 1 NP = $\pi d_p^3/6$ = 5.839 * 10⁻²⁵ m³
- 116 Density of silver = 10500 kg/m^3
- 117 Mass of 1 NP = Volume * density = 6.13×10^{-21} kg
- 118 Molar mass of Ag = 107.87 g/mol
- 119 Number of Ag⁰ atoms per NP (N_{batch}) = Mass of 1 NP * N_A * 1000 / Molar mass of Ag \approx 34226

120 The absorbance ($A_{batch standard}$) for the Ag NP sample is measured. A plot for the absorbance 121 at various dilutions of the Ag NP sample is constructed to ensure that $A_{batch standard}$ is in the linear 122 range. The absorbance ($A_{batch standard}$) for the Ag NP sample is measured. A plot for the absorbance 123 at various dilutions of the Ag NP sample is constructed to ensure that $A_{batch standard}$ is in the linear 124 range. All dilutions prepared are with respect to the original as-synthesized Ag NP standard batch 125 sample. This plot is shown in Figure S2.



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Figure S2. Plot of absorbance measured by UV-Vis against the concentration of several dilutions of a standard Ag NP batch synthesis. All dilutions prepared are with respect to the as-synthesized sample that has a relative concentration of 1.

From the high R² value of the plot, the absorbance at the as-synthesized Ag NP concentration
falls in the linear concentration range and is used.

For a path length (*L*) of 1 cm, the Beer-Lambert law is used to calculate particle concentration (C_{NP}) and further the Ag⁰ concentration (C_{Ag}^{0}) in the sample.

$$A = \epsilon * C_{NP} * L$$

135 $C_{NP} = 2.6 * 10^{-9} \text{ M}$

136 $C_{Ag}^{0} = C_{NP} * N_{batch} = 8.9 * 10^{-5} \text{ M}$

From the initial concentration of $AgNO_3$ after mixing the standard reactant solutions ($C_{initial}$), the conversion is calculated.

 $C_{initial} = 0.1 \text{ mM}$ 139

% Conversion = $(C_{Ag}^{0} / C_{initial}) * 100 = 88.9\%$ 140

141 S4.2. Jet-mixing synthesis

For jet-mixing synthesized Ag NPs, the volume-weighted average particle size is 142 calculated to be 6.2 nm. An external source is used to calculate the ε at this size.⁵ From the 143 absorbance and concentration specifications of commercial citrate-capped 5 nm Ag NP particles,⁵ 144 the ε is calculated from the Beer-Lambert law to be, 145

146
$$\epsilon_{5nm} = 5.39 * 10^7 \ M^{-1} cm^{-1}$$

From the ε found by Paramelle et. al. for 8 nm particles ($\epsilon_{8nm} = 1.84 * 10^8 M^{-1} cm^{-1}$), a line was 147 fit between $\varepsilon_{5 nm}$ and $\varepsilon_{8 nm}$ to find the ε for 6.2 nm Ag NPs, resulting in, 148

149
$$\epsilon_{6.2 nm} = 1.004 * 10^8 M^{-1} cm^{-1}$$

Similar to the batch synthesis yield calculations, the number of Ag⁰ atoms per nanoparticle for 6.2 150

nm Ag NPs (N_{JM}) is calculated to be, 151

The absorbance for the standard Aq NP sample (AJM standard) is measured and several dilutions of 153

154 the as-synthesized sample are prepared to ensure the concentration falls in the linear absorbance

range. A plot for the absorbance at various dilutions of the Ag NP sample is constructed to ensure 155 156 that A_{JM standard} is in the linear range. All dilutions are prepared with respect to the original as-

synthesized Ag NP standard JM sample. This plot is shown in Figure S3. 157



158

Figure S3. Plot of absorbance measured by UV-Vis against the concentration of several dilutions 159 of a standard Ag NP JM synthesis. All dilutions prepared are with respect to the as-synthesized 160

sample that has a relative concentration of 1. 161

The particle concentration is calculated in a manner similar to that for batch synthesized 162 Ag NPs. 163

 $C_{NP} = 1.12 * 10^{-8} \text{ M}$ 164

165
$$C_{Ag}^{0} = C_{NP} * N_{JM} = 8.3 * 10^{-5} \text{ M}$$

From the initial concentration of $AgNO_3$ after mixing the standard reactant solutions ($C_{initial}$), the conversion is calculated.

