Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts

Automated method for determining the flow of surface functionalized nanoparticles through a mineral formation using plasmonic silver nanoparticles

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Electronic Supplementary Information

Experimental Details

Steady state analysis. A schematic of the steady state experiment setup is shown in Fig 1. A UV-visible Agilent® 4853 spectrometer (Fig. 1b-d) was attached to a UV-Vis workstation (Fig. 1a) with Agilent® ChemStation software in kinetic mode. The spectrometer was equipped with a UV-Vis quartz flow through cell (Fig. 1c) (Hellma, QS 1.000, 1 mm path, 62 μL 35x12x5x12, rectangular aperture 15 mm) that was attached to a conical flask with Teflon stirrer bar, stirrer hot plate, and rubber stopper containing nanoparticle solution analyte (Fig. 1f), via PEEK tubing (Fig. 1g) on the in-flow to the UV cell, the outflow of the cell is attached via PEEK tubing (Fig. 1h) to a Cole Palmer® Variable-Flow peristaltic pump model 73160-20 (Fig. 1e), the out-flow from the peristaltic pump returns to the conical flask via PEEK tubing (Fig. 1i).

The interior surfaces (Fig. 1c, and e-i) were cleaned between measurements sequentially with dilute 5% aqueous HCl solution using ACS grade 37% HCl in DI, a 1 M aqueous solution of sodium thiosulfate in DI and finally by DI only. This sequence was achieved by recycling through the experimental setup using the peristaltic pump (Fig. 1e). The cleaning solutions were flushed from the experimental setup by directing the return flow to waste until the experimental setup is empty of cleaning fluid. Measurements were carried out using both the tungstem and deuterium lamps with the software set to kinetic mode, and experimental values of a) time: 86400, b) trace: 400, c) display spectrum: 190 to 1100, and d) cycle interval: 300, were fixed using the Agilent® UV-Vis ChemStation online program.

The blank matrix is then cycled through the system prior to experimentation. After which a "Time based measurement" is begun by injecting an aliquot of MSA-Ag NPs into the conical flask. The aliquot pH is shown in Table 1.

Kinetic mobility analysis. A schematic of the kinetic mobility experimental setup is shown in Fig. 2. The UV-Vis Agilent® 4853 spectrometer (Fig. 2b-d) was equipped with a PC workstation and operated by Agilent® ChemStation in Kinetic mode (Fig. 2a). A quartz flow-through cell (Hellma, QS 1.000, 1 mm path, 62 μL 35x12x5x12, rectangular aperture 15 mm) (Fig. 2c) was equipped with a PEEK in-flow line (Fig. 2p) and waste line (Fig. 2n) via Teflon PEEK fittings. The waste line (Fig. 2n) led to a waste sampler (Fig. 2j), the waste line can be used to take physical samples if necessary. The UV-visible in-flow line (Fig. 2p) was attached to the out-flow access port (Fig. 2o) of the Combiflash gear pump (Fig. 2f), which in turn was attached to either flow line (Fig. 2l) or a Redisep Teflon column 2 cm in diameter and 6.5 cm in length (Fig. 2i) containing a solid phase and flow line (Fig. 2m), either Fig. 2l or Fig. 2i, (Fig. 2m) were attached to gear pump top access port (Fig. 2r). The gear pump (Fig. 2f) is a Combiflash Companion altered by removing the electronic three-way flow switch and replacing it with a union PEEK 1/8" thus by-passing the waste outlet. The dispenser outlet of the gear pump (Fig. 2f) was also disconnected from the dispenser arm and attached to a PEEK tube (Fig. 2p) and then connected to the UV flow through cell (Fig. 2c). The gear pump (Fig. 2f) was controlled via a laptop workstation with Combiflash Companion software (Fig. 2e). Two in-flow tubes (Fig. 2q) displayed as solvent A and B on the Combiflash gear pump led to either a matrix solution container (Fig. 2g), which is called solvent A in Combiflash software or nanoparticle/matrix solution container (Fig. 2h), called solvent B in Combiflash software. Both containers for solvent A and B were equipped with a Teflon stirrer bar, and stirrer hot plate. Two different injection methodologies were used, either long curve or multi-curve. This analysis steps were setup in the Combiflash Companion software (Fig. 2a). To setup a method, open Companion software, click Method editor, select "Run Units" option as Time. Select Redisep 12 g column, Enter run length as 225 mins for multi-curve and 73 min for long-curve analysis. Enter 10 for flow rate mL/min. Select equilibration volume as 150. Enter 0 for initial waste volume. Enter 0 for % B. Enter Max % B as 100. For Long curve Insert 6 rows, in duration column enter 0, 5, 0, 53, 0, and 15. In Solvent % B enter 0, 0, 100, 100, 0 and 0. For Multicurve Insert 22 rows, in duration column, enter 0, 10, 0, 20, 0, and 20. Repeat the last four digits of this sequence four more times and insert 30 in the last row. In solvent % B insert 0, 0, 100, 100, insert this sequence five times with 0, 0 entered in last two rows. Save both methods.

