

Supporting Information

One-Step Colorimetric Acid-Base Titration Sensor using Complementary Color Changing Coordination System

Hui Hun Cho,^a Si Hyun Kim,^a Jun Hyuk Heo,^b Young Eel Moon,^c Young Hun Choi,^c Dong Cheol Lim,^d Kwon-Hoon Han,^b Jung Heon Lee^{a,b*}

^a *SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea*

^b *School of Advanced Materials Science and Engineering, Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea*

^c *Citrus Research Institute, National Institute of Horticulture and Herbal Science in RDA, Jeju Special Self-Governing Province 63607, Republic of Korea*

^d *Sunforest Inc., Incheon IT Tower #507, Gyeongin-ro 229, Nam-gu, Incheon-city 22106, Republic of Korea*

**correspondence should be addressed to Jung Heon Lee (jhlee7@skku.edu)*

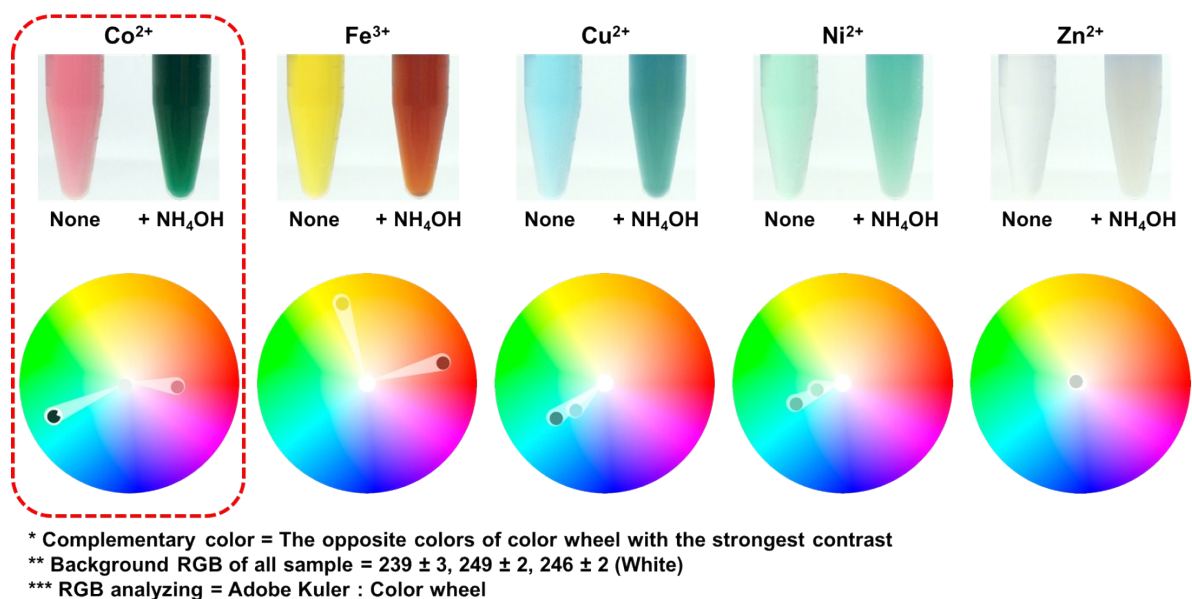


Fig. S1 The color changes and RGB analyses of five transition metals (Co^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , and Zn^{2+} respectively) before and after NH_4OH treatment in 1 : 3 molar ratio. The background color of each sample was fixed a color coordinate (239, 249, 246). All colors were analyzed by Adobe Kuler : Color wheel.