168 $C_{initial} = 0.1 \text{ mM}$

169 % Conversion = $(C_{Ag}^{0} / C_{initial}) * 100 = 82.7\%$

170 S5. Effect of unequal flowrates in Y-joint on Ag NP synthesis in standard jet-mixing

The Y-joint that separates the fluidic lines going to the two jets in the JM reactor could 171 potentially yield unequal flowrates. To test the effect of an unequal split on the Ag NPs 172 173 synthesized, the Y-joint is removed from the system and the flows for the jet lines are instead provided by two separate syringe pumps, giving a total of three syringe pumps (one for the main 174 line; one for each the jet line). Standard reagent concentrations are used. The main line flowrate 175 is maintained at 48 mL/h (Q₀). The total flowrate from both jet lines (Q₁ = Q_{1-jet1} + Q_{1-jet2}) is 176 177 maintained at 48 mL/h, as in the standard synthesis; however, the ratio of the flowrates in the two jet lines is varied. Three scenarios are tested – (1) Q_{1-jet1} : Q_{1-jet2} = 24:24; (2) Q_{1-jet1} : Q_{1-jet2} = 16:32; 178 179 (3) $Q_{1-jet1}: Q_{1-jet2} = 2:46$.

180 The UV-vis spectra from each run have been shown in Figure S4 and the change in 181 properties (FWHM, absorbance, λ_{max}) from the control (standard synthesis) listed in Table S1.



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Figure S4. UV-vis spectra of Ag NPs obtained at the standard reaction conditions in the JM reactor, and at various ratios of the split jet lines – 24:24, 16:32 and 2:46. Synthesis conditions are as follows: $[NaBH_4] = 0.6 \text{ mM}, [AgNO_3] = 0.2 \text{ mM}, [TSC] = 0.2 \text{ Mm}.$

187 **Table S1.** Comparison of the properties of UV-vis spectra (absorbance, FWHM and λ_{max}) obtained

on varying the ratio of flowrate in the the split jet lines, against the control (standard JM run). The

189 % change for each property in each run is with respect to that obtained for the control.

Q _{1-jet1} :Q _{1-jet2}	% Change in FWHM (nm)	% Change in absorbance	% Change in λ_{max} (nm)
24:24	3.36	5.12	0.26
16:32	1.94	1.49	0.26
2:46	4.71	7.11	0

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191 Comparing the UV-vis spectra of the Ag NP synthesized at various flowrates in the two jet 192 lines, it is observed that there is no significant difference in their properties. This suggests that 193 any potential difference in the flowrates delivered to the two jet inlets of JM reactor does not affect 194 Ag NP synthesis.

195 S6. UV-vis, DLS and TEM data for Ag NP syntheses



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Figures S5. TEM images (a) and (b) of the standard jet-mixing sample used for PSD analysis using ImageJ. Synthesis conditions: main line flow rate = jet line flow rate = 48 mL/h; Reagent

concentrations: $AgNO_3 = 0.2 \text{ mM}$, $NaBH_4 = 0.6 \text{ mM}$, TSC = 0.2 mM.



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Figure S6. PSDs obtained from DLS of standard (a) batch $(13\pm3 \text{ nm})$ and (b) jet-mixing $(7\pm2 \text{ nm})$ syntheses. The PSD is based on the average of three runs.

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Table S2. The PSD of standard Ag NP batch and jet-mixing syntheses calculated based on
DLS data for different runs.