The experimental setup internal surfaces (Fig. 2c, f-i, and k-p) were cleaned sequentially with dilute 5% aqueous HCl solution using ACS grade 37% HCl in DI, a 1 M aqueous solution of sodium thiosulfate in DI and finally by DI by flushing through the experimental setup from both (Fig. 2g) and (Fig. 2h) using the gear pump (Fig. 2f). The cleaning solutions were flushed from the experimental setup by selecting air purge on the Companion software. To begin a measurement go to the UV-visible workstation open the Agilent® ChemStation online program, turn on tungsten and deuterium lamps, select kinetics mode. Make the kinetic settings as follows: a) Time: 4000 s (for Long curve analysis), 14000 (for Multicurve analysis), b) Trace: 400 enter this in WL1 box this number should be the maximum absorbance recorded for a particular nanoparticle/matrix solution, c) Display Spectrum: 190 to 1100, d) Cycle Interval: 0.5 seconds, e) Start time: 1. Press "Ok". For each experimental analysis either Long curve or Multicurve curves, two measurements must be taken C and C_0. Both require a slightly different experimental setup. C requires solid phase column (Fig. 2i) and the flow line (Fig. 2m) to be attached to the pump/mixer top access port (Fig. 2k) and pump/mixer bottom out-flow access port (Fig. 2o), C_0 requires the flow line (Fig. 2o) to be attached to (11) and (15).

When a measurement is to be taken go to gear pump workstation (Fig. 2a), open program interface Companion. Do not choose the default column option. In the program interface open a directory folder, which will have the Long Curve and Multicurve methodologies saved in the Companion program. Once the method is selected, select no to default column size. Press the play button. Select "Bottles" for "Rack" from the drop down window, click "Start" position 1, press "Ok", the experiment will begin to equilibrate for the amount of time that was entered into the method usually 10 mins. The equilibration solution is the blank matrix taken from (Fig. 2f).

Equilibration forces out all air from the experimental setup. It also allows the background matrix to wash out on soluble particles contained on the solid phase in (Fig. 2i) as well as setup a thermodynamic equilibrium across the solid phase surface for that particular environment. After equilibration is complete on the pump workstation (Fig. 2e) click “Start” when the window appears prompting you to inject samples. After this directly go to UV-visible workstation (Fig. 2a) press “Blank”, Press “Time based measurement” at the bottom of the screen, type in the name to save the spectrum under and press “Start”.

