

Supporting Information

A Simple and Highly Sensitive Colorimetric Detection Method for Gaseous Formaldehyde

Liang Feng^{†‡}, Christopher J. Musto[†], Kenneth S. Suslick^{†*}

[†] Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Ave., Urbana, Illinois 61801 USA

[‡] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, P.R. China

Experimental:

All reagents used were analytical-reagent grade, obtained from Sigma-Aldrich, and used without further purification unless otherwise specified. A certified, premixed formaldehyde gas tank was obtained from Matheson Tri-Gas Corp. through S. J. Smith, Co. (Urbana, IL). Polyvinylidene difluoride (PVDF, [CH₂CF₂]_n) membrane (thickness: 165 μm; pore size: 0.45 μm) was obtained from VWR Scientific. (Batavia, IL).

For printing of the sensor arrays, we prepared polymer-colorant solutions in 2-methoxyethanol using commercially available poly(ethyleneglycol) bis(3-amino-propyl)-terminated (MW 1500), butyl benzyl phthalate, and poly(ethyleneglycol) (MW 400) with a variety of chemically responsive indicators (Supporting Information Table S1). The solutions were loaded into a multihole Teflon ink well. Sensor arrays were printed by a robotic printer (Nanoprint Microarray Printer, ArrayIt Co., Mountain View, CA) using an array of 30 or 36 floating slotted pins (which delivered approximately 130 nL each) by dipping into the ink well and transferring to a hydrophobic PVDF membranes. Once printed, the arrays were vacuum dried for 24 hours and aged in a sealed bag under nitrogen for at least 2 days before sensing experiments were performed.

Gas streams containing formaldehyde at lower concentrations were prepared by mixing the prediluted formaldehyde gas from the premixed tank with dry and wet nitrogen gas. Importantly, in all cases, gas stream concentrations and relative humidity were confirmed by in-line analysis using an FTIR multi-gas analyzer,

MKS Instruments model 2030. MKS digital mass flow controllers were used to achieve the desired concentrations and relative humidity (cf. SI Figures S1). For high concentrations of formaldehyde (i.e., 15 and 20 ppm), gas streams were produced by flushing dry nitrogen through a Teflon tube containing paraformaldehyde fine powder, and mixing with dry and wet nitrogen gas. Again concentrations were confirmed by in-line FTIR analysis.

For all sensing experiments, the arrays were imaged on an ordinary flatbed scanner (Epson Perfection V200); the before-exposure image was acquired after 2 min. flow of 50% RH N₂ flow at 500 sccm. After-exposure images were acquired every minute again at 500 sccm. Difference maps were obtained by taking the difference of the red, green, and blue (RGB) values from the center of every colorant spot (~300 pixels) from the “before” and “after” images; all difference maps shown here are averages of multiple trials. Digitization of the color differences can be performed using Adobe Photoshop[™] or with a customized software package, ChemEye[™] (ChemSensing, Inc., Champaign, IL).

The chemometric analysis was carried out on the color difference vectors (provided as a database in Supporting Information, Table S3) using the Multi-Variant Statistical Package[™] (MVSP v.3.1, Kovach Computing); in all cases, minimum variance (i.e., “Ward’s Method”) was used for the HCA clustering.

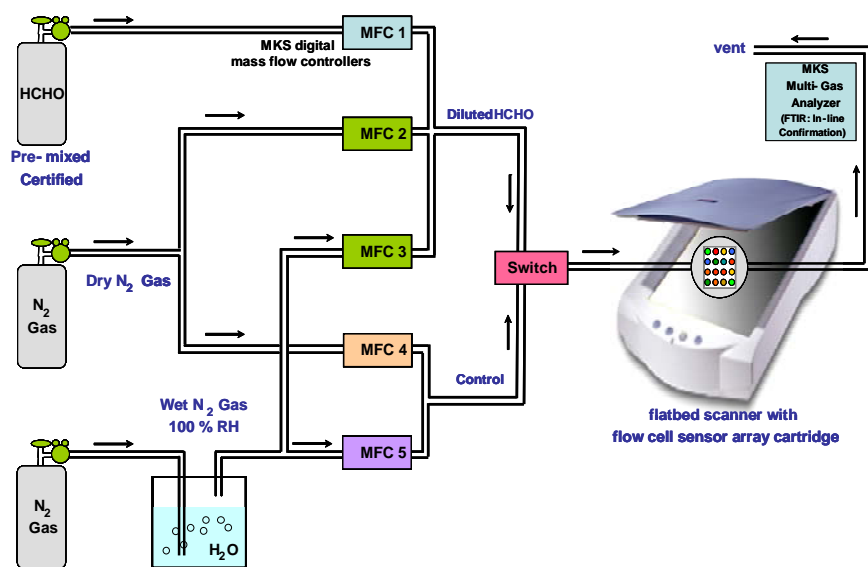


Figure S1. Gas mixing rig used for exposure of colorimetric sensor arrays. The box labeled “switch” is actually a series of three three-way valves, which allows for venting and also diversion of analyte stream to the MKS multi-gas analyzer. MFC = mass flow controller.

