Supplementary Information for:

Simplified Determination of Complex Stoichiometry for Colorimetric Metal Indicators by Inkjet Printing

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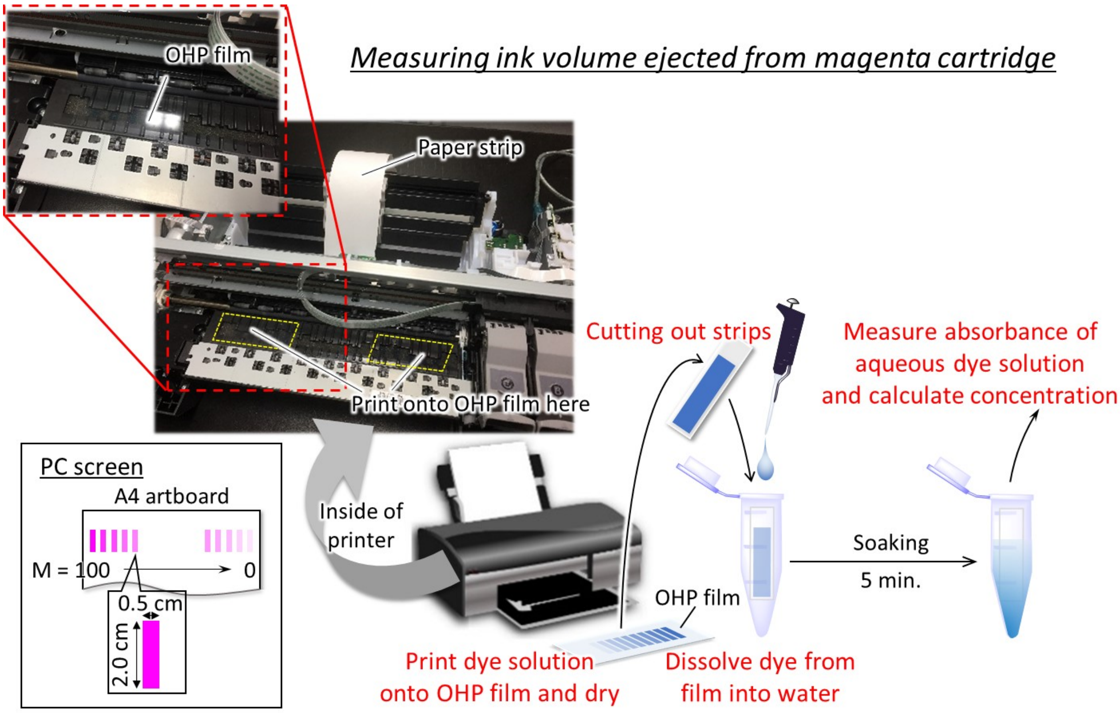
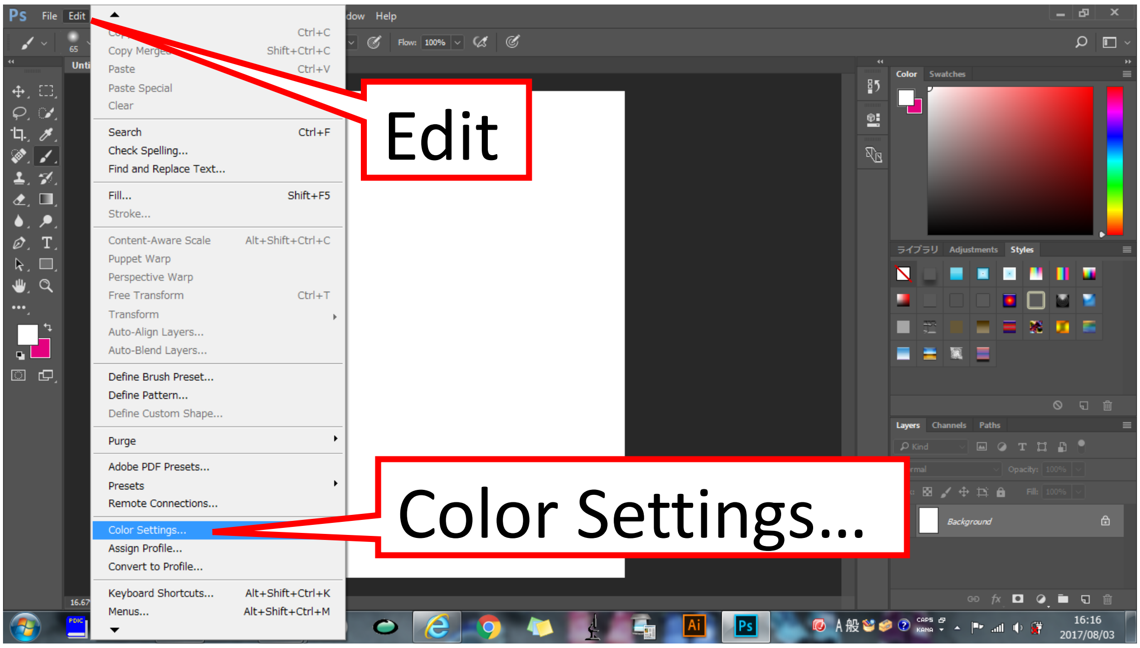


Figure S1. Schematic outline of the determination method of inkjet-ejected liquid volume. The figure shows the case of the magenta ink cartridge as an example. An aqueous dye solution filled in the magenta reservoir was inkjet-printed onto two sheets of OHP film (7 x 3 cm^2) fixed inside the printer. For the recognition of the correct paper feeding by the printer, a copy paper strip ("Paper strip" in the figure) was fed from the paper feeder and was passed between the fixed OHP sheets. Inkjet-printing of dye solutions onto an A4-sized OHP sheet using the "standard" feeding mode is not achievable, because the paper feeding rollers inside the printer unavoidably come into contact with the inks deposited on the surface of the OHP film.