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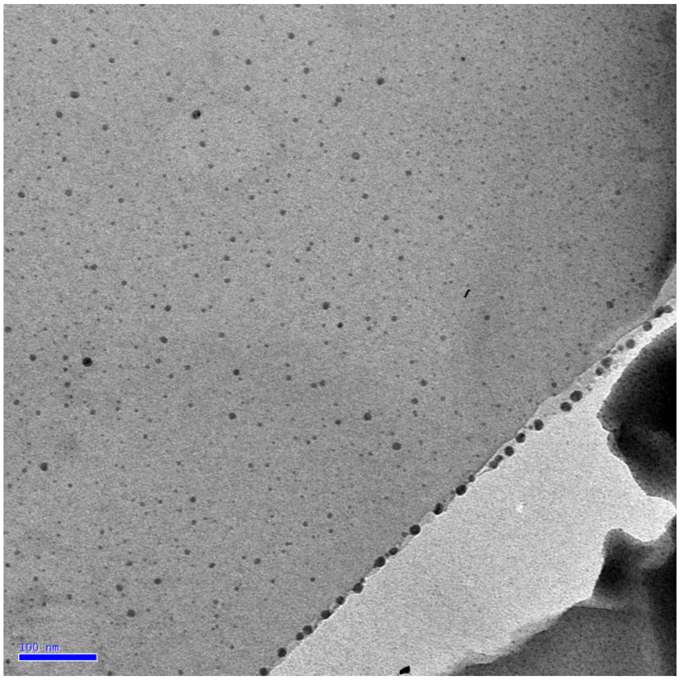

Fig. S1 TEM of cystamine Ag NP pH 2.

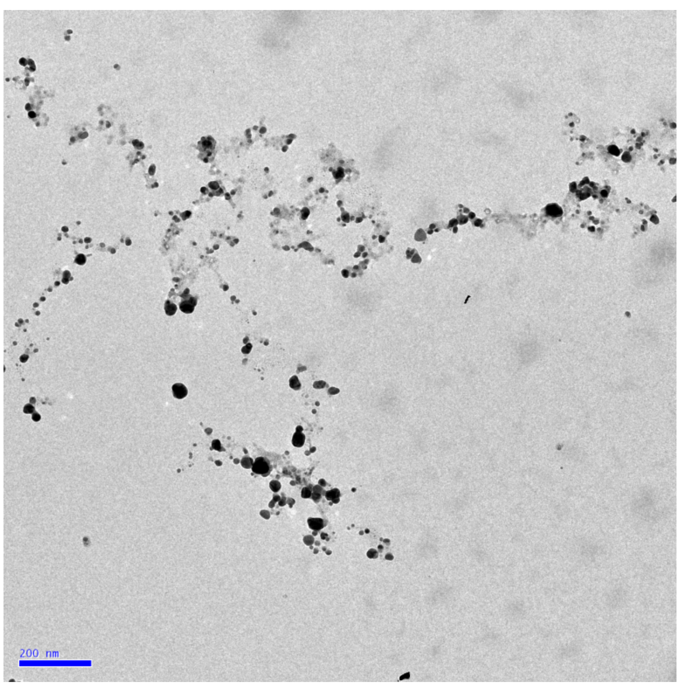

Fig. S2 TEM image of cystamine Ag NP pH 3.

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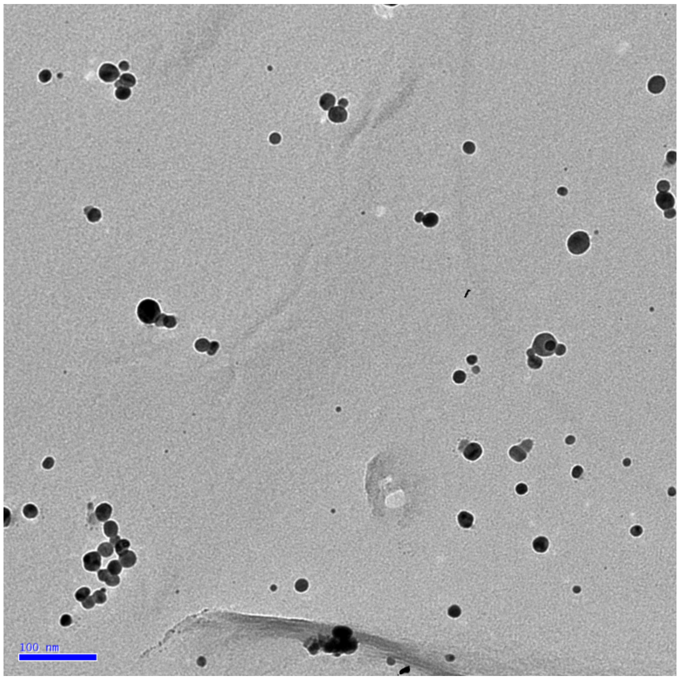

Fig. S4 TEM image of cystamine Ag NP at pH 4.