Run no.	Batch synthesis (nm)	Jet-mixing synthesis (nm)
1	13 <u>+</u> 3	7 <u>+</u> 2
2	11 <u>+</u> 3	9 <u>+</u> 2
3	10 <u>+</u> 3	8 <u>+</u> 2

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209

210 Figures S7. TEM images (a), (b) and (c), of the standard batch sample used for PSD analysis

using ImageJ. Synthesis conditions: reagent concentrations – $AgNO_3 = 0.2 \text{ mM}$, $NaBH_4 =$

212 0.6 mM, TSC = 0.2 mM.

Table S3. The variability in the properties of the surface plasmon resonance (i.e. absorbance,
wavelength of maximum absorbance and FWHM) measured by UV-vis in a single standard jet-

216 mixing synthesis, within samples (Sample 1 - 5) taken at 15 minute time intervals, showing a 217 difference in properties of <5%. This data is used to construct Figure 4.

	Absorbance	Wavelength of maximum absorbance (nm)	FWHM (nm)
Sample 1	0.614	392	59.81
Sample 2	0.561	392	55.03
Sample 3	0.608	391	56.68
Sample 4	0.576	392	54.93
Sample 5	0.55	391	54.64
Mean	0.58	391.6	56.22
Std. Dev.	0.02	0.55	2.16
% Std. Dev.	4.86	0.14	3.84

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219

- 220 **Table S4.** The variability in the properties of the surface plasmon resonance (i.e. absorbance,
- wavelength of maximum absorbance, and full width at half maximum (FWHM) measured by UV-

vis for six different batch syntheses, used to construct Figure	5(a	а	I)
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Run no.	Absorbance	Wavelength of max abs (nm)	FWHM (nm)
1	0.71	391.00	58.95
2	0.68	389.00	64.35
3	0.75	384.00	70.00
4	0.76	384.00	70.33
5	0.72	385.00	65.97
6	0.61	388.00	75.50
Mean	0.71	386.83	67.52
Std. Dev.	0.05	2.93	5.72
% Std. dev.	7.45	0.76	8.47

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Table S5. The variability in the properties of the surface plasmon resonance (i.e. absorbance,

wavelength of maximum absorbance, and FWHM) measured by UV-vis for six different jetmixing syntheses, used to construct Figure 5(b).

Run no.	Absorbance	Wavelength of max. abs (nm)	FWHM (nm)
1	0.64	391.00	56.25
2	0.64	391.00	57.05
3	0.59	390.00	61.34
4	0.60	391.00	59.67
5	0.57	391.00	58.86
6	0.61	389.00	55.68
Mean	0.61	390.50	58.14
Std. Dev.	0.03	0.84	2.19
% Std. dev.	4.55	0.21	3.76

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Figure S8. Plot of the FWHM obtained as a function of NaBH₄ concentration for a standard jetmixing synthesis, analyzed via UV-vis. Other synthesis conditions are as follows: $Q_r = Q_i =$

232 48 mL/h; [AgNO₃] = 0.2 mM, [TSC] = 0.2 mM.

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Table S6. The effect of concentration of NaBH₄ on the FWHM of Ag NPs for jet-mixing. All runs
considered to plot Figure S5 have been reported. The mean and standard deviation is

calculated based on at least 2 runs.

NaBH₄ concentration (mM)	Mean FWHM (nm)	Standard deviation FWHM (nm)
0.03	76.16	1.61
0.15	62.23	0.30
0.60	57.32	2.08
2.40	54.81	2.35

237

Table S7. The effect of concentration of TSC on the FWHM of Ag NPs for jet-mixing. All runs

considered to plot Figure 6 have been reported. The mean and standard deviation is calculatedbased on at least 2 runs.