A)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Free Transform
Transform
Auto-Align Layers...
Auto-Blend Layers...
Define Brush Preset...
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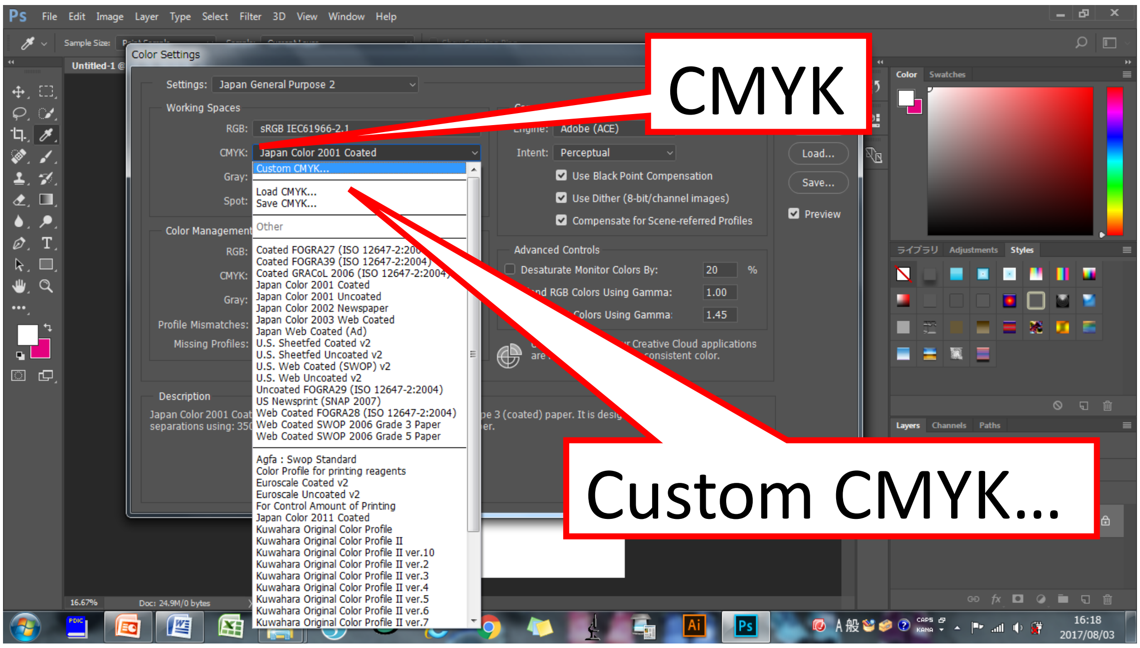
Menus...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CMYK: Japan Color 2001 Coated
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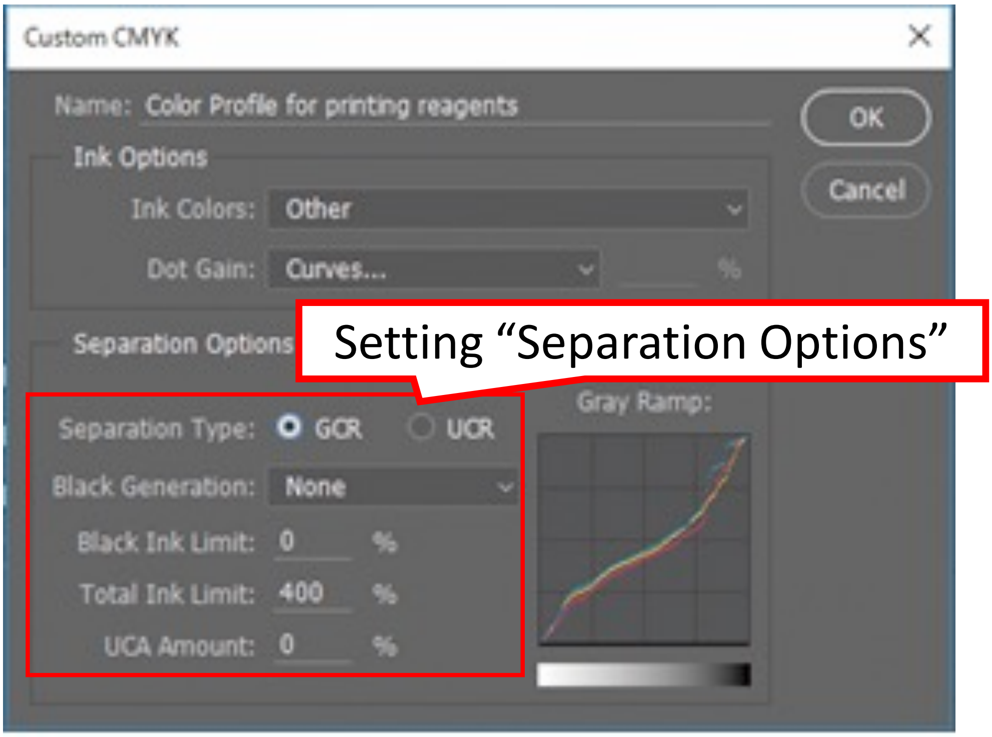
Load CMYK...
Save CMYK...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Dot Gain: Curves...