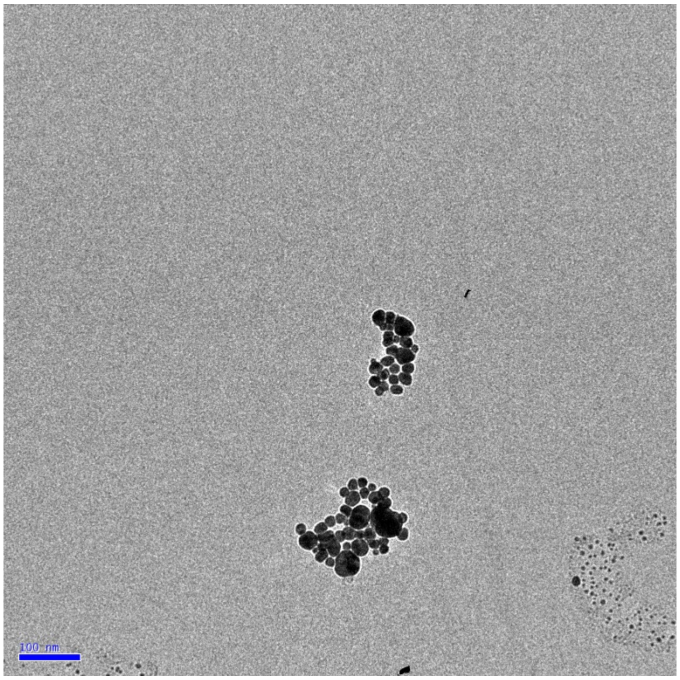

Fig. S5 TEM image of cystamine Ag NP at pH 9.

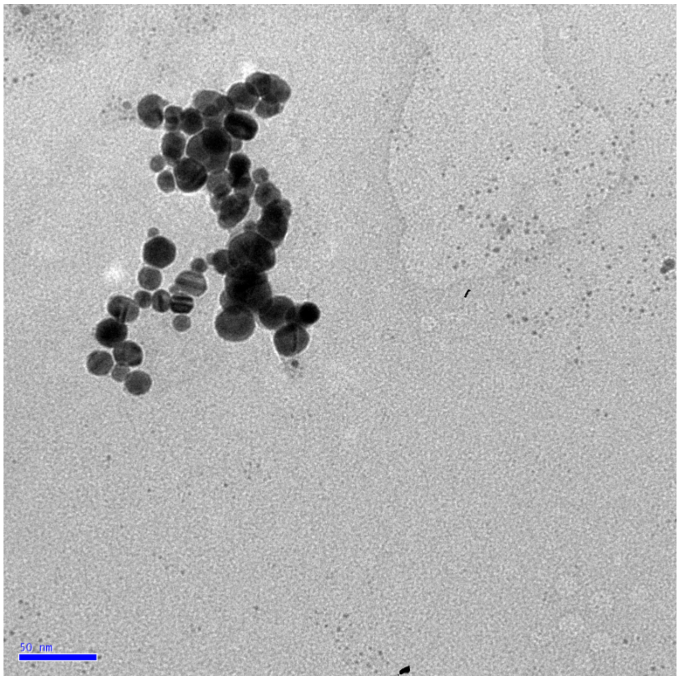

Fig. S6 TEM image of cystamine Ag NP at pH 12.