TSC concentration (mM)	Mean FWHM (nm)	Standard deviation FWHM (nm)
0.001	66.71	2.40
0.003	66.99	4.29
0.01	60.15	1.76
0.05	52.17	0.42
0.2	57.30	2.08
0.8	63.50	2.26



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Figure S9. TEM images of (a) batch and (b) jet-mixing syntheses at 0.05 mM TSC. Other synthesis conditions are as follows: $Q_r = Q_j = 48$ mL/h for jet-mixing; [NaBH₄] = 0.6 mM, [AgNO₃] = 0.2 mM for both syntheses.

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Figure S10. FWHMs obtained from UV-vis spectra taken after adding 32 mM NaNO₃ to precursor solutions for Ag NP jet-mixing syntheses while varying the TSC concentration. Other synthesis conditions are as follows: $Q_r = Q_j = 48 \text{ mL/h}$; [NaBH₄] = 0.6 mM, [AgNO₃] = 0.2 mM for both syntheses.



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Figure S11. Solutions of Ag NPs prepared via jet-mixing using different TSC concentrations and with pre-synthetic addition of solid 32 mM NaNO₃ to both reactant solutions. From left to right, the concentrations of TSC are 0.01 mM, 0.05 mM and 0.2 mM. Other synthesis conditions are as follows: $Q_r = Q_i = 48 \text{ mL/h}$; [NaBH₄] = 0.6 mM, [AgNO₃] = 0.2 mM.



Figure S12. UV-vis spectra comparing the Ag NP solution synthesized by standard jet-mixing before and after the post-synthetic addition of solid NaNO₃ of concentration (a) 32 mM (b) 64 mM. The spectra are taken 20 minutes after salt addition. Synthesis conditions are as follows: $Q_r = Q_j$ = 48 mL/h; [NaBH₄] = 0.6 mM, [AgNO₃] = 0.2 mM, [TSC] = 0.2 mM.



Figure S13. TEM images of samples synthesized by standard jet-mixing synthesis with 0.2 mM

TSC, treated with (a) $32 \text{ mM} \text{ NaNO}_3$; (b) $64 \text{ mM} \text{ NaNO}_3$. Other synthesis conditions are as follows:

267 $Q_r = Q_j = 48 \text{ mL/h}; \text{[NaBH_4]} = 0.6 \text{ mM}, \text{[AgNO_3]} = 0.2 \text{ mM}.$



Figure S14. UV-vis spectra of Ag NP batches synthesized with standard reagent concentrations and otherwise standard conditions, with different orders of addition of reagents: standard addition of AgNO₃ and TSC to NaBH₄ (*blue*), and reversed addition of NaBH₄ added to AgNO₃ and TSC (*red*). Other synthesis conditions are as follows: [NaBH₄] = 0.6 mM, [AgNO₃] = 0.2 mM, [TSC] = 0.2 mM.

Table S8. Stability of batch-synthesized Ag NP samples with 0.05 mM TSC over time, as indicated
by their FWHMs obtained from the UV-vis spectra taken at fixed time intervals. All times are
measured post-synthesis.

277	Time of	Mean	Standard
278	sampling	FWHM (nm)	deviation FWHM
270			(nm)
2/5	15 minutes	72.6	0.65
280	1 hour	77.1	4.29
201	2 days	80.0	1.55
201	1 week	81.7	1.88
282	2 weeks	81.8	0.09
283	1 month	86	3.31

Table S9. Stability of JM-synthesized Ag NP samples with 0.05 mM TSC over time, as indicated

by their FWHMs obtained from the UV-vis spectra taken at fixed time intervals. All times are measured post collection of sample.

Time	Mean FWHM (nm)	Standard deviation FWHM (nm)
15 minutes	54.0	0.00
1 hour	60.4	0.07
2 days	64.4	0.08
1 week	65.9	0.04
2 weeks	67.3	0.14
1 month	67.6	0.55

289 Notations

- Q_r = solution flowrate in the main line.
- Q_i = the solution flowrate in the jet line.
- 292 [A] = Molar concentration of species A in solution.

294 References

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