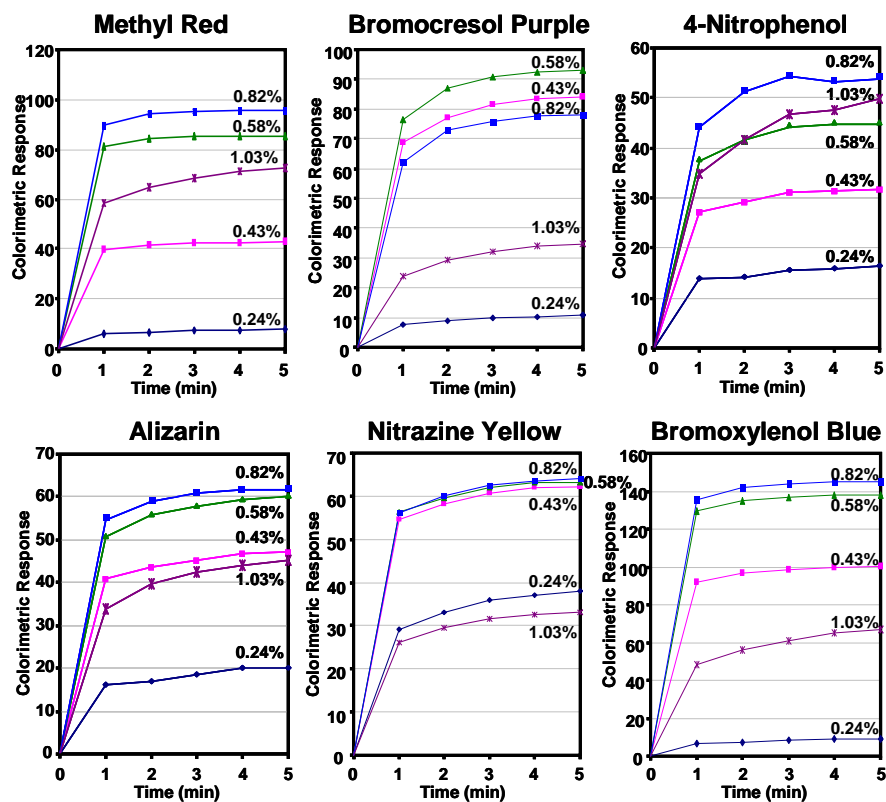


Figure S2. Colorimetric response (i.e., $(\Delta_R^2 + \Delta_G^2 + \Delta_B^2)^{1/2}$) of each pH indicator versus response time at various polymeric amine wt. % after exposure 20 ppm formaldehyde, at 500 sccm, 50% relative humidity and 298 K.

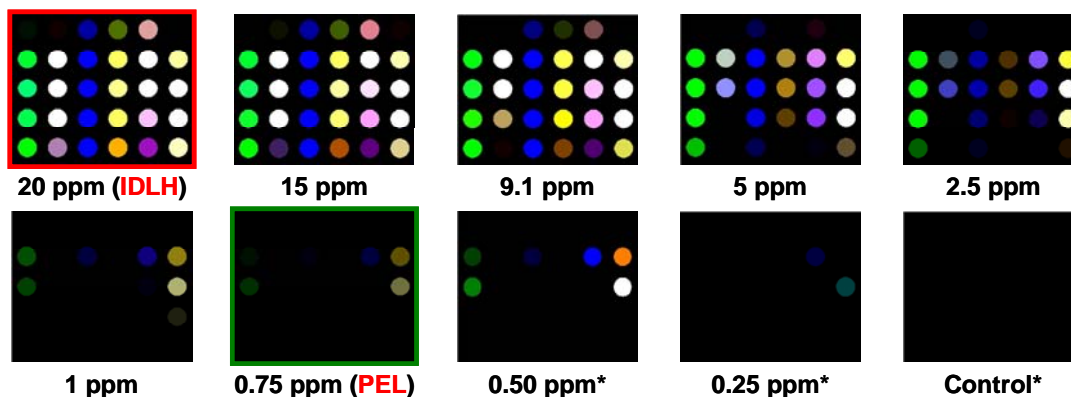


Figure S3. Color difference maps of formaldehyde at nine different concentrations after 1 minute exposure at 500 sccm, 50% relative humidity and 298 K. A full digital database is provided in the Supporting Information Table S3. For display purposes, the color range of these difference maps are expanded from 4 to 8 bits per color (RGB range of 4-19 expanded to 0-255), except for control and several weak responses that are marked with asterisk (RGB range of 2-5 expanded to 0-255).