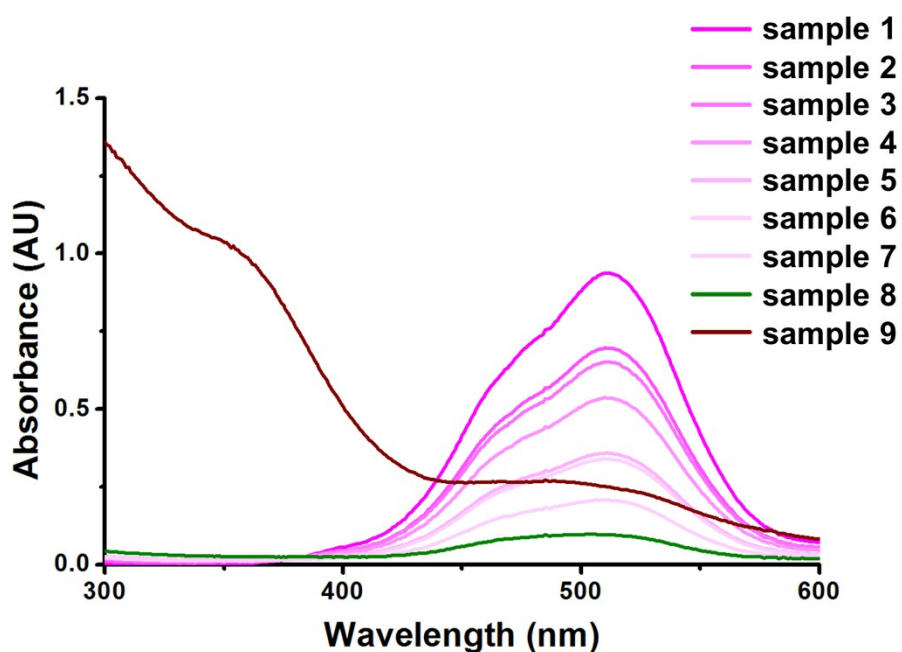


Fig. S2 Absorption spectra of the supernatant of samples treated with various concentrations of NH_4OH (sample 0 to 0.73). The concentration noted next to each sample name in the legend is the final molarity of NH_4OH treated.