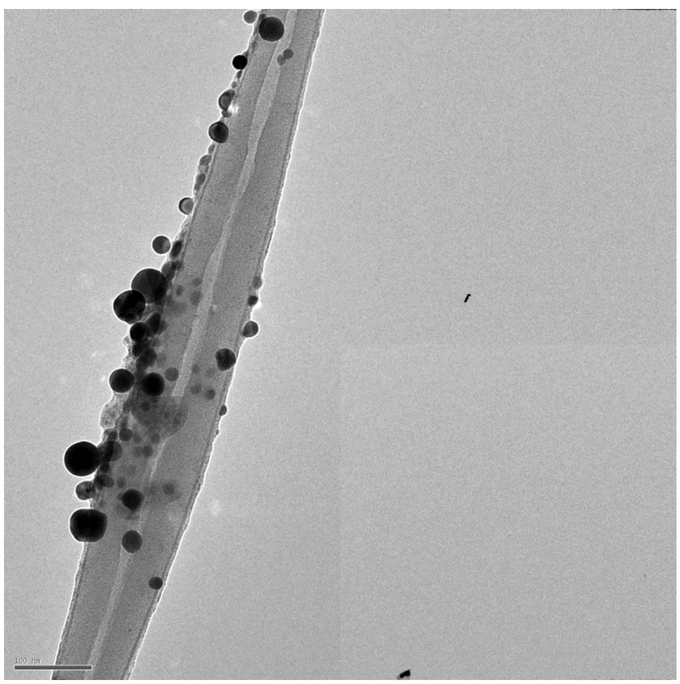

Fig. S7 TEM image of MSA Ag NP at pH 4.

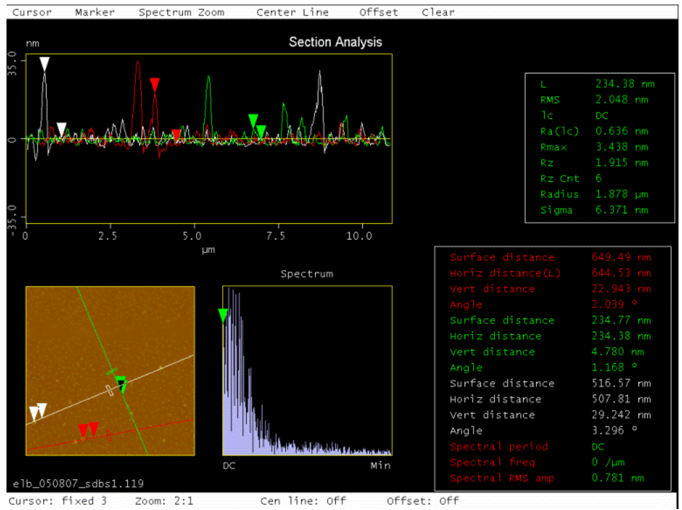

Fig. S8 AFM of MSA-AgNP.

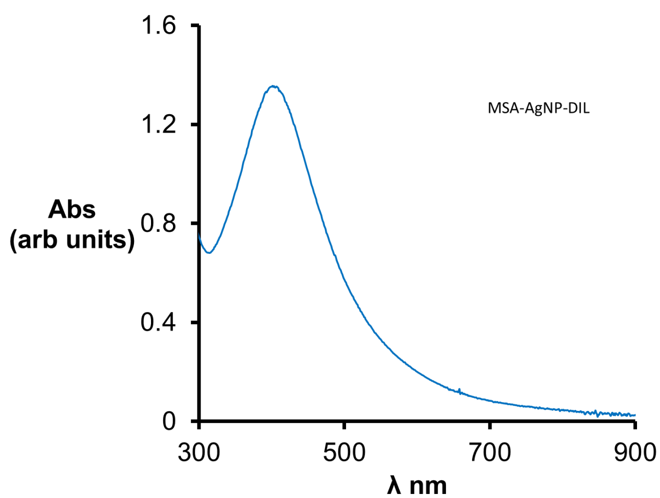

Fig. S9 UV-visible spectrum of MSA-AgNP.