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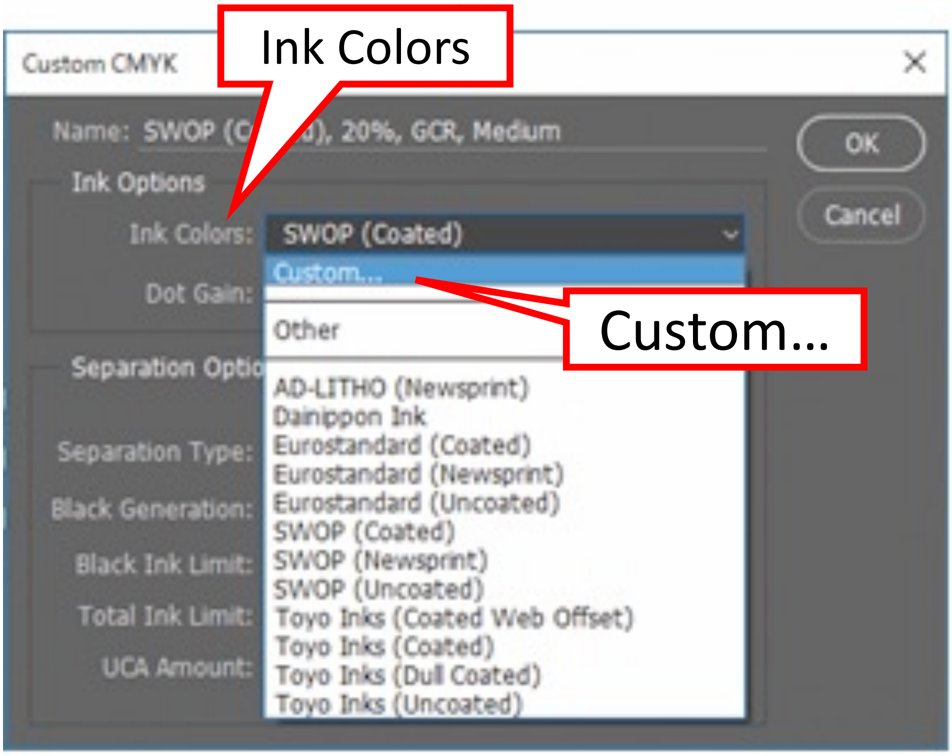
UCA Amount: 0 %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Custom...
Dot Gain:
Other
Custom...
Separation Optio
AD-LITHO (Newsprint)
Dainippon Ink
Eurostandard (Coated)
Eurostandard (Newsprint)
Eurostandard (Uncoated)
SWOP (Coated)
SWOP (Newsprint)
SWOP (Uncoated)
Toyo Inks (Coated Web Offset)
Toyo Inks (Coated)
Toyo Inks (Dull Coated)
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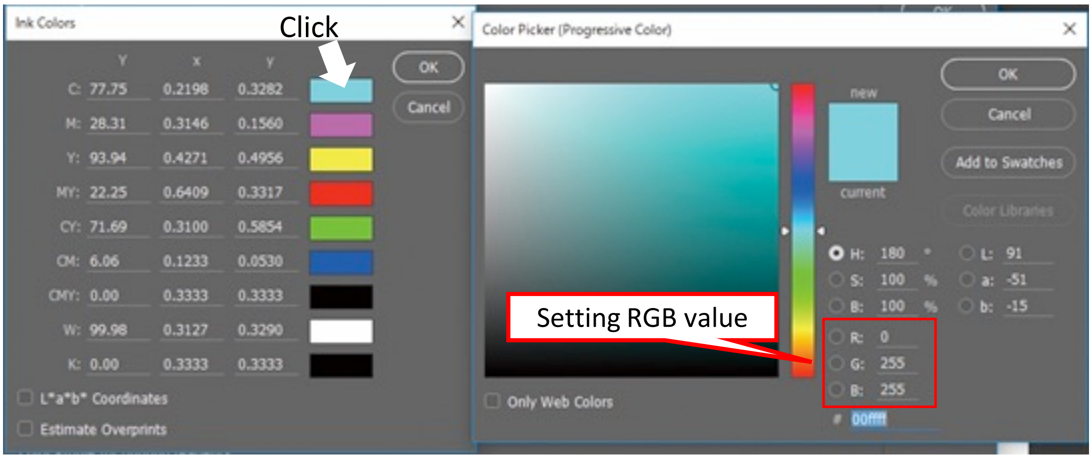
Black Generation:
Black Ink Limit:
Total Ink Limit:
UCA Amount:



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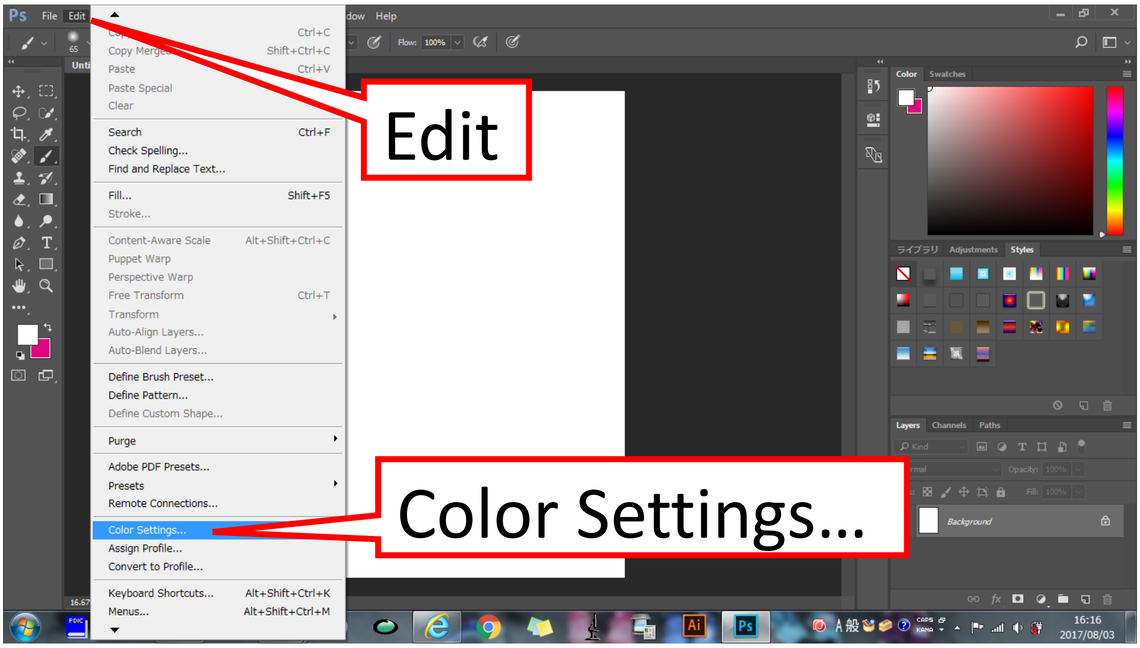
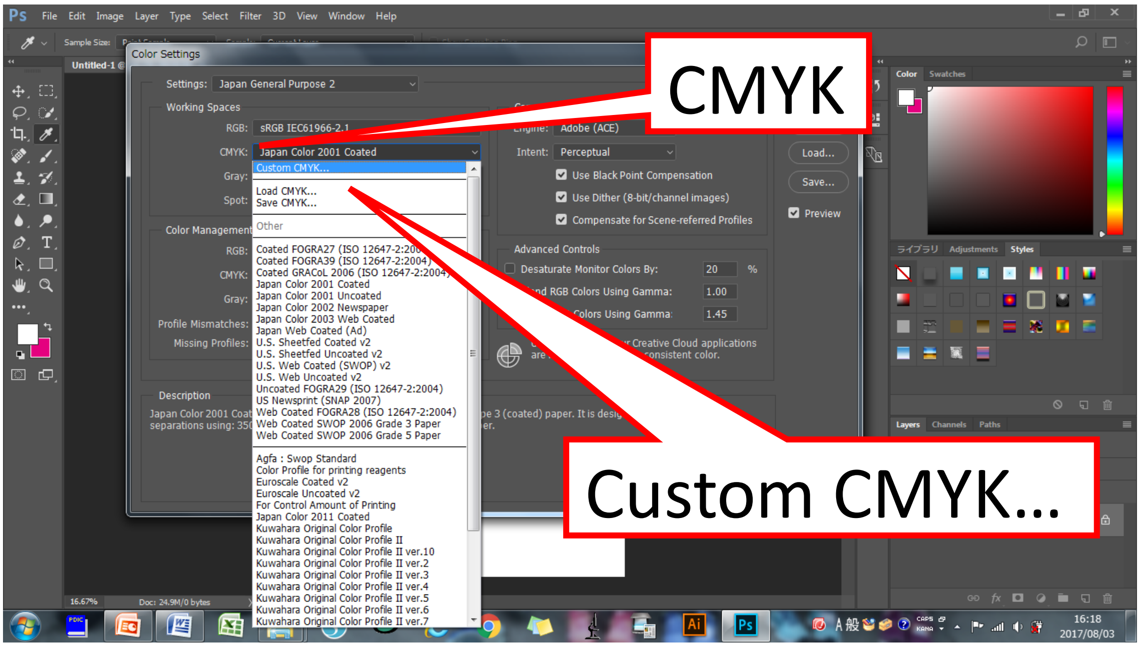
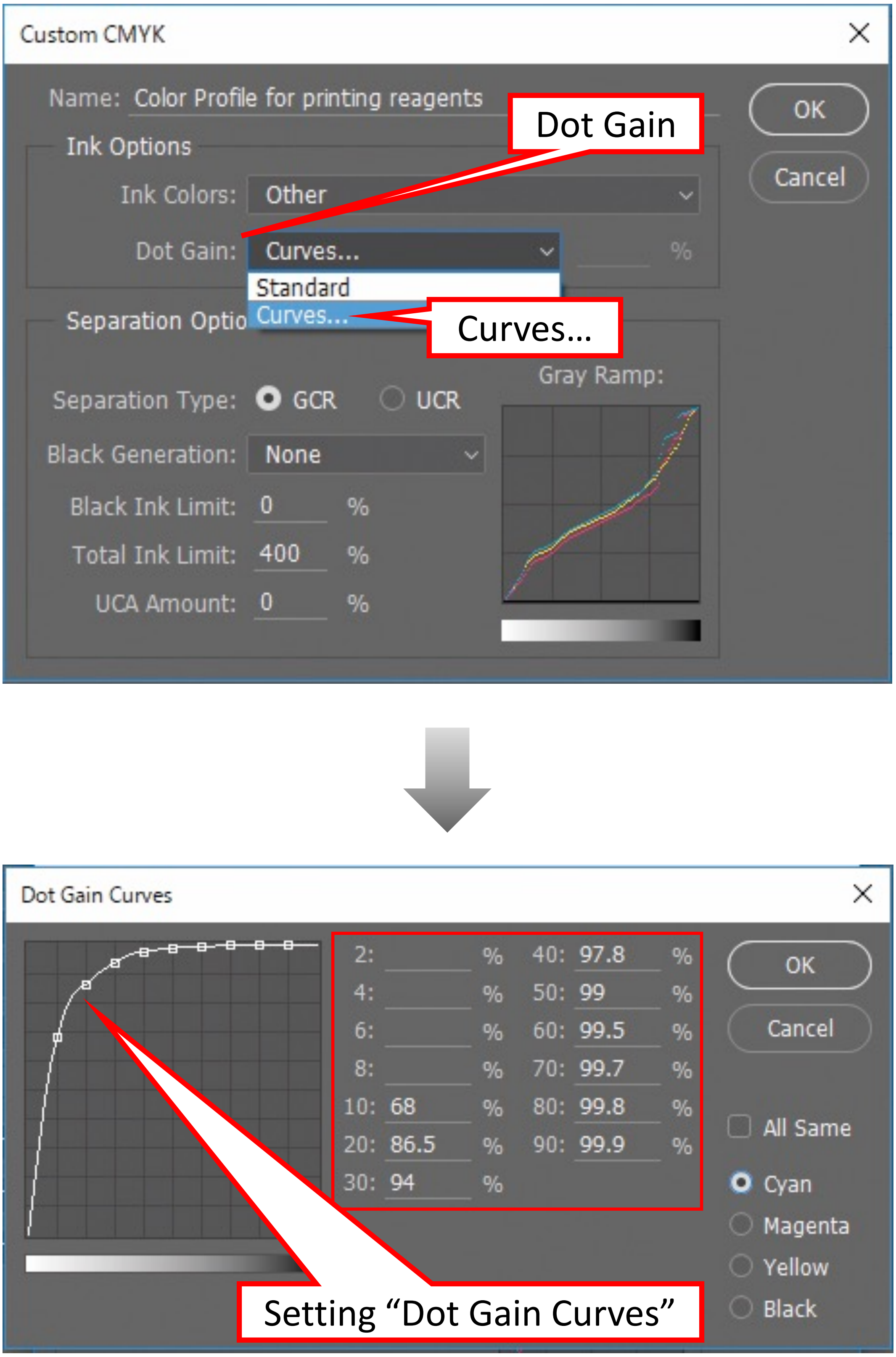
G	255	0	255	0	255	0	0	255	0
B	255	255	0	0	0	255	0	255	0

