

# CoMnO<sub>x</sub> Nanoflower-Based Smartphone Sensing Platform and Virtual Reality Display for Colorimetric Detection of Ziram and Cu<sup>2+</sup>

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## Reagents and Chemicals

Cobaltous nitrate (Co(NO<sub>3</sub>)<sub>2</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), tert-butanol (TBA), sodium azide (NaN<sub>3</sub>), potassium permanganate (KMnO<sub>4</sub>), dimethyl sulfoxide (DMSO), ethylenediamine tetraacetic acid disodium salt (EDTA), riboflavin, *p*-benzoquinone (PBQ), and ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) were supplied by KeLong (Chengdu, China, <http://www.cdkelong.com/>). Ziram was purchased from Macklin Biochemical Co. Ltd. (Shanghai, China, <http://www.macklin.cn/>). 3,3',5,5'-Tetramethylbenzidine (TMB) was obtained from Shanghai Ryon Biological Technology Co. Ltd. (Shanghai, China, <http://ruien.company.lookchem.cn/>). All the chemicals used in experiments were analytically pure. All experiments used deionized water (18.25 MΩ·cm<sup>-1</sup>).

## Characterization Equipment

The crystal structure, morphological structure, elemental composition and surface functional groups were analyzed by X-ray diffraction (XRD, DX-2700, Dandong, China), transmission electron microscope (TEM, JSM4800F, JEOL, Japan), scanning electron microscope (SEM, JEOL-2100F, Japan), X-ray photoelectron spectroscopy

(XPS, ESCALAB-250Xi, China), and Fourier transform infrared spectrometer (FTIR, Bruker Vertex 70, China), respectively.

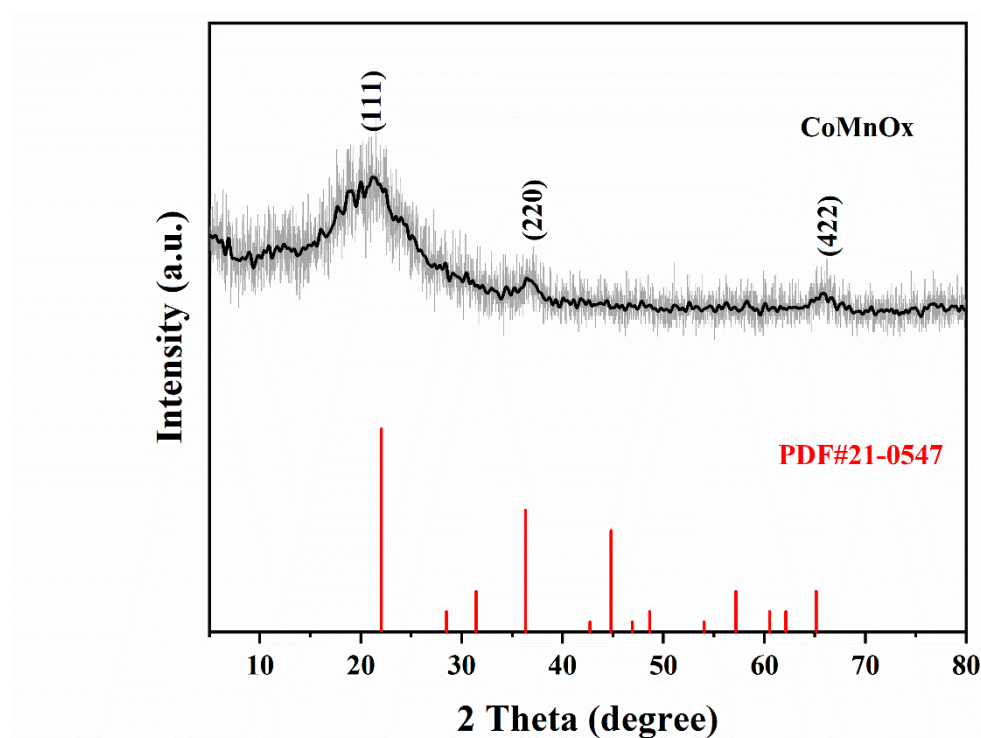


Figure S1. XRD image of CoMnO<sub>x</sub>.