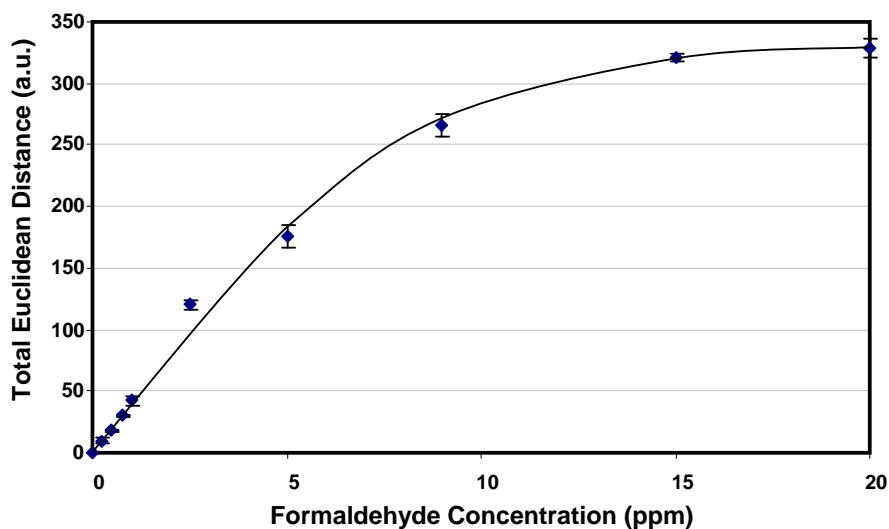


Figure S4. The total Euclidean distance of the color change of the array versus formaldehyde concentration. A 90-dimensional vector is defined from the changes (after 1 min. exposure minus before exposure) in the red, green and blue values of the thirty spots in our 6x5 array. The Euclidean distance is simply the total length of this 90-dimensional color-difference vector.

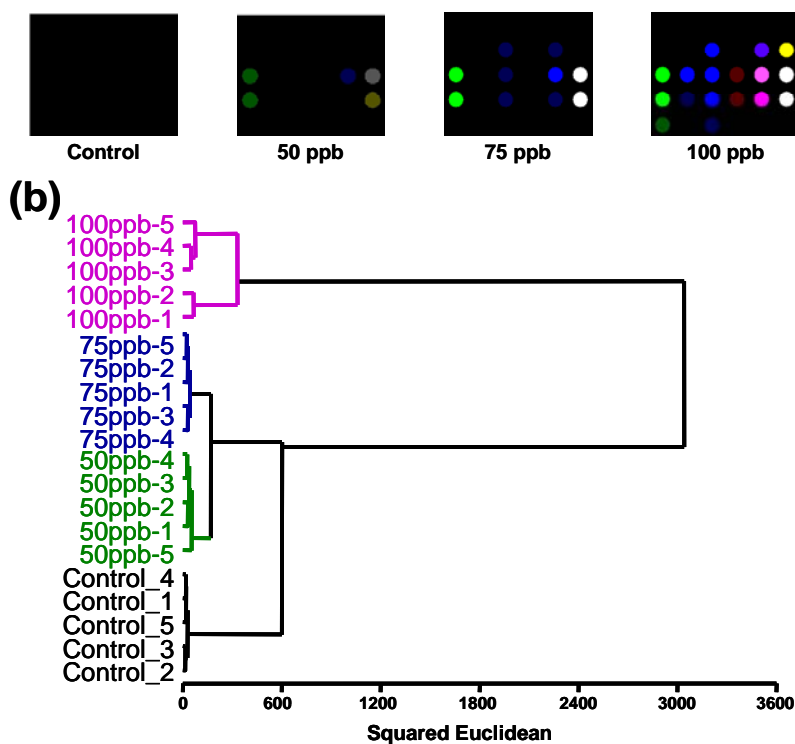


Figure S5. (a) Color difference maps of formaldehyde at 100 ppb, 75 ppb, 50 ppb, and a control after 10 minutes of exposure at 500 sccm, 50% relative humidity and 298 K. For display purposes, the color range of these difference maps are expanded from 2 to 8 bits per color (RGB range of 1-3 expanded to 0-255). (b) Hierarchical cluster analysis (HCA) for formaldehyde at 100 ppb, 75 ppb, and 25 ppb concentrations and a control. All experiments were run in quintuplicate trials; no confusions or errors in classification were observed in 20 trials, as shown.

