# A Portable Paper-Based and Smartphone-Assisted Colorimetric Sensor for Copper Oxychloride

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## Supplementary Material

1. **Synthesis of coumarin triazole**

### Step 1: Synthesis of 4-(3-bromopropoxy)-3-methoxybenzaldehyde

Vanillin (152 mg, 1 mmol), potassium carbonate (137 mg, 1 mmol), and acetone (10 mL, HPLC grade) were added into a 50 mL round-bottom flask. The mixture was refluxed at 60 °C for 2 h. After this time, 1,3-dibromopropane (200 µL, 2 mmol) was added dropwise, and the reaction mixture was refluxed for a further 12 h at the same temperature. After completion (monitored by TLC), the reaction was cooled to room temperature and quenched with water. The inorganic salts were removed by aqueous washing, and the organic product was extracted with dichloromethane (DCM). The combined organic extracts were dried and concentrated to afford 4-(3-bromopropoxy)-3-methoxybenzaldehyde.

### Step 2: Synthesis of 4-(3-azidopropoxy)-3-methoxybenzaldehyde

The brominated intermediate obtained from step 1 was dissolved in absolute ethanol (7 mL). Sodium azide (325 mg, 5 mmol) was added, and the mixture was stirred at 80 °C for 12 h. Upon completion (TLC monitoring), the reaction mixture was cooled to room temperature, diluted with

water to dissolve excess sodium azide, and extracted with DCM. The organic phase was dried and concentrated to afford 4-(3-azidopropoxy)-3-methoxybenzaldehyde.

**Step 3: Synthesis of 4-(prop-2-yn-1-yloxy)-2H-chromen-2-one**

4-Hydroxycoumarin (162 mg, 1 mmol) was dissolved in acetone (7 mL), and potassium carbonate (137 mg, 1 mmol) was added. The mixture was refluxed at 60 °C for 30 min, followed by the dropwise addition of propargyl bromide (150 µL). The mixture was refluxed for 8 h, and the progress of the reaction was monitored by TLC (n-hexane/ethyl acetate). After completion, the mixture was cooled, diluted with water, and extracted with DCM. The organic phase was dried and concentrated to yield 4-(prop-2-yn-1-yloxy)-2H-chromen-2-one.

**Step 4: Click Reaction (CuAAC) to Form the Final Triazole-Linked Hybrid**

The alkyne derivative (200 mg, 1 mmol) and the azide derivative (235 mg, 1 mmol) were dissolved in DMF (5 mL) in a 50 mL round-bottom flask. Copper sulfate (5 mol%) and sodium ascorbate (20 mol%) were added as the catalytic system. The reaction was stirred at 70 °C for 4 h. After completion (TLC monitoring), the mixture was cooled, and ice-cold water was added to precipitate the product. The precipitate was collected by filtration, dried, and further purified by column chromatography (n-hexane/ethyl acetate). The final product was obtained as a brown crystalline solid in good yield.