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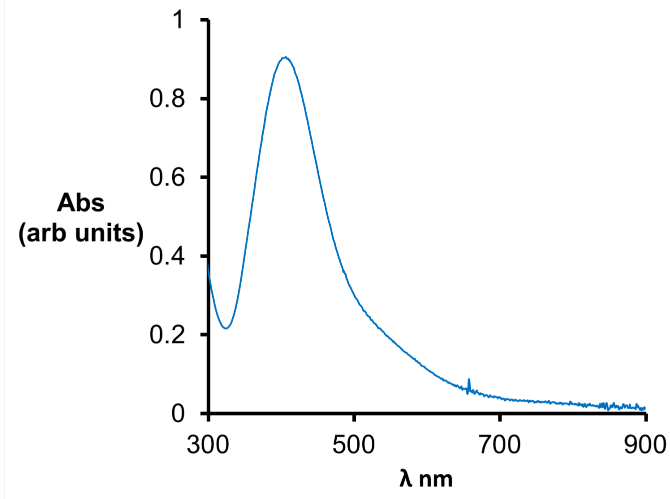

Fig. S10 UV-visible spectrum of CYS-AgNP.

Table S1 R^2 fit of C and C_0 curves for MSA and CYS breakthrough curves.

Coating	C-C_0	pH	Injection	Rank	r^2 Coef Def	DF Adj r^2	Fit Std Err	F-value
MSA	C_0	4	1	2	0.99880888	0.99880696	0.016584072	650502.1196
MSA	C_0	4	2	2	0.99902229	0.99902127	0.015160952	765806.3618
MSA	C_0	4	3	7	0.998292835	0.998288945	0.01790507	320890.6354
MSA	C_0	4	4	5	0.999100081	0.999098534	0.014570405	807678.4409
MSA	C_0	4	5	3	0.998948498	0.998947183	0.01548416	949545.4337
MSA	C	4	1	1	0.998494474	0.998491957	0.018468699	495922.6138
MSA	C	4	2	2	0.998609596	0.998607275	0.017855019	537943.2964
MSA	C	4	3	3	0.998635101	0.998632823	0.017796933	548009.595
MSA	C	4	4	2	0.998720006	0.99871787	0.017321025	584410.1839
MSA	C	4	5	1	0.998771487	0.998769436	0.01696923	608931.2862
MSA	C_0	5	1	4	0.999765886	0.999765551	0.007046293	3732351.35
MSA	C_0	5	2	1	0.999782709	0.999782346	0.005906669	3446235.205
MSA	C_0	5	3	1	0.999775926	0.999775552	0.00620088	3341899.462
MSA	C_0	5	4	2	0.999764154	0.99976376	0.006502118	317297.343
MSA	C_0	5	5	1	0.999753419	0.999753007	0.006808512	3036786.018
MSA	C	5	1	1	0.999837405	0.999837052	0.005288079	3538895.628
MSA	C	5	2	2	0.999883851	0.999883698	0.005049199	8169582.098
MSA	C	5	3	1	0.999851056	0.999850848	0.005627056	6034905.885
MSA	C	5	4	1	0.999836956	0.999836729	0.005955891	5512955.792
MSA	C	5	5	1	0.999861487	0.999861294	0.005548456	6489453.216
MSA	C_0	6	1	5	0.999543913	0.999543201	0.009955607	1755989.289
MSA	C_0	6	2	3	0.999815311	0.999815065	0.006443004	5087329.867
MSA	C_0	6	3	9	0.999254049	0.99253053	0.013341836	1253838.834
MSA	C_0	6	4	1	0.999885641	0.99988549	0.005230504	8297484.427
MSA	C_0	6	5	2	0.999861051	0.999860873	0.005754804	7026779.524
MSA	C	6	1	6	0.999687227	0.999686751	0.008438551	2627281.964
MSA	C	6	2	2	0.999711127	0.999710645	0.006953341	2592085.228
MSA	C	6	3	1	0.999764921	0.999764528	0.00676033	3185408.505
MSA	C	6	4	2	0.999806964	0.999806668	0.006353999	4219897.207
MSA	C	6	5	1	0.999714204	0.999713673	0.007051212	2353279.359
MSA	C_0	7	1	14	0.999679186	0.999678739	0.008539687	2799786.21
MSA	C_0	7	2	4	0.998323805	0.999832171	0.006211193	5958926.502
MSA	C_0	7	3	1	0.999909652	0.999909539	0.004641733	1.11E+07
MSA	C_0	7	4	1	0.999860311	0.999860078	0.005350806	5361164.277
MSA	C_0	7	5	1	0.99988371	0.999883515	0.005103004	6440022.031