B)






Custom CMYK
Name: Color Profile for printing reagents
OK
Cancel
Dot Gain
Ink Options
Ink Colors: Other
Dot Gain: Curves...
Standard
Curves...
Curves...
Separation Optio
Gray Ramp:
Separation Type: GCR UCR
Black Generation: None
Black Ink Limit: 0 %
Total Ink Limit: 400 %
UCA Amount: 0 %
Dot Gain Curves
2: %
4: %
6: %
8: %
10: 68 %
20: 86.5 %
30: 94 %
40: 97.8 %
50: 99 %
60: 99.5 %
70: 99.7 %
80: 99.8 %
90: 99.9 %
OK
Cancel
All Same
Cyan
Magenta
Yellow
Black
Setting “Dot Gain Curves”

Set values

	Cyan	Magenta	Yellow	Black
10	68	66.5	58	60
20	86.5	85	81	84
30	94	92.9	90.9	91
40	97.8	96.9	96.3	94.6
50	99	98.6	98.2	96.3
60	99.5	99.4	99.1	97.5
70	99.7	99.6	99.6	98.4
80	99.8	99.8	99.9	99.3
90	99.9	99.9	100	99.8

Figure S2. Screenshots of the Adobe Photoshop software for colour profile editing; A) procedure for editing the "Ink Colors" and "Separation Option" settings; B) procedure for editing the "Dot Gain" setting.