**Yield**: 304.5 mg, 70 %, brown crystalline solid

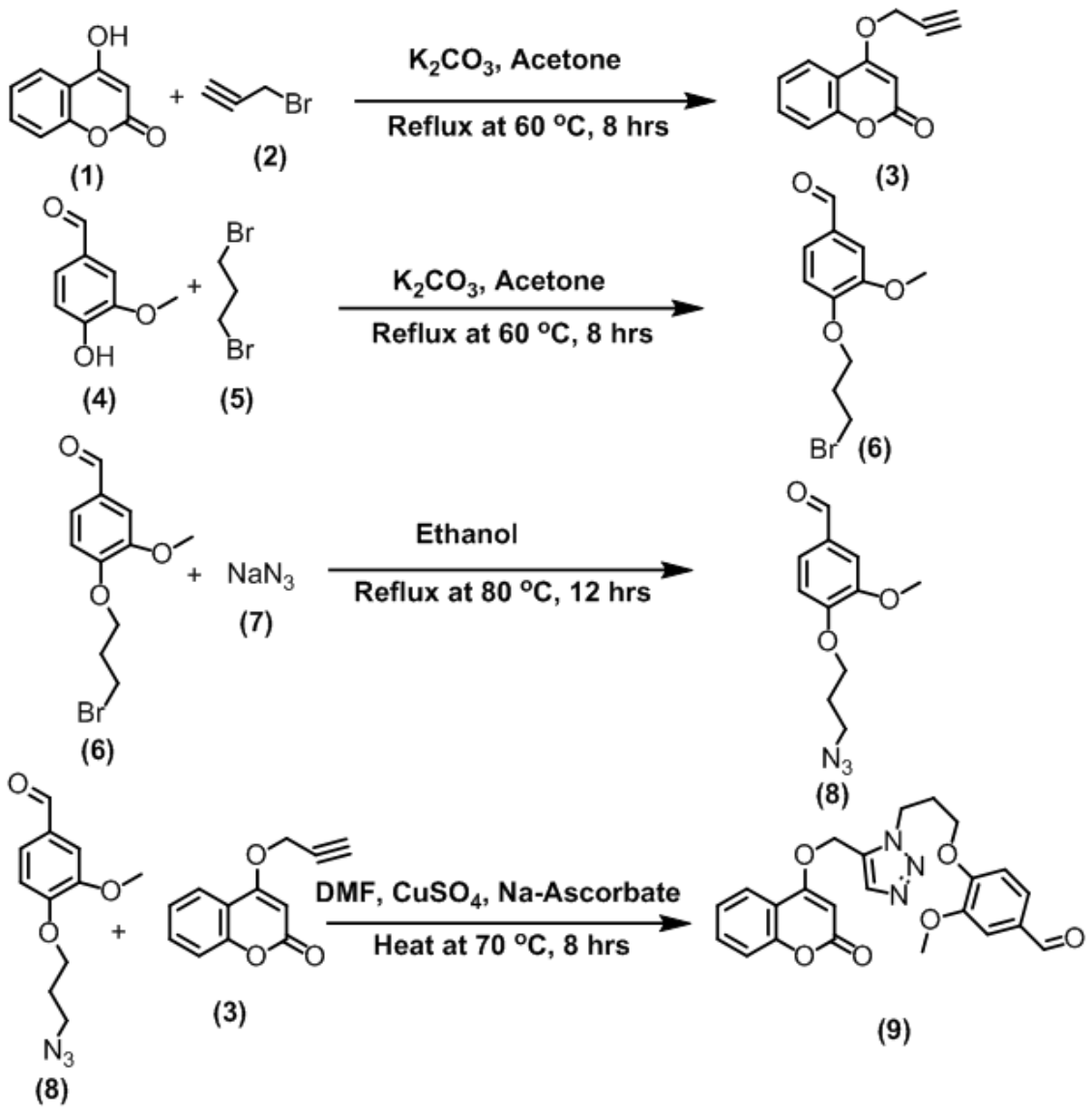
**FAB-MS**: the observed mass 436 *m/z* and calculated mass 435.15 *m/z*

**$^1$HNMR (400 MHz, CDCl3) δ**: 3.89 (s, 3H, -$OCH_3$), 4.03 (q, 2H, $CH_2$, *J*: 5.6 Hz), 4.63 (t, 2H, $CH_2$, *J*: 1.6 Hz), 5.12 (s, 1H, CH), 5.21 (s, 2H, $CH_2$), 6.21 (t, 1H, CH, *J*: 9.6 Hz), 6.73 (d,d, 1H, CH, *J*: 2.4 Hz), 6.85 (d, 1H, CH, *J*: 2.4 Hz), 6.87 (d, 1H, CH, *J*: 1.2 Hz), 7.33 (t, 1H, CH, *J*: 1.6 Hz), 7.38 (t, 1H, CH, *J*: 1.6 Hz), 7.58 (d, 1H, CH, *J*:9.6 Hz), 7.69 (s, 1H, CH), 9.9 (d, 1H, aldehyde, *J*: 16.4 Hz).

## 2. Results and discussions

CT was synthesized via a click reaction and characterized by FAB-MS to determine its molecular mass. A molecular ion peak was observed at *m/z* 436, which is in agreement with the calculated mass of 435.15 (*m/z*) for the molecular formula $C_{23}H_{21}N_3O_6$ (Figure S1).