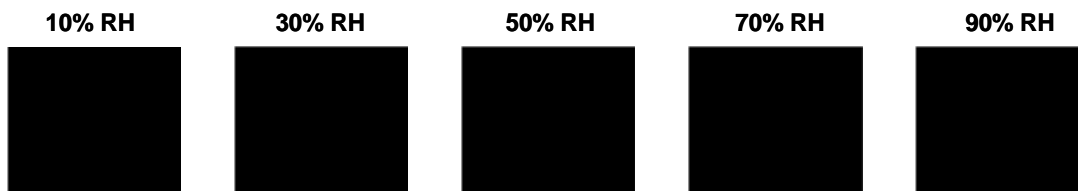


Figure S6. The response of array to variations in humidity from 10% to 90% RH; average of three trials is shown. For display purposes, the color range of these difference maps is expanded from 4 to 8 bits per color (RGB range of 4-19 expanded to 0-255).

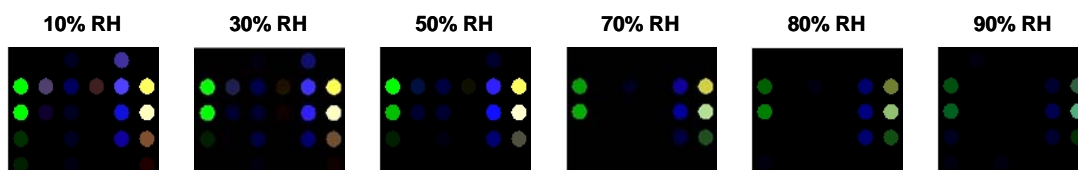


Figure S7. Difference maps of the colorimetric sensor array for formaldehyde at 1.5 ppm at different relative humidities at room temperature, after one minute exposure time, 500 sccm. For display purposes, the color range of these difference maps are expanded from 4 to 8 bits per color (RGB range of 4-19 expanded to 0-255).

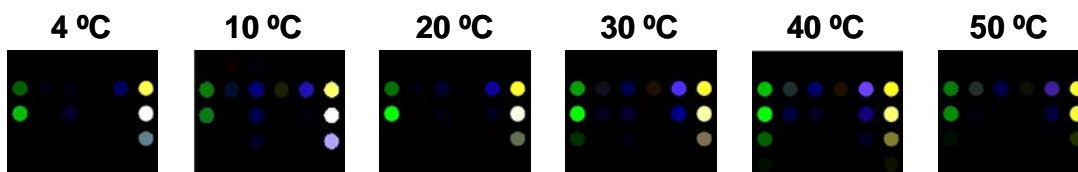


Figure S8. Difference maps of the colorimetric sensor array for formaldehyde at 1.5 ppm concentration at 50% RH and different temperatures, after one minute exposure time, 500 sccm. For display purposes, the color range of these difference maps are expanded from 4 to 8 bits per color (RGB range of 4-19 expanded to 0-255).

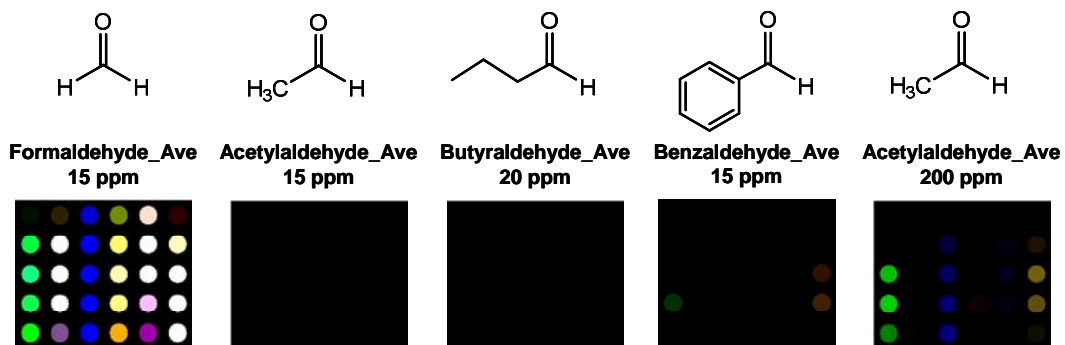


Figure S9. Difference maps of the colorimetric sensor array for several aldehydes at room temperatures and 50% RH, after one minute exposure time, 500 sccm. For display purposes, the color range of these difference maps are expanded from 4 to 8 bits per color (RGB range of 4-19 expanded to 0-255).