MSA	C	7	1	2	0.999645701	0.999645258	0.00898931	2817246.073
MSA	C	7	2	1	0.999530177	0.999529523	0.010203421	1912585.955
MSA	C	7	3	1	0.999663053	0.999662638	0.008694023	3006140.235
MSA	C	7	4	1	0.999668681	0.999668163	0.008429278	2410775.493
MSA	C	7	5	2	0.999562649	0.999562005	0.009834522	1941524.313
MSA	C_0	8	1	2	0.999550075	0.999549324	0.009712841	1662862.622
MSA	C_0	8	2	2	0.999498121	0.999497283	0.010662214	1491642.287
MSA	C_0	8	3	2	0.999285113	0.999283919	0.012972827	1046968.627
MSA	C_0	8	4	3	0.999146679	.99914561-5	0.013964312	1169720.35
MSA	C_0	8	5	1	0.998755702	0.998753622	0.014788138	600394.1477
MSA	C	8	1	13	0.999728535	0.999728195	0.007281952	3677193.5
MSA	C	8	2	1	0.999866076	0.999865908	0.005640721	7458431.787
MSA	C	8	3	3	0.999828086	0.999827799	0.005884639	4356072.549
MSA	C	8	4	2	0.999859229	0.999858994	0.005565852	5319953.649
MSA	C	8	5	27	0.999040083	0.999038263	0.014408548	686639.1318
MSA	C_0	9	1	2	0.999550075	0.999549324	0.009712841	1662862.622
MSA	C_0	9	2	2	0.999348684	0.999347671	0.011542776	1232852.972
MSA	C_0	9	3	2	0.998962265	0.998960566	0.014454752	734973.7172
MSA	C_0	9	4	2	0.99814131	0.998138207	0.016071763	402222.9826
MSA	C_0	9	5	1	0.998762351	0.998760283	0.014663732	604026.9618
MSA	C	9	1	14	0.999327682	0.999326756	0.01198495	1349643.812
MSA	C	9	2	2	0.999487233	0.99948652	0.010656729	1753795.65
MSA	C	9	3	1	0.999215811	0.999214502	0.012401117	954378.0917
MSA	C	9	4	1	0.999270463	0.999269328	0.012381254	1100238.19
MSA	C	9	5	1	0.999224268	0.999223123	0.012951622	1091024.705
MSA	C_0	10	1	10	0.999536093	0.999535329	0.009664638	1635882.531
MSA	C_0	10	2	1	0.999770029	0.999769723	0.007189345	4084352.865
MSA	C_0	10	3	2	0.999694962	0.999694453	0.007571351	2454685.532
MSA	C_0	10	4	1	0.999671422	0.999670913	0.008193537	2458269.806
MSA	C_0	10	5	1	0.999677536	0.999677039	0.008237736	2512649.118
MSA	C	10	1	1	0.999140779	0.999139196	0.009055162	789280.527
MSA	C	10	2	1	0.998463484	0.998460369	0.008844072	400940.6745
MSA	C	10	3	2	0.999534141	0.999533429	0.009570277	1755613.514
MSA	C	10	4	5	0.999127479	0.999125968	0.011275774	827051.01
MSA	C	10	5	1	0.99931948	0.999318373	0.011836407	1128882.304
CYS	C_0	4	1	1	0.999241097	0.999240069	0.013276995	1215306.444
CYS	C_0	4	2	5	0.998270371	0.998268181	0.019884914	5699.89403
CYS	C_0	4	3	5	0.998120418	0.99811728	0.01888599	397742.8284
CYS	C_0	4	4	9	0.991494907	0.991486241	0.035609105	143039.496