The $^1$H-NMR spectrum of CT was recorded in $CDCl_3$ using tetramethylsilane (TMS) as an internal reference on a Bruker 400 MHz spectrometer. A singlet corresponding to three protons of the methoxy group appeared at δ 3.89 ppm. A quartet for two protons of a –$CH_2$– group was observed at δ 4.03 ppm (J = 5.6 Hz), while a triplet for two protons of another –$CH_2$– group appeared at δ 4.63 ppm (J = 1.6 Hz). A singlet corresponding to one proton of a –CH– group was observed at δ 5.12 ppm, and another singlet for two protons of –$CH_2$– appeared at δ 5.21 ppm. A triplet corresponding to one proton of a –CH– group was observed at δ 6.21 ppm (J = 9.6 Hz). Aromatic signals were observed as follows: a doublet for one proton at δ 6.73 ppm (J = 2.4 Hz), a doublet for one proton at δ 6.85 ppm (J = 2.4 Hz), a doublet for one proton at δ 6.87 ppm (J = 1.2 Hz), a triplet for one proton at δ 7.33 ppm (J = 1.6 Hz), a triplet for one proton at δ 7.38 ppm (J = 1.6 Hz), and a doublet for one proton at δ 7.58 ppm (J = 9.6 Hz). A singlet corresponding to one proton of a –CH– group was observed at δ 7.69 ppm. Finally, a singlet for the aldehyde proton appeared at δ 9.90 ppm (Figure S2).