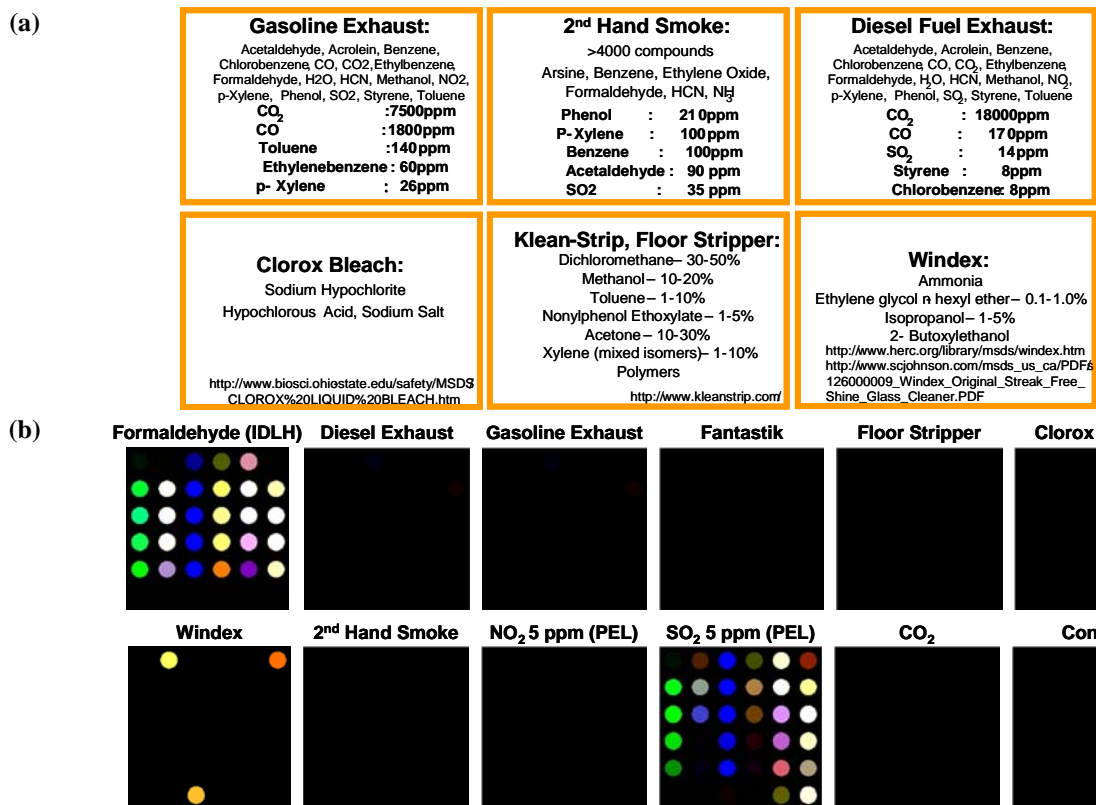


Figure S10. (a) The compositions for several vapor phase interferents. (b) Difference maps of the colorimetric sensor array for 10 interferents after one minute exposure at 500 sccm. For display purposes, the color range of these difference maps are expanded from 4 to 8 bits per color (RGB range of 4-19 expanded to 0-255). Interferents tested: second-hand smoke, diesel fuel exhaust, gasoline exhaust, floor stripper, Windex[®], Fantastik[®], and Clorox[®] bleach at 2% of their saturation vapor concentrations; sulfur dioxide and nitrogen dioxide at their respective PEL concentrations; and the carbon dioxide concentration at ~375 ppm (i.e., approximately ambient atmospheric concentration).