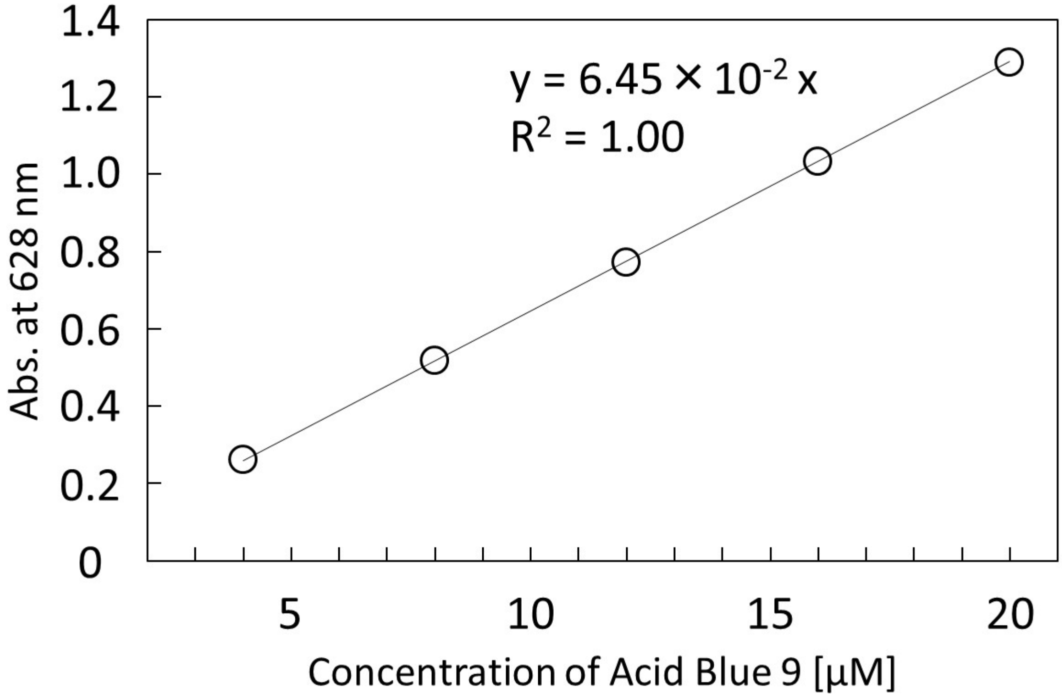


Figure S3. Calibration curve representing the relationship between the concentration of Acid Blue 9 in aqueous solution and absorbance at 628 nm

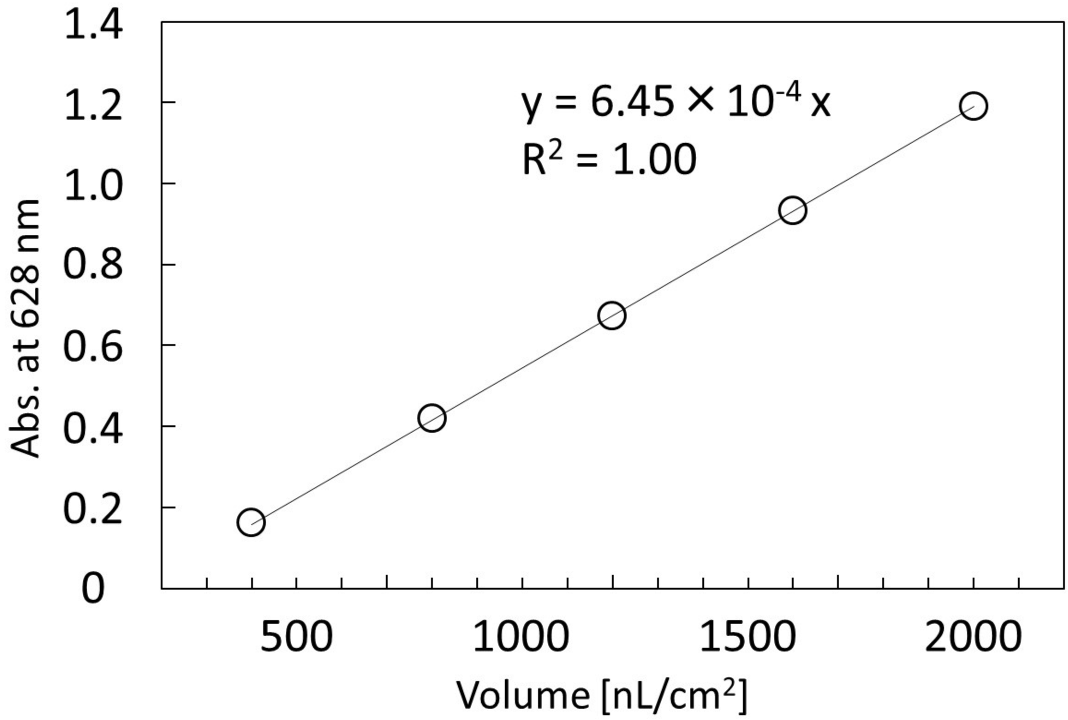


Figure S4. The calibration curve for determination of ejected ink volume from the absorbance of Acid Blue 9 dye dissolved into water.