**Scheme S1**. Synthesis scheme of coumarin triazole.

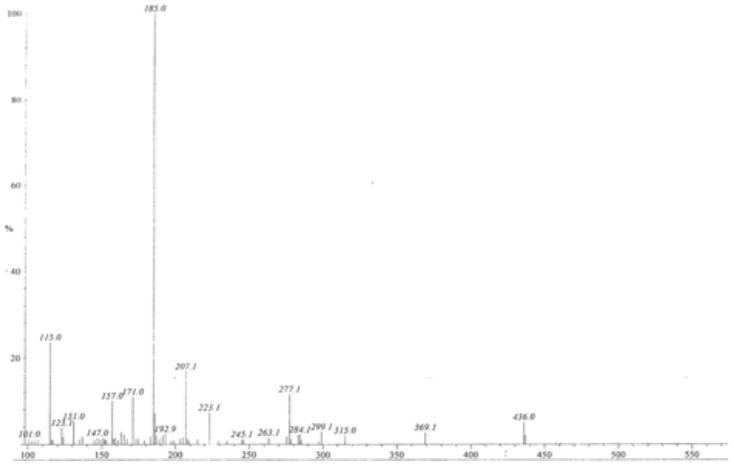



**Figure S1.** FAB-MS spectrum of C.

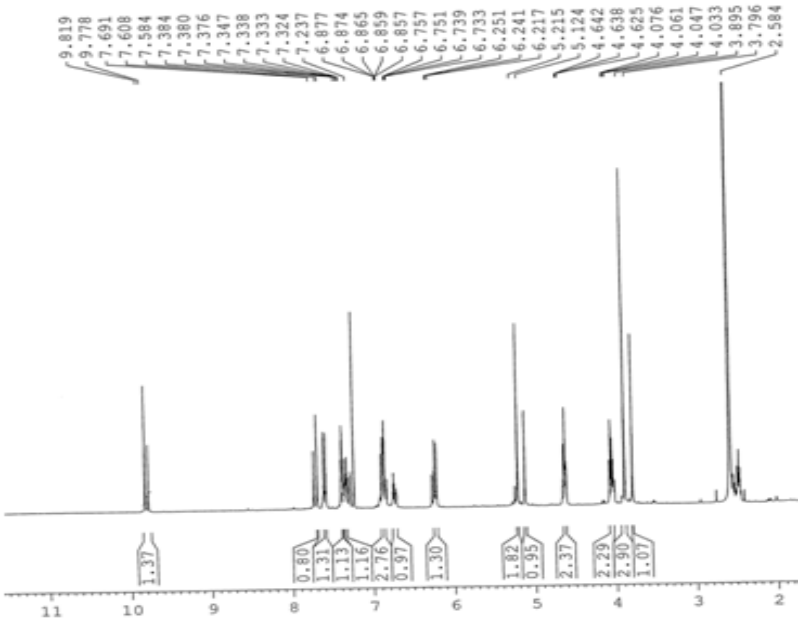



**Figure S2.** $^{1}$H-NMR spectrum of CT.

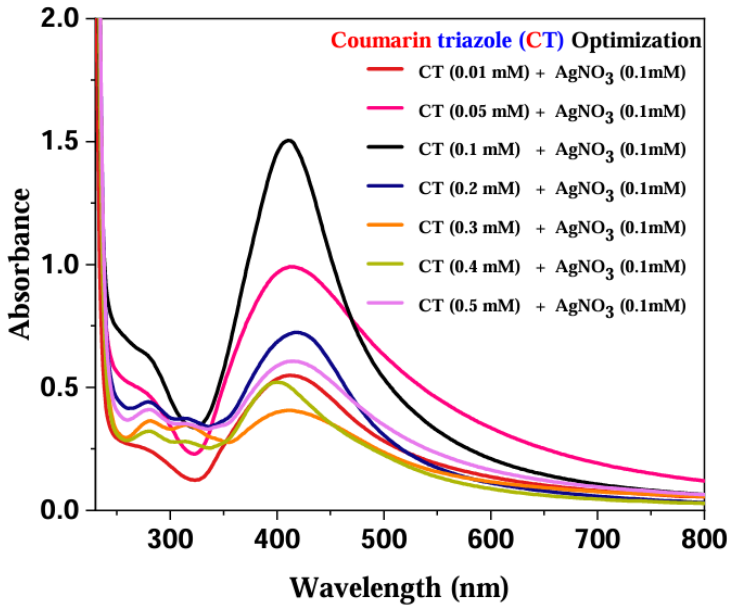



**Figure S3.** Optimization of CT concentration with 0.1 mM $AgNO_3$ for formation of CT-AgNPs through UV-Vis analysis.

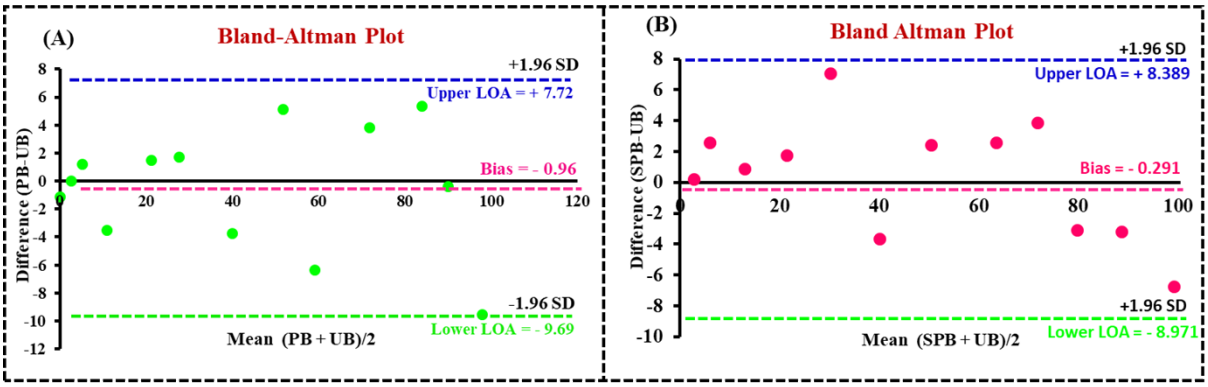



**Figure S4.** Bland–Altman plots comparing copper oxychloride concentrations determined by the paper-based (PB) (A) and smartphone-based (SPB) (B) methods with the UV–visible spectrophotometric reference method.