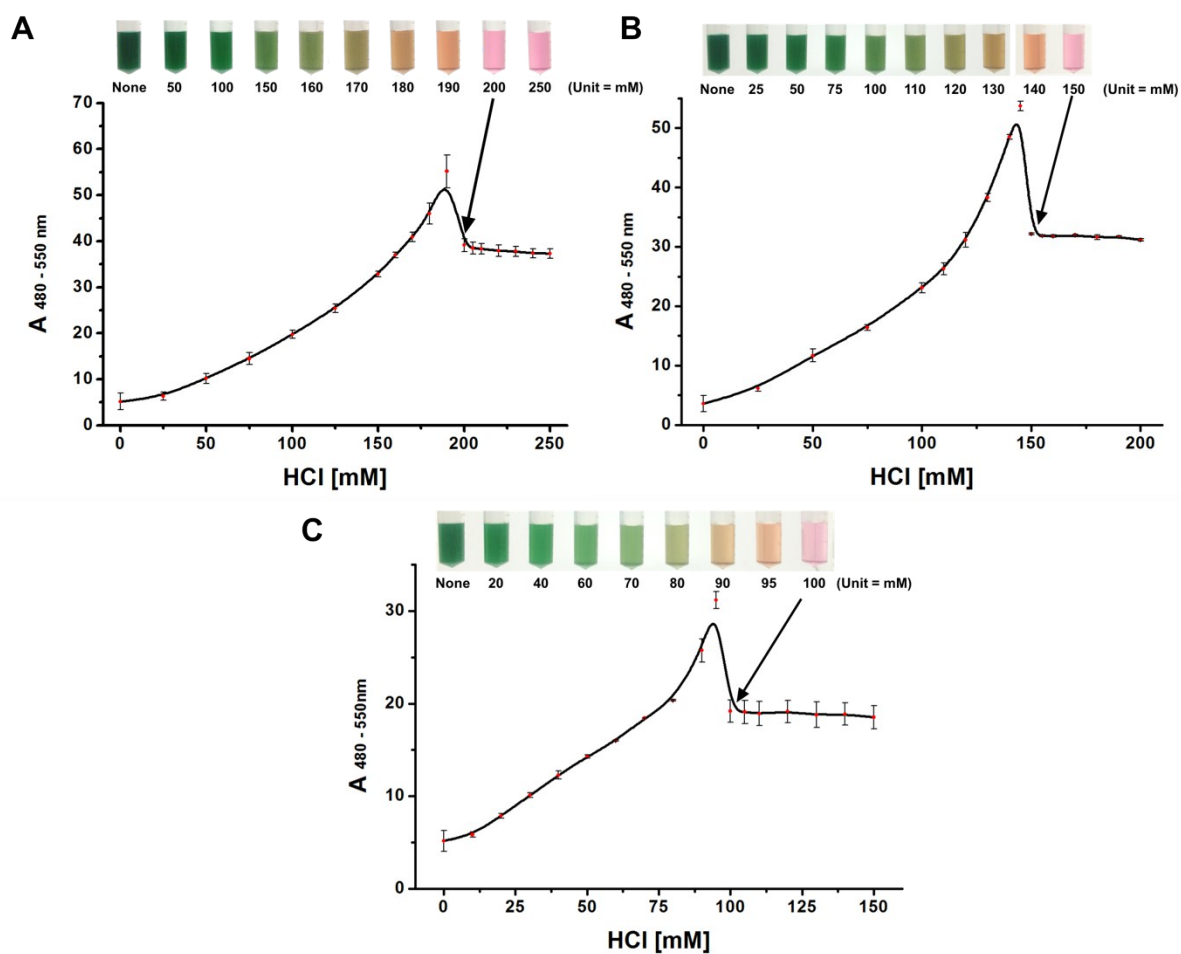


Fig. S3 Photograph and absorbance within 480 – 550 nm of the supernatant of Co-complex sensor after treatment with different concentrations of hydrochloric acid (HCl, Unit = [mM]). The concentration of Co-complex sensor tested is 100 mM (A), 75 mM (B), and 50 mM (C), respectively. The absorbance of supernatant of the Co-complex sensor in 480 – 550 nm range showed increase with the concentration of hydrochloric acid up to 200, 150, and 100 mM HCl, respectively, which corresponds to the equivalent point of 100, 75, and 50 mM Co-complex sensor. The detection limit of 100, 75, and 50 mM Co-complex sensor turned out to be 52.0 mM, 30.1 mM, and 18.8 mM HCl, respectively.

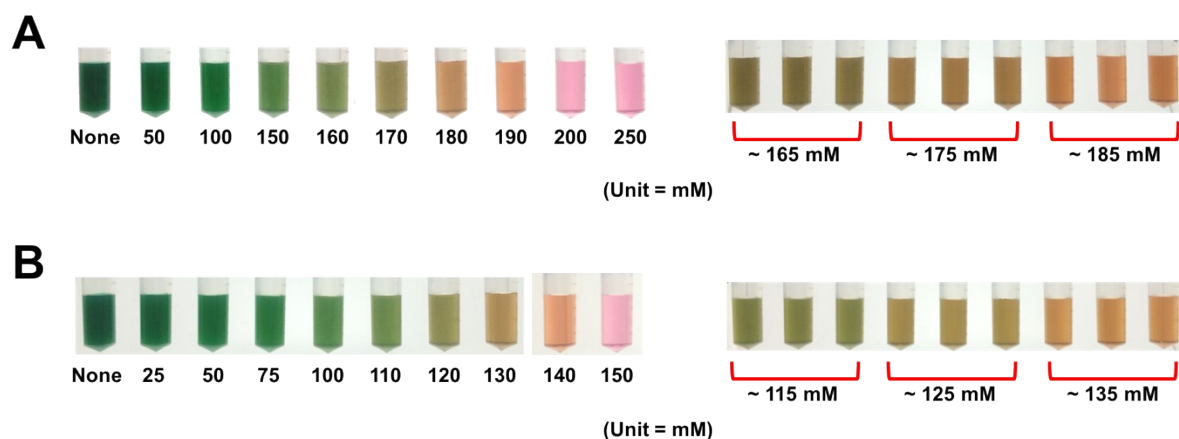


Fig. S4 Quantitative acid content measurement carried out with Co-complex sensor. (A) 100 mM and (B) 75 mM Co-complex sensor were treated with triplet HCl samples of three unknown concentrations, respectively. The actual HCl concentration of tested samples were 165, 175, and 185 mM for 100 mM Co-complex sensor and 115, 125, and 135 mM for 75 mM Co-complex sensor.