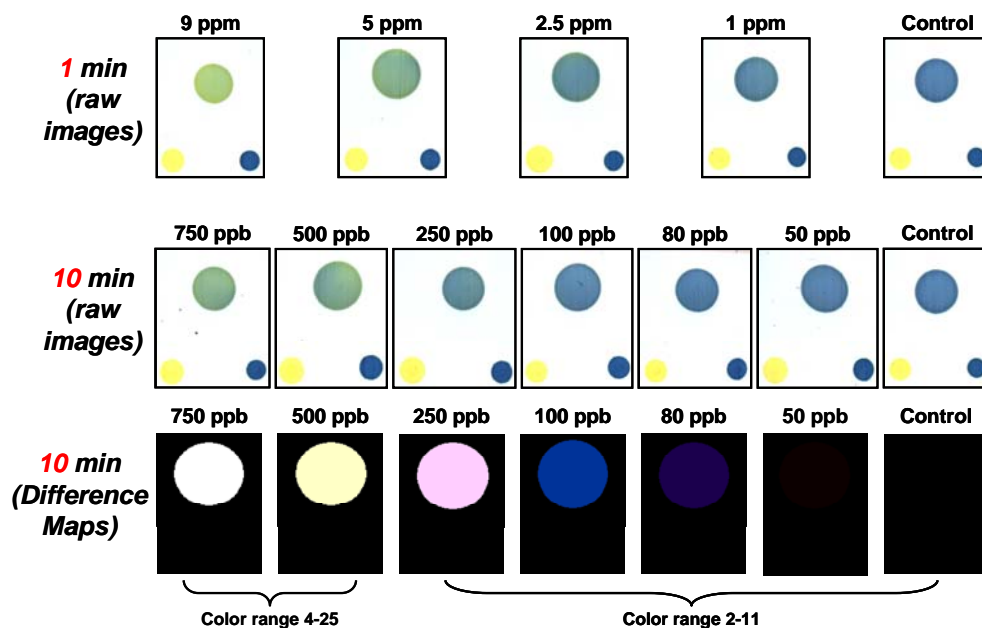


Figure S11. A simplified formaldehyde sensor showing the response after 1 minutes exposure (1~9 ppm) or 10 minutes exposure (50~750 ppb). The top spot is used for detection of formaldehyde and consists of bromoxylenol blue in a 0.6 wt.% amine-PEG film; the bottom two spots (left and right) are indicators for acidic and basic interferents vapors (respectively) and consist of bromoxylenol blue (lower left spot) and tetrabutylammonium hydroxide treated nitrazine yellow (lower right spot) in a non-amine PEG film.

Table S1. List of indicators and formulations.

Spot #	Name
1	Methyl Red + Formulation I
2	Bromocresol Purple + Formulation I
3	4-Nitrophenol + Formulation I
4	Alizarin + Formulation I
5	Nitrazine Yellow + Formulation I
6	Bromoxyleneol Blue + Formulation I
7	Methyl Red + Formulation II
8	Bromocresol Purple + Formulation II
9	4-Nitrophenol + Formulation II
10	Alizarin + Formulation II
11	Nitrazine Yellow + Formulation II
12	Bromoxyleneol Blue + Formulation II
13	Methyl Red + Formulation III
14	Bromocresol Purple + Formulation III
15	4-Nitrophenol + Formulation III
16	Alizarin + Formulation III
17	Nitrazine Yellow + Formulation III
18	Bromoxyleneol Blue + Formulation III
19	Methyl Red + Formulation IV
20	Bromocresol Purple + Formulation IV
21	4-Nitrophenol + Formulation IV
22	Alizarin + Formulation IV
23	Nitrazine Yellow + Formulation IV
24	Bromoxyleneol Blue + Formulation IV
25	Methyl Red + Formulation V
26	Bromocresol Purple + Formulation V
27	4-Nitrophenol + Formulation V
28	Alizarin + Formulation V
29	Nitrazine Yellow + Formulation V
30	Bromoxyleneol Blue + Formulation V

Spot numbering from left to right, top to bottom for 6x5 array shown in Figure 1.

TBAH: 1.0 M tetrabutylammonium hydroxide in 2-methoxyethanol; amino-PEG: poly(ethylene glycol) bis(3-aminopropyl)terminated

Formulation I: amino-PEG (100mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

Formulation II: amino-PEG (200mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

Formulation III: amino-PEG (300mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

Formulation IV: amino-PEG (500mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

Formulation V: amino-PEG (750mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

Table S2. List of indicators and formulations for interferents test.