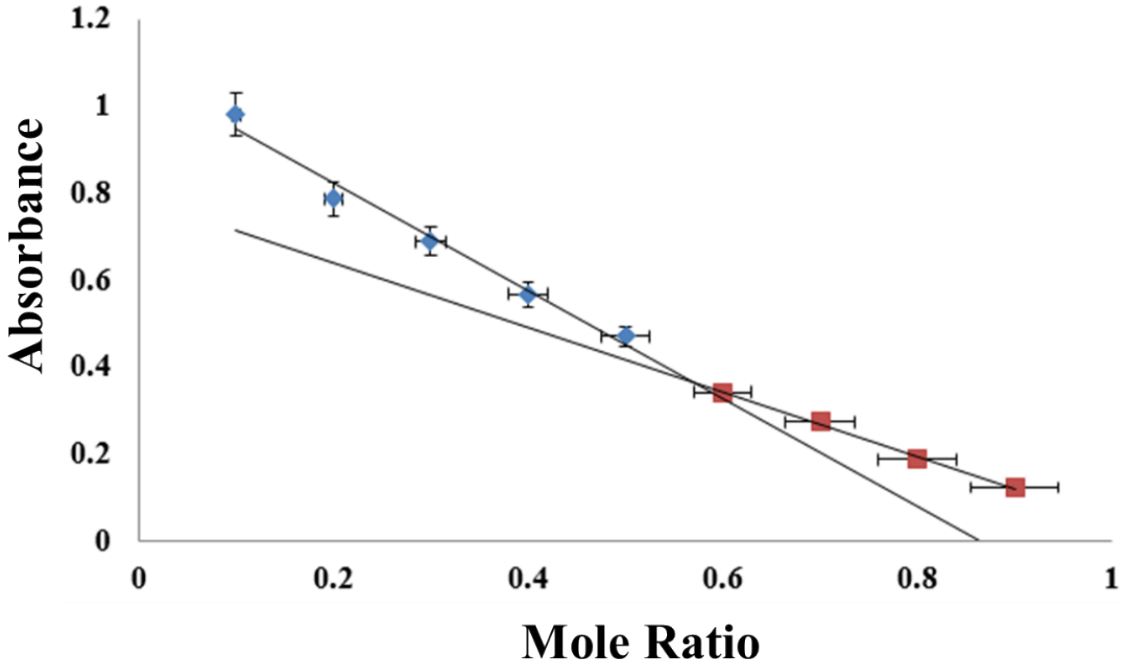



**Figure S5.** Job plot of CT-AgNPs and CuOxy.

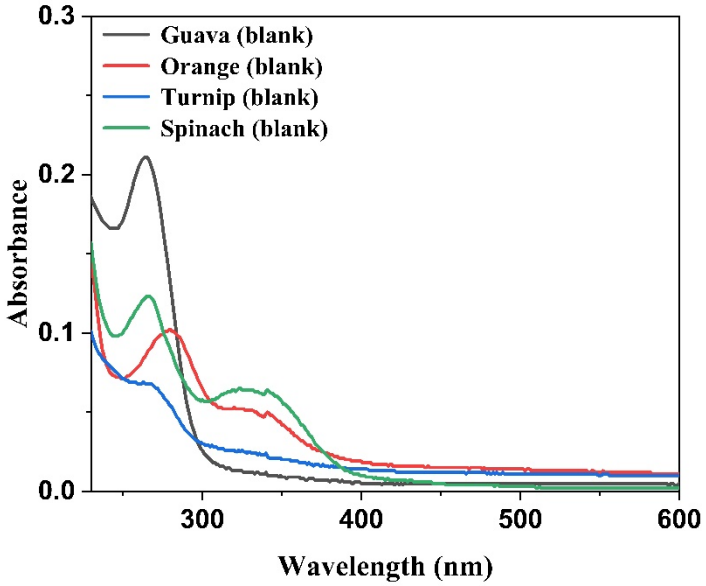



**Figure S6.** Matrix blank for real samples (Guava, Orange, Turnip, Spinach).

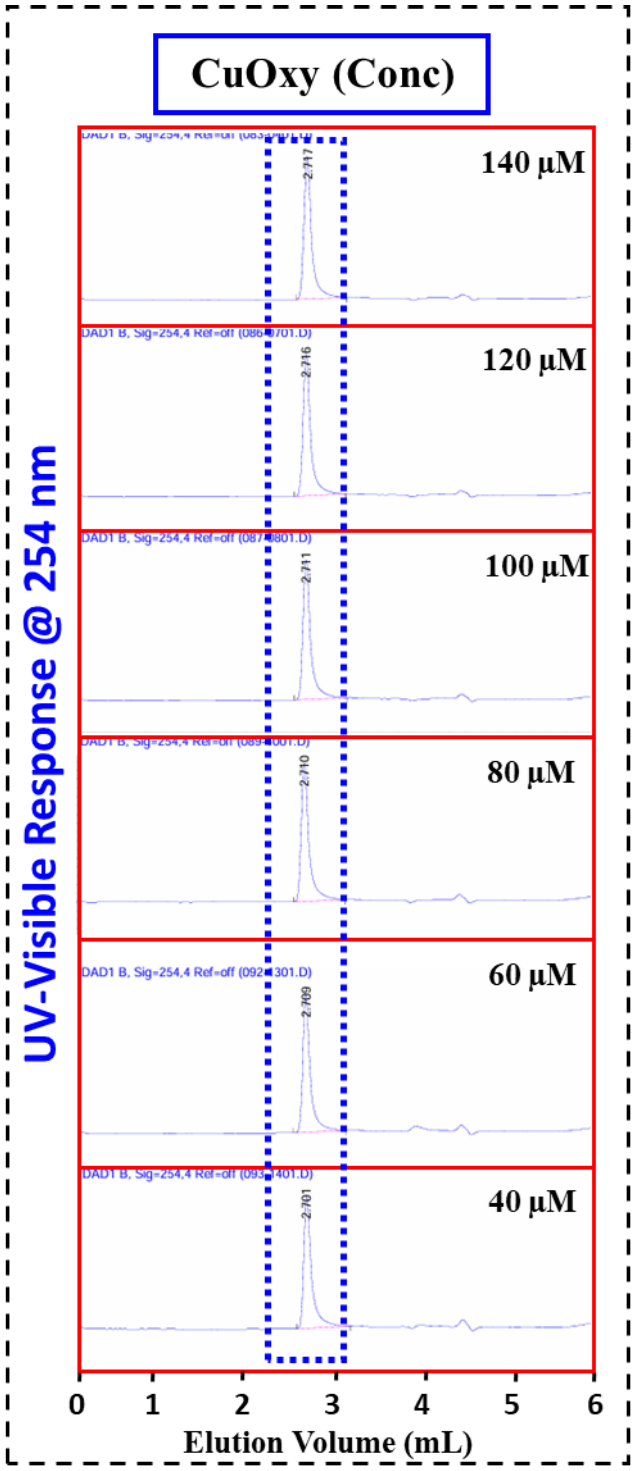



**Figure S7.** UPLC elugrams of different concentrations of Cuoxy chloride in DI water, Column: Octadecyl Silica column (250 × 6.0 mm, JH08S04-2506WT), mobile phase: 30% Milli-Q water and 70% acetonitrile (ACN), flow rate: 1.0 mL $min^{-1}$, UV-detection at 254 nm.