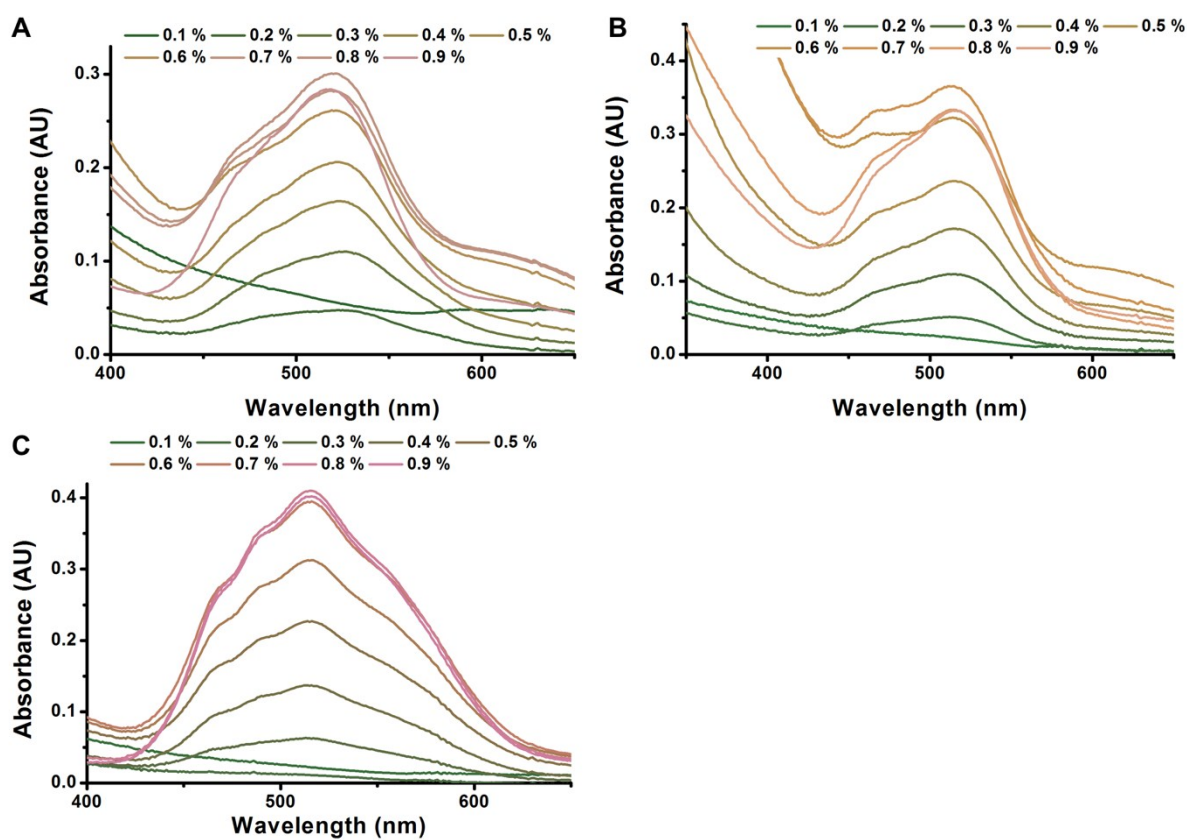


Fig. S5 Absorption spectra of the supernatant of Co-complex sensor after treatment with various concentration of citric acid (A), malic acid (B), and tartaric acid (C).

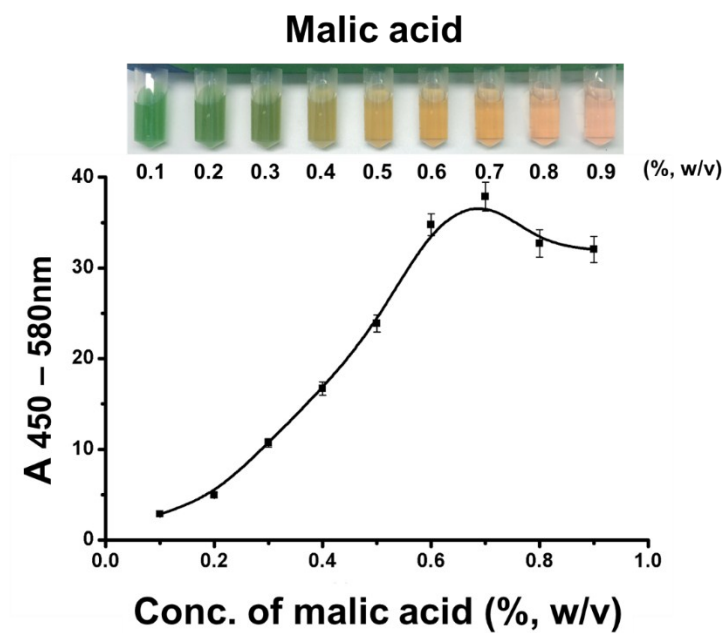


Fig. S6 Photograph of the supernatant of Co-complex sensor after treatment with malic acid of 0 to 0.9 % (w/v). The absorbance curve of supernatant of the Co-complex sensor in 450 – 580 nm range showed linear increase as the concentration of malic acid increase from 0.2 – 0.7 %.