Spot #	Name
1	Methyl Red + Formulation I
2	Bromocresol Purple + Formulation I
3	4-Nitrophenol + Formulation I
4	Alizarin + Formulation I
5	Nitrazine Yellow + Formulation I
6	Bromoxyleneol Blue + Formulation I
7	Methyl Red + Formulation II
8	Bromocresol Purple + Formulation II
9	4-Nitrophenol + Formulation II
10	Alizarin + Formulation II
11	Nitrazine Yellow + Formulation II
12	Bromoxyleneol Blue + Formulation II
13	Methyl Red + Formulation III
14	Bromocresol Purple + Formulation III
15	4-Nitrophenol + Formulation III
16	Alizarin + Formulation III
17	Nitrazine Yellow + Formulation III
18	Bromoxyleneol Blue + Formulation III
19	Methyl Red + Formulation IV
20	Bromocresol Purple + Formulation IV
21	4-Nitrophenol + Formulation IV
22	Alizarin + Formulation IV
23	Nitrazine Yellow + Formulation IV
24	Bromoxyleneol Blue + Formulation IV
25	Methyl Red + Formulation V
26	Bromocresol Purple + Formulation V
27	4-Nitrophenol + Formulation V
28	Alizarin + Formulation V
29	Nitrazine Yellow + Formulation V
30	Bromoxyleneol Blue + Formulation V
31	Methyl Red + Formulation VI
32	Alizarin + Formulation VI
33	Nitrazine Yellow + Formulation VI
34	Methyl Red + TBAH + Formulation VI
35	Alizarin + TBAH + Formulation VI
36	Nitrazine Yellow + TBAH + Formulation VI

Spot numbering from left to right, top to bottom for 6x6 array shown in Figure 1.

The first 30 spots are identical with Table S1.

TBAH: 1.0 M tetrabutylammonium hydroxide in 2-methoxyethanol; amino-PEG: poly(ethylene glycol) bis(3-aminopropyl)terminated

Formulation I: amino-PEG (100mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

Formulation II: amino-PEG (200mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

Formulation III: amino-PEG (300mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

Formulation IV: amino-PEG (500mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

Formulation V: amino-PEG (750mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

Formulation VI: PEG 1500 (300mg) + Benzyl butyl phthalate (500mg) + PEG 400 (300mg) + 10mL 2-Methoxyethanol