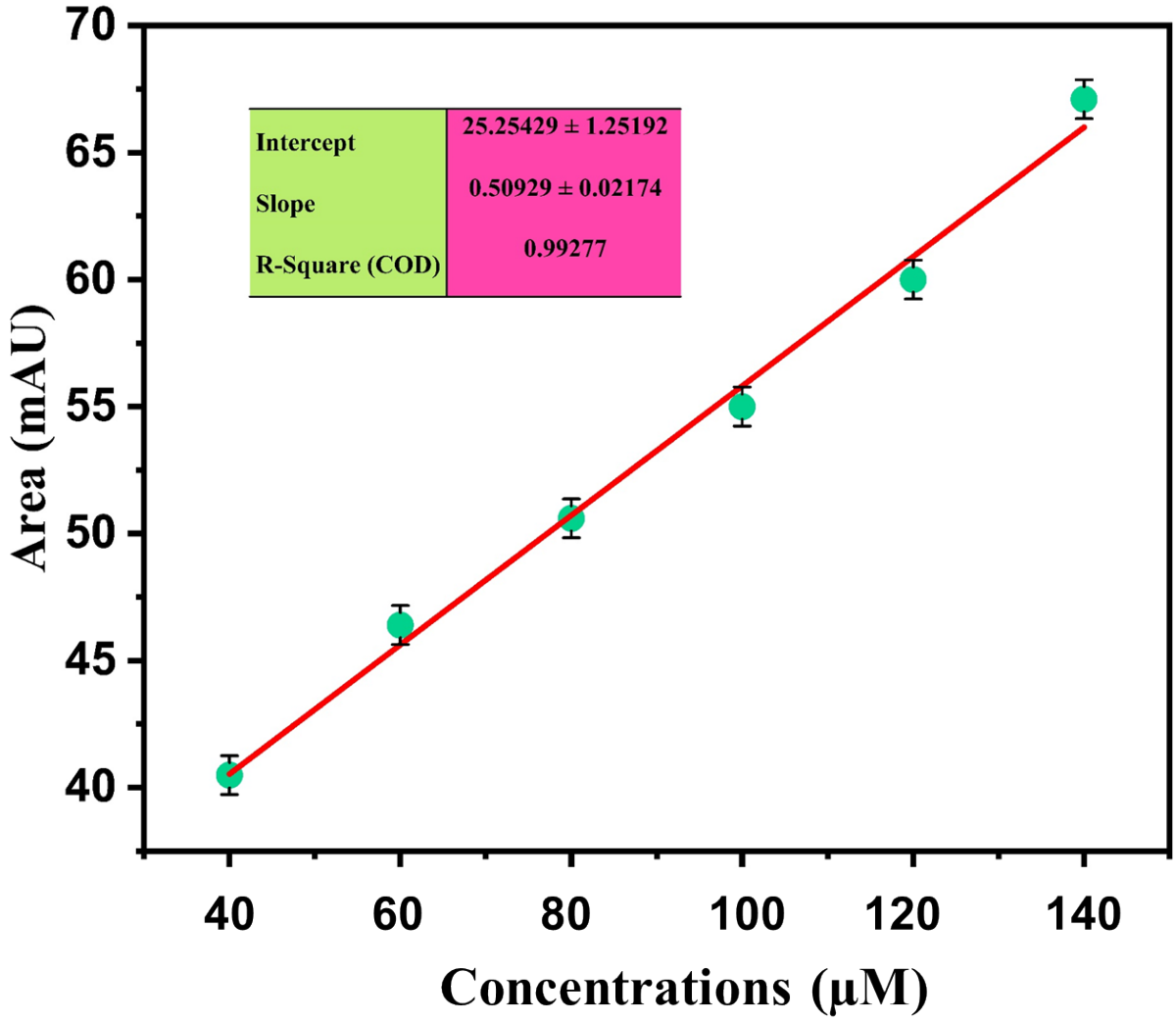



**Figure S8.** Area of the detector curve (2.8 mL) as a function of different concentrations of Cuoxy chloride, Column: Octadecyl Silica column (250 × 6.0 mm, JH08S04-2506WT), mobile phase: 30% Milli-Q water and 70% acetonitrile (ACN), flow rate: 1.0 mL $min^{-1}$, UV-detection at 254 nm.