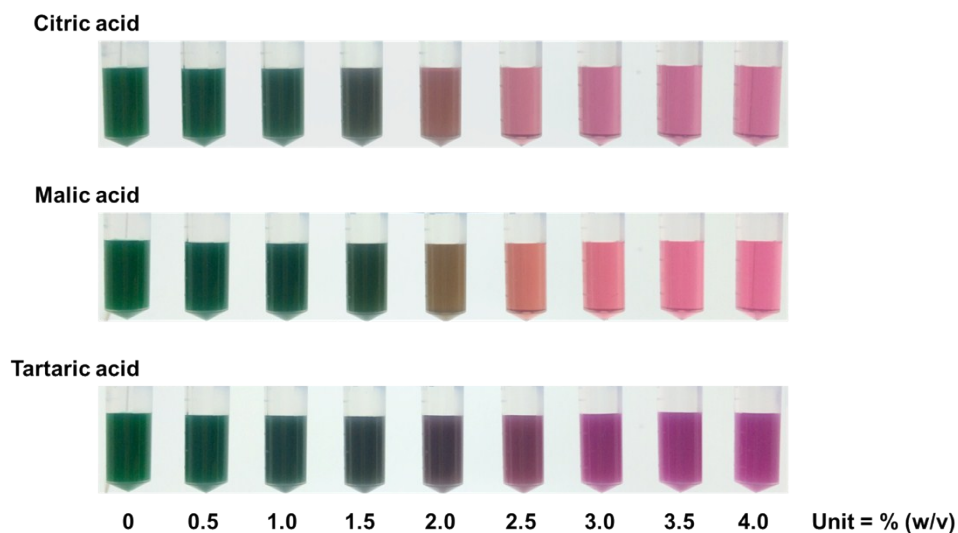


Fig. S7 Photograph of Co-complex sensors treated with used here is 4 times concentrated then those used in Fig. 3A, B and Fig. S4. This shows that the dynamic range of this sensor can be tuned by changing its concentration.