CYS	C	4	1	5	0.97265894	0.972593904	0.068057642	18703.57033
CYS	C	4	2	4	0.989504506	0.989486303	0.033990979	67975.144
CYS	C	4	3	7	0.983913806	0.983886951	0.054725114	45812.66773
CYS	C	4	4	7	0.978632504	0.978611115	0.058203943	57204.26931
CYS	C_0	5	1	3	0.998860675	0.998859089	0.015723762	787726.065
CYS	C_0	5	2	7	0.999441321	0.999440533	0.011157616	1585893.349
CYS	C_0	5	3	1	0.999988915	0.999988901	0.001617771	8.65E+07
CYS	C_0	5	4	2	0.999975797	0.999975767	0.002415395	4.17E+07
CYS	C_0	5	5	1	0.999969839	0.999969802	0.002698677	3.43E+07
CYS	C	5	1	7	0.988887015	0.988870806	0.036293952	7.63E+04
CYS	C	5	2	5	0.997749929	0.997746932	0.022383278	4.16E+05
CYS	C	5	3	1	0.999959081	0.999959028	0.003086189	2.33E+07
CYS	C	5	4	2	0.99988582	0.999885667	0.005155349	8.16E+06
CYS	C	5	5	1	0.999367858	0.999366782	0.010717383	1.16E+06
CYS	C_0	6	1	1	0.999658285	0.999657857	0.008774634	2.92E+06
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CYS	C_0	6	3	1	0.999984532	0.999845121	0.00191588	6.33E+07
CYS	C_0	6	4	1	0.999965249	0.999965204	0.002874776	2.79E+07
CYS	C_0	6	5	1	0.999980754	0.999980728	0.002133996	4.89E+07
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CYS	C	6	3	2	0.999325385	0.999324471	0.012352162	1.37E+06
CYS	C	6	4	1	0.999881333	0.999881163	0.005223335	7.33E+06
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CYS	C	9	2	8	0.979370201	0.979341013	0.059282808	4.20E+04
CYS	C	9	3	4	0.993279555	0.993268961	0.035968173	1.17E+05
CYS	C	9	4	1	0.999051588	0.999049691	0.008990642	6.58E+05
CYS	C	9	5	1	0.999827308	0.999827052	0.00614062	4.89E+06
CYS	C_0	10	1	5	0.997529316	0.999752588	0.007509989	3.64E+06
CYS	C_0	10	2	1	0.999966491	0.999966447	0.002760994	2.88E+07
CYS	C_0	10	3	1	0.999965135	0.999965087	0.00278435	2.56E+07
CYS	C_0	10	4	1	0.999976437	0.999976405	0.002322738	3.86E+07
CYS	C_0	10	5	1	0.999963707	0.999963655	0.002843777	2.42E+07
CYS	C	10	1	2	0.996497056	0.99649189	0.027871565	2.41E+05
CYS	C	10	2	3	0.998633025	0.998631095	0.017504554	6.47E+05
CYS	C	10	3	5	0.997592587	0.997590441	0.02158284	5.81E+05
CYS	C	10	4	3	0.998464622	0.998463341	0.017161703	9.75E+05

Eq. S1 Deconvolved Gaussian used to fit to C and C_0 breakthrough curves.

$$y = \frac{a}{2}\left|1 + erf\left(\frac{x-b}{\sqrt{2}c}\right) - \left(\frac{d}{|d|} + erf\left(\frac{x-b}{\sqrt{2}c} - \frac{c}{\sqrt{2}d}\right)\right) exp\left(\frac{c^2}{2d^2} + \frac{b-x}{d}\right)\right|$$

Transition height: a

Transition center for deconvolved Gaussian cumulative: b

Transition width for deconvolved Gaussian cumulative: 1.348979501c

Exponential time constant: d