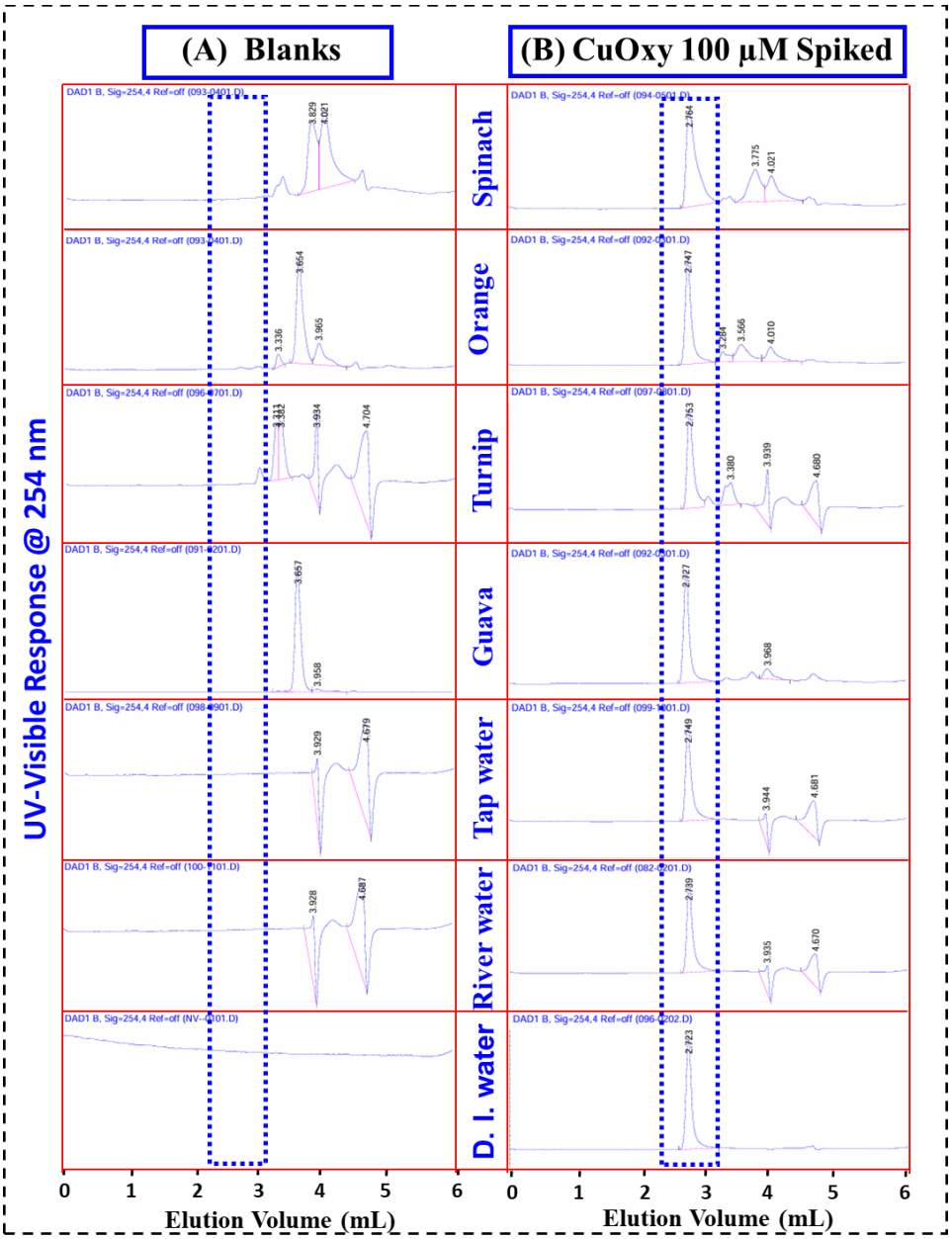



**Figure S9.** Analysis of real samples for CuOxy chloride concentration, (A) Blanks, (B) spiked with 100 µM, Column: Octadecyl Silica column (250 × 6.0 mm, JH08S04-2506WT), mobile phase: 30% Milli-Q water and 70% acetonitrile (ACN), flow rate: 1.0 mL $min^{-1}$, UV-detection at 254 nm.

**Table S1.** Recoveries of the spiked amount of CuOxy in the presence of an equal amount of potential interfering compounds (70 µM CuOxy chloride + 70 µM interferent) using the UV-Visible spectroscopic *method.*

| **CT-AgNPs + CuOxy chloride (70 µM) + Interferent (70 µM)** | **Detected CuOxy (µM)** | **Recovery (%)** |
|---|---|---|
| CT-AgNPs + CuOxy chloride + **blank** | 69.85 ± 0.20 | 99.79 ± 0.28 |
| CT-AgNPs + CuOxy chloride + **Isoproturin** | 71.57 ± 0.72 | 102.25 ± 1.03 |
| CT-AgNPs + CuOxy chloride + **Chlorothalonil** | 69.51 ± 0.53 | 99.29 ± 0.75 |
| CT-AgNPs + CuOxy chloride + **Abamectin** | 68.69 ± 1.22 | 98.13 ± 1.74 |
| CT-AgNPs + CuOxy chloride + **Propanil** | 71.69 ± 0.60 | 102.41 ± 0.86 |
| CT-AgNPs + CuOxy chloride + **Trifluralin** | 73.30 ± 1.22 | 104.72 ± 1.74 |
| CT-AgNPs + CuOxy chloride + **Urea** | 70.76 ± 1.22 | 101.09 ± 1.74 |
| CT-AgNPs + CuOxy chloride + **Imidacloprid** | 72.15 ± 0.53 | 103.07 ± 0.75 |