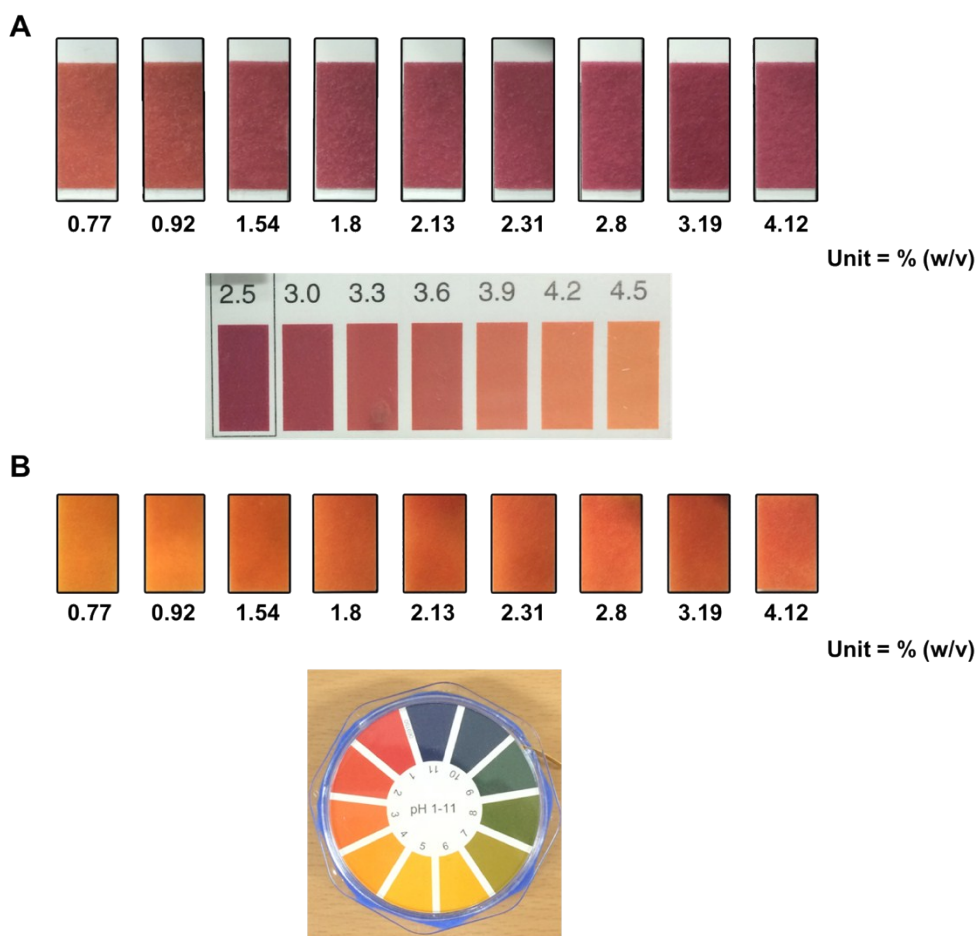


Fig. S8 Photograph of real tangerine juice samples tested with (A) pH indicator strips ranging from 2.5 to 4.5 (Merck KGaA) and (B) pH indicator paper ranging from 1 to 11 (Macherery-Nagel GmbH). The change of the color of pH strips or papers was negligible when they were treated with real tangerine juice samples with different concentrations of citric acid. On the other hand, the color change was significant when Co complex sensor was treated with the same real tangerine juice samples (see Fig. 3C).

Calculation of pK_a , pK_b , and equivalent point of Cobalt hydroxide precipitate

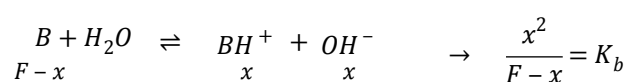
Table S1 The total pH values of Co-complex sensor treated with hydrochloride acid

(Average values of three samples)

| [HCl] | pH |
|-------|-------------|
| 0 | 9.76 ± 0.02 |
| 25 | 8.58 ± 0.01 |
| 50 | 8.21 ± 0.02 |
| 75 | 8.04 ± 0.01 |
| 100 | 7.92 ± 0.01 |
| 125 | 7.82 ± 0.02 |
| 150 | 7.73 ± 0.01 |
| 160 | 7.62 ± 0.01 |
| 170 | 7.70 ± 0.01 |
| 180 | 7.54 ± 0.01 |
| 190 | 7.24 ± 0.17 |
| 195 | 5.21 ± 0.59 |
| 200 | 3.17 ± 0.26 |
| 205 | 2.64 ± 0.04 |
| 210 | 2.38 ± 0.03 |
| 220 | 2.14 ± 0.02 |
| 230 | 1.98 ± 0.01 |
| 240 | 1.83 ± 0.02 |
| 250 | 1.77 ± 0.01 |
| 300 | 1.45 ± 0.02 |

From Table S1, [HCl] = 0 mM, pH = 9.76

According as the equation of titration and dissociation constant,¹

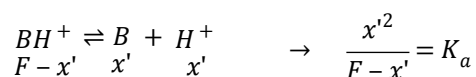


$B = \text{Basic analyte}$, $F = [\text{analyte}] = 1 : 1$ (v/v) reaction of cobalt precipitate $\approx \frac{0.2 M}{2} \approx 0.1 M$

$$x = 10^{-pOH} = 10^{-(14 - 9.76)} = 5.75 \times 10^{-5} M, F - x \approx F (x \ll F)$$

$$pK_b = 7.48 \leftrightarrow pK_a = 6.52 (\because pK_b + pK_a = 14)$$

From pK_a , pH of equivalent point is calculated below.



$F \approx 0.1 \text{ M}$, $pK_a = 6.52$, and assume that $F - x' \approx F$ ($x' \ll F$)

$$x' = 1.74 \times 10^{-4} \text{ M} \leftrightarrow \text{pH} = 3.76$$

According to Table S1, concentration of [HCl] at equivalent point (A mM) is followed below.

| | | | |
|-------|-----------------|------|-----------------|
| [HCl] | 195 mM | A mM | 200 mM |
| pH | 5.21 ± 0.59 | 3.76 | 3.17 ± 0.26 |

A comes between 195 and 200 mM, and final concentration of cobalt precipitate is 0.1 M

Accordingly, cobalt precipitation: [HCl] \approx 1 : 2

Table S2 The pH values of real tangerine juice and artificial citric acid solution with identical concentrations of citric acid. The pH value of each solution at 0.77 % is 2.08 and 3.28 respectively.

| Concentration of citric acid (% w/v) | 0.77 | 0.92 | 1.54 | 1.8 | 2.13 | 2.31 | 2.8 | 3.19 | 4.12 |
|--|------|------|------|------|------|------|------|------|------|
| pH of artificial citric acid solution | 2.08 | 2.02 | 1.91 | 1.86 | 1.82 | 1.77 | 1.72 | 1.70 | 1.62 |
| pH of real tangerine juice | 3.28 | 3.16 | 2.74 | 2.54 | 2.52 | 2.45 | 2.36 | 2.33 | 2.30 |

1 D. C. Harris, *Quantitative chemical analysis*, W. H. Freeman and Company, 7 edn. 2007.