	R28	G28	B28	R29	G29	B29	R30	G30	B30
20ppm_1	18.36232	11.22319	-5.472458	14.28406	5.18261	-18.71594	21.71884	20.28406	-17.87247
20ppm_2	22.12391	15.68333	-1.595652	13.72391	4.923189	-15.72609	30.52464	27.67681	-16.22609
20ppm_3	21.91305	15.09855	-0.971016	13.75652	4.231884	-17.45217	34.67536	32.07826	-16.93044
20ppm_4	22.09275	15.67536	-1.536232	12.9942	5.249275	-13.7971	34.70435	30.0058	-17.4
20ppm_5	26.76811	20.86087	-1.057968	17.7971	6.495655	-18.0145	33.70435	30.72463	-15.68695
15ppm_1	16.23478	9.255074	-2.156525	10.91014	3.837681	-14.02898	18.49565	17.48116	-14.73624
15ppm_2	18.56812	11.89565	-0.437683	11.68696	4.463768	-11.3913	19.95652	18.60001	-10.66666
15ppm_3	15.27536	8.788406	-0.953621	10.51014	3.510143	-12.51014	18.85218	16.96522	-11.34782
15ppm_4	14.85507	9.028984	-2.918839	10.64638	3.388405	-12.28406	18.89855	16.75072	-13.49855
15ppm_5	15.02029	8.91304	-2.226089	10.57392	3.371014	-14.38261	17.96812	16.22029	-15.00579
9ppm_1	12.15942	7.391304	3.249275	9.942028	4.313042	-12.3913	18.1913	19.24638	-8.553619
9ppm_2	10.25797	8.379715	1.655075	8.507248	3.417389	-11.06957	15.42899	15.86957	-9.666672
9ppm_3	14.82609	10.6087	3.681152	9.171015	3.449276	-10.96522	26.9855	26.51304	-14.86377
9ppm_4	11.08985	7.843483	3.765213	10.14493	4.301449	-11.21159	15.96522	16.25217	-8.544922
9ppm_5	11.77971	7.599998	2.828987	9.753622	4.344925	-12.02898	14.15942	14.36232	-7.382607
5ppm_1	4.373917	3.028992	2.985504	2.857971	1.431885	-6.240578	8.426088	8.136234	-6.608696
5ppm_2	3.078262	1.562317	1.289856	2.205797	1.185509	-3.81739	5.434782	4.107243	-5.472458
5ppm_3	4.930435	3.344933	1.965218	4.994204	2.286957	-7.014496	17.04348	16.88696	-8.626083
5ppm_4	5.214493	3.44928	3.04348	3.57971	1.428986	-5.588409	12.54493	12.06377	-7.362328
5ppm_5	3.973915	1.968109	1.014496	2.826086	1.489853	-4.866669	6.88406	6.272465	-7.162315
2.5ppm_1	1.081161	0.698547	1.626091	1.834784	0.527538	-1.881165	6.611595	6.489853	-4.933334
2.5ppm_2	2.460869	1.347824	2.597099	4.098549	2.663769	0.165222	7.037682	5.652176	-4.982613
2.5ppm_3	2.727539	2.469566	2.617393	1.750725	0.886959	-2.098549	6.165218	5.460869	-4.150726
2.5ppm_4	3.121742	1.704346	2.113045	1.968117	0.756523	-3.643478	9.686958	9.113037	-5.843475
2.5ppm_5	2.554591	1.44058	2.307246	1.548793	0.622223	-2.254107	6.176812	5.69082	-3.690821
1ppm_1	0.09565	0.231888	1.359421	0.031883	-0.130432	-0.228981	1.284058	1.510147	-1.365211
1ppm_2	0.072464	0.426086	0.611595	0.200001	-0.069565	-1.202896	1.504345	0.759422	-2.107246
1ppm_3	0.228989	0.495651	0.289856	0.733334	0.414494	-0.289856	3.144928	2.727539	-2.481155
1ppm_4	-0.052177	0.892754	0.437683	0.252172	0.25507	-0.118835	1.82029	2.344925	-1.391304
1ppm_5	0.234787	-0.4058	0.402901	0.060869	-0.434784	-1.156517	1.324638	1.565216	-2.217392
0.75ppm_1	-0.257973	-0.678261	-0.292755	-0.095654	-0.466663	0.617393	0.321739	0.191307	-1.220284
0.75ppm_2	0.031891	-0.41449	0.324638	0.672462	0.171013	-0.159424	0.779711	0.365219	-1.492752
0.75ppm_3	-0.118835	-0.052177	0.020287	0.33913	0.110146	-0.211594	0.672462	0.90435	-1.284058
0.75ppm_4	0.026085	-0.515938	-0.376816	0.408695	-0.344925	-1.344925	1.330433	1.078262	-1.976814
0.75ppm_5	0.747826	0.142029	1.234787	0.623188	-0.130436	-1.368118	1.463768	0.486954	-1.895653
0.5ppm_1	-0.652168	0.110146	0.284058	0.191303	0.626087	-0.066666	0.547829	0.5942	-0.936226
0.5ppm_2	0.301453	-0.515938	-0.220291	0.24058	-0.507244	-0.50145	-0.02319	-0.13913	-1.22319
0.5ppm_3	-0.127533	-0.211594	0.4058	0.472464	-0.492752	-1.342033	0.597099	0.449276	-0.075363
0.5ppm_4	-0.599998	-0.77681	0.034782	-0.031883	-0.45507	-1.055077	0.77681	0.440582	-0.855072
0.5ppm_5	-0.576813	-0.611595	0.336235	-0.226088	0.084057	-0.469559	1.008698	0.434784	-0.168114
0.25ppm_1	-0.020294	-0.327538	0.571014	0.371014	0.162319	0.718842	0.26667	0.234779	-0.037682
0.25ppm_2	-0.446381	-0.884056	0.333328	-0.014494	-0.130432	-0.281158	0.38261	-0.13913	0.086952
0.25ppm_3	-0.695648	-0.533333	-0.614494	-0.231884	-0.70145	-0.515945	-1.460869	-1.49855	-1.805801
0.25ppm_4	-0.339127	0.089859	-0.475357	-0.04348	-0.284058	-0.060867	-0.113045	-0.962318	-1.295654
0.25ppm_5	-0.475357	0.063774	-0.133331	0.747826	0.49855	-0.150719	-0.092754	-0.356522	-0.915939
Control_1	0.101448	0.144928	-0.449272	-0.12174	0.400002	-0.115944	-0.182606	-0.498558	-0.272461
Control_2	0.095657	0.234787	0.710144	0.147827	-0.150726	-0.536232	0.092754	0.481163	-0.011581
Control_3	-0.942032	-0.081154	-0.866661	0.27536	0.005798	-0.107246	-0.278263	-0.307251	-0.579712
Control_4	0.197105	0.107246	0.837685	-0.484056	-0.072464	0.846375	-0.34203	0.026085	1.171021
Control_5	-0.017387	-0.237686	-0.402901	-0.037682	0.585506	0.011597	-0.449274	0.18261	0.356522