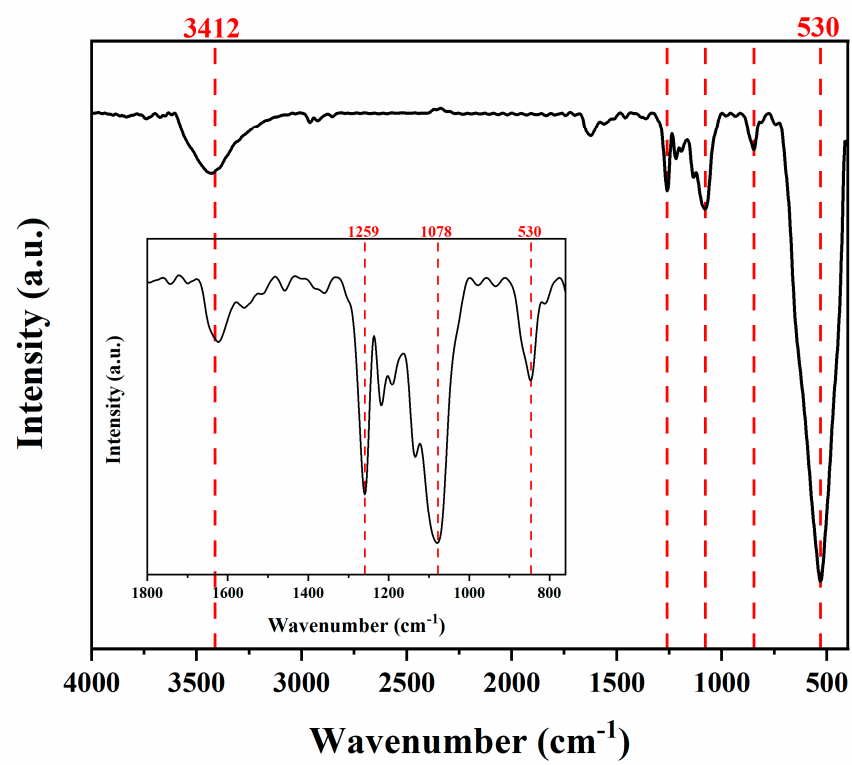


Figure S2. FTIR spectrum of CoMnO<sub>x</sub>.

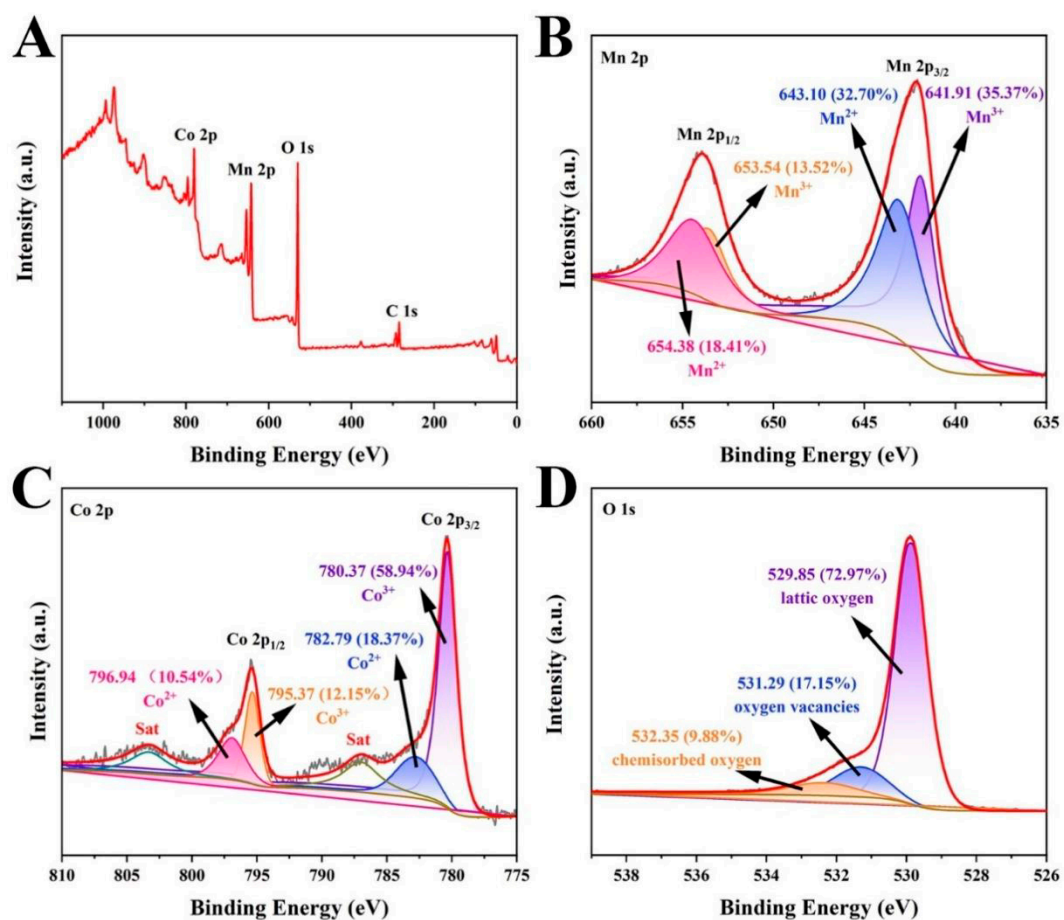


Figure S3. (A) XPS full spectrum; (B) Mn 2p, (C) Co 2p and (D) O 1s spectra of CoMnO<sub>x</sub>.