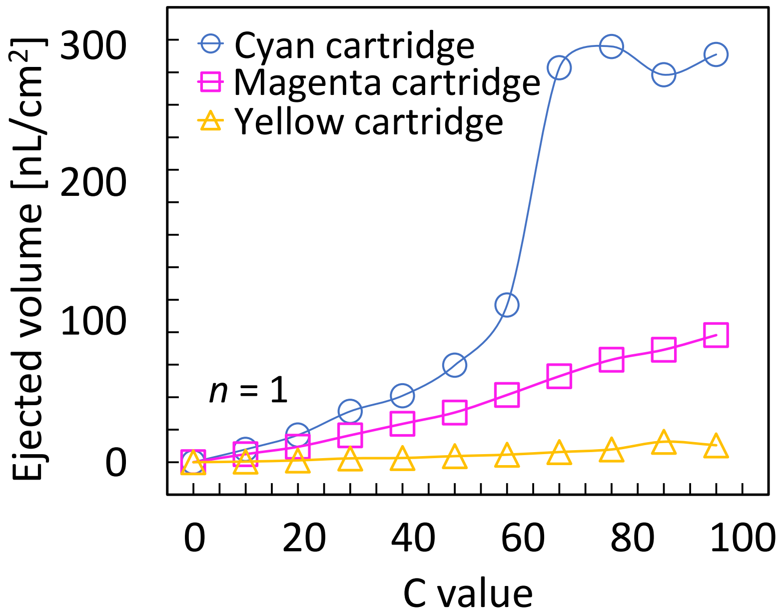


Figure S5. Ink ejection volumes from non-intended cartridges when using a common colour profile (Coated GRACOL 2006). The graph shows the ejected ink volumes from the cyan (blue curve), magenta (pink curve) and yellow (yellow curve) cartridges, respectively. The software set printing colour values were varied between 0 and 100 for cyan while magenta and yellow values were kept at 0 in the colour printing mode (*i.e.* ink dispensing intended from the cyan cartridge, only). Although the ink volume dispensed from the "intended" cyan cartridge increased with increasing C values, the use of the common colour profile resulted in ink ejection also from "non-intended" magenta and yellow cartridges, making precise control of ink dispensing ratios unachievable.

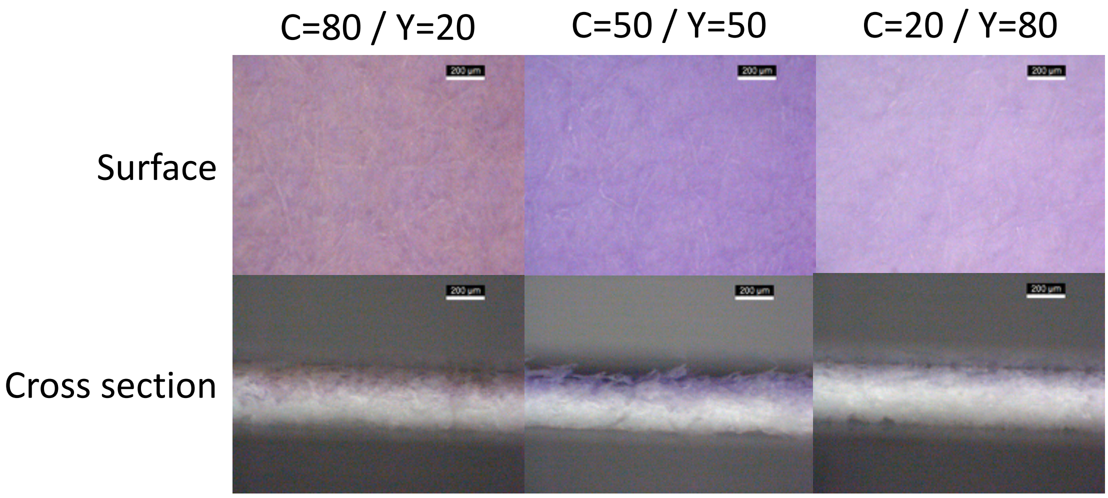


Figure S6: Surface and cross-sectional views of filter papers with inkjet-deposited reagents for the Nitro-PAPS/Ni^{2+} system after the completed printing process.

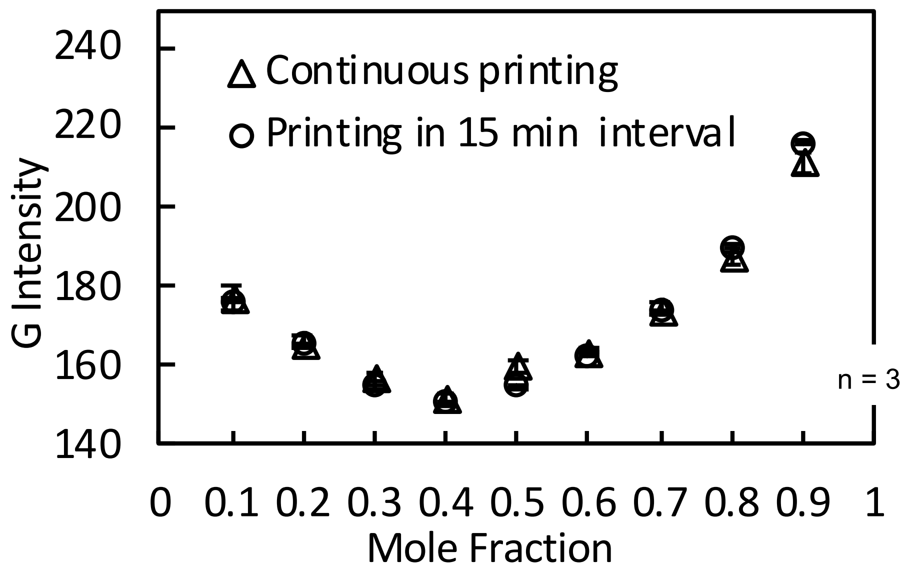


Figure S7. Comparison of inkjet-based Job plots for the Nitro-PAPS/Ni^{2+} system with and without an interval time between multiple reagent print cycles.

Table S1. Detailed inkjet-printing conditions of reagents for the Job plot analysis on paper.