| CT-AgNPs + CuOxy chloride + **DAP** | 68.82 ± 0.72 | 98.31 ± 1.03 |
| CT-AgNPs + CuOxy chloride + **Cymoxanil** | 72.72 ± 1.50 | 103.89 ± 2.15 |
| CT-AgNPs + CuOxy chloride + **Amonium Sulphate** | 72.03 ± 0.91 | 102.91 ± 1.30 |
| CT-AgNPs + CuOxy chloride + **Emamectin** | 69.85 ± 0.20 | 99.79 ± 0.28 |
| CT-AgNPs + CuOxy chloride + **Daconil** | 71.57 ± 0.72 | 102.25 ± 1.03 |

**Table S2.** Recoveries of the spiked amount of CuOxy (100 µM) in real samples using UV-Visible, smar*tphone-assisted* solution-based and paper-based methods, along with UPLC, for the sake of validation.

| Matrix | Recovery (%) | | | |
|---|---|---|---|---|
| | **UV-Visible** | **Smartphone solution-based method** | **Smartphone paper-based method** | **UPLC** |
| **DI water** | 101.91 ± 0.20 | 99.08 ± 0.30 | 101.19 ± 1.59 | 99.12 ± 0.57 |
| **River water** | 113.64 ± 1.06 | 105.27 ± 0.19 | 113.84 ± 0.39 | 102.29 ± 0.21 |
| **Tap water** | 113.66 ± 0.69 | 108.13 ± 0.35 | 112.85 ± 0.44 | 106.95 ± 1.55 |
| **Guava** | 98.59 ± 0.69 | 98.85 ± 0.32 | 98.84 ± 1.90 | 91.44 ± 0.53 |
| **Orange** | 93.41 ± 0.69 | 94.97 ± 1.34 | 95.94 ± 0.46 | 90.24 ± 0.53 |
| **Turnip** | 102.49 ± 0.72 | 102.51 ± 1.06 | 104.63 ± 0.97 | 93.75 ± 0.32 |
| **Spinach** | 112.51 ± 3.21 | 107.03 ± 0.58 | 109.35 ± 0.58 | 104.92 ± 1.72 |