System	Reagent inks			Buffer ink		Used colour coordinate
	Ink composition	Printing cycles	Solute wt%	Buffer condition	Printing cycles	
Zincon /Cu^{2+}	Zincon 2.0 mM aq. with 2 mM of NaOH	5	0.100	9.0	2	Red
	$CuCl_2$ 2.0 mM aq.	5	2.69×10^{-2}			
Nitro-PAPS /Ni^{2+}	Nitro-PAPS 2.0 mM aq.	5	0.101	6.0	2	Green
	$NiCl_2$ 2.0 mM aq.	5	2.59×10^{-2}			
BCS/Cu^{+}	BCS 4.0 mM aq.	10	0.226	6.0 (10 mM of ascorbic acid is added)	2	Grey
	$CuCl_2$ 4.0 mM aq.	10	5.38×10^{-2}			
Tiron/Fe^{3+}	Tiron 50 mM aq.	5	1.66	-	-	Grey
	$FeCl_3\cdot6H_2O$ 50 mM aq. with 10 mM H_2SO_4	5	0.909			
Nitroso-PSAP /Fe^{2+}	Nitroso-PSAP 2.0 mM aq.	10	6.05×10^{-2}	7.5 (5 mM of ascorbic acid is added)	2	Red
	$FeCl_3\cdot6H_2O$ 2.0 mM aq. with 10 mM H_2SO_4	10	0.131			

Table S2. Evaluation of Acid Blue 9 rehydration efficiency.

Pipetted amount of Acid Blue 9		Absorbance at 629 nm[a]	Rehydrated moles[b]	Recovery[c]
Volume of 10 mM solution	Moles			
1 μL	10 nmol	0.643 ± 0.003	9.96 ± 0.05 nmol	99.6 %

[a] The average and standard deviations were calculated from four independent measurements. [b] Calculated based on the measured absorbance and the calibration curve shown in Figure S3. [c] Recovery (%) calculated as 100 × (rehydrated mole/pipetted mole).

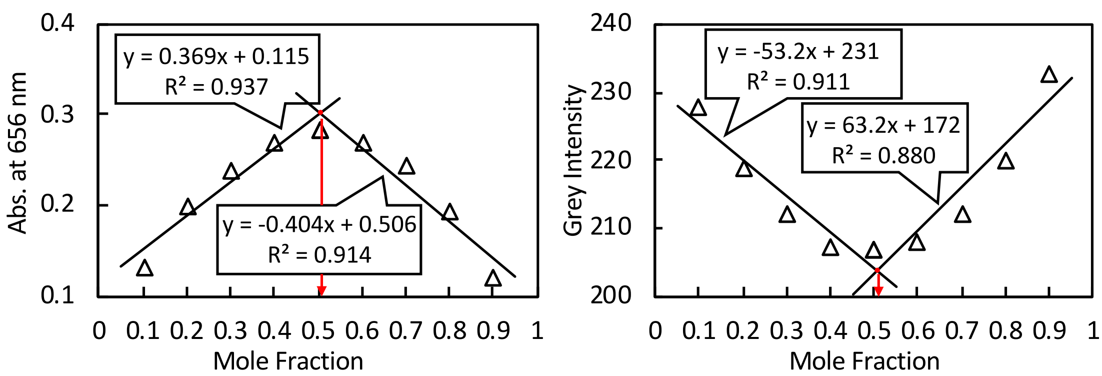
Table S3. Properties of the examined indicator-metal ion complexes.

Indicator-metal ion complex	Colorimetric response of indicator		Reported stoichiometry (metal ion : indicator)	Reference
	Metal-free form	After complexation		
Zincon/Cu^{2+}	Pink	Blue	1 : 1	1
Nitro-PAPS/Ni^{2+}	Orange	Purple	1 : 2	2
BCS/Cu^{+}	Colourless	Orange	1 : 2	3
Tiron/Fe^{3+} at pH<2.5	Colourless	Blue	1 : 1	4
Nitroso-PSAP/Fe^{2+}	Red	Yellowish green	1 : 3	5

Table S4. Mole fractions of highest complex concentrations obtained by linear curve fitting (for details, see below).

	Zincon/Cu^{2+}	Nitro-PAPS/Ni^{2+}	BCS/Cu^{+}	Tiron/Fe^{3+} pH<2.5	Nitroso-PSAP/Fe^{2+}
Absorbance-based	0.53	0.39	0.29	0.51	0.28
Inkjet-based	0.53	0.42	0.29	0.51	0.27
Expected	0.50	0.33	0.33	0.50	0.25

Curve fitting method: A very simple curve fitting procedure has been applied to estimate the mole fraction of highest complex concentration. Independent of the actual shape of the plot, two linear regression curves were fitted into each job plot, and their intersection is reported as the mole fraction of highest complex concentration in the table above. Linear regression was performed between the maximum and minimum color intensities (inkjet-based data) or the minimum and maximum absorbance values (and the minimum color intensity (solution-based data), wherein the minimum color intensity and the maximum absorbance value was included into both line segments, as shown representatively for Tiron/Fe^{3+} in the graph below:



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(3) Campos, C.; Guzmán, R.; López-Fernández, E.; Casado, Ángela. *Anal. Biochem.* **2009**, *392* (1), 37–44.

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(5) Nakagawa, K.; Tsujimoto, T.; Nishino, S.; Teramoto, M.; Kawase, Y. Colorimetric method and reagent used for the same. U.S. Patent 8,574,896, Nov. 5, 2013.