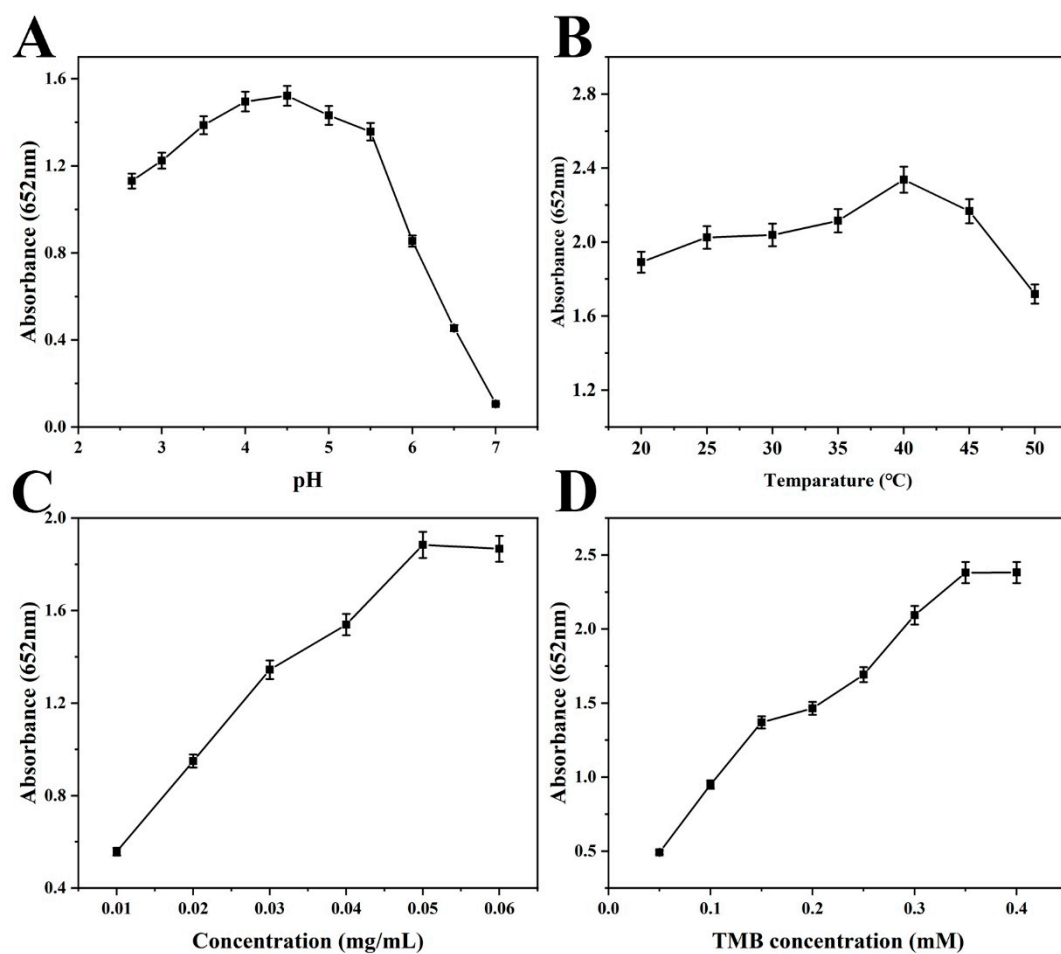


Figure S4. Optimization of reaction conditions for CoMnO<sub>x</sub> oxidase-like activity. (A) pH; (B) Temperature; (C) Material concentration; (D) TMB concentration ( $n=3$ ).

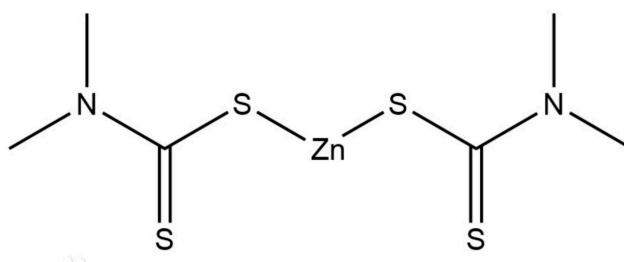


Figure S5. Chemical structure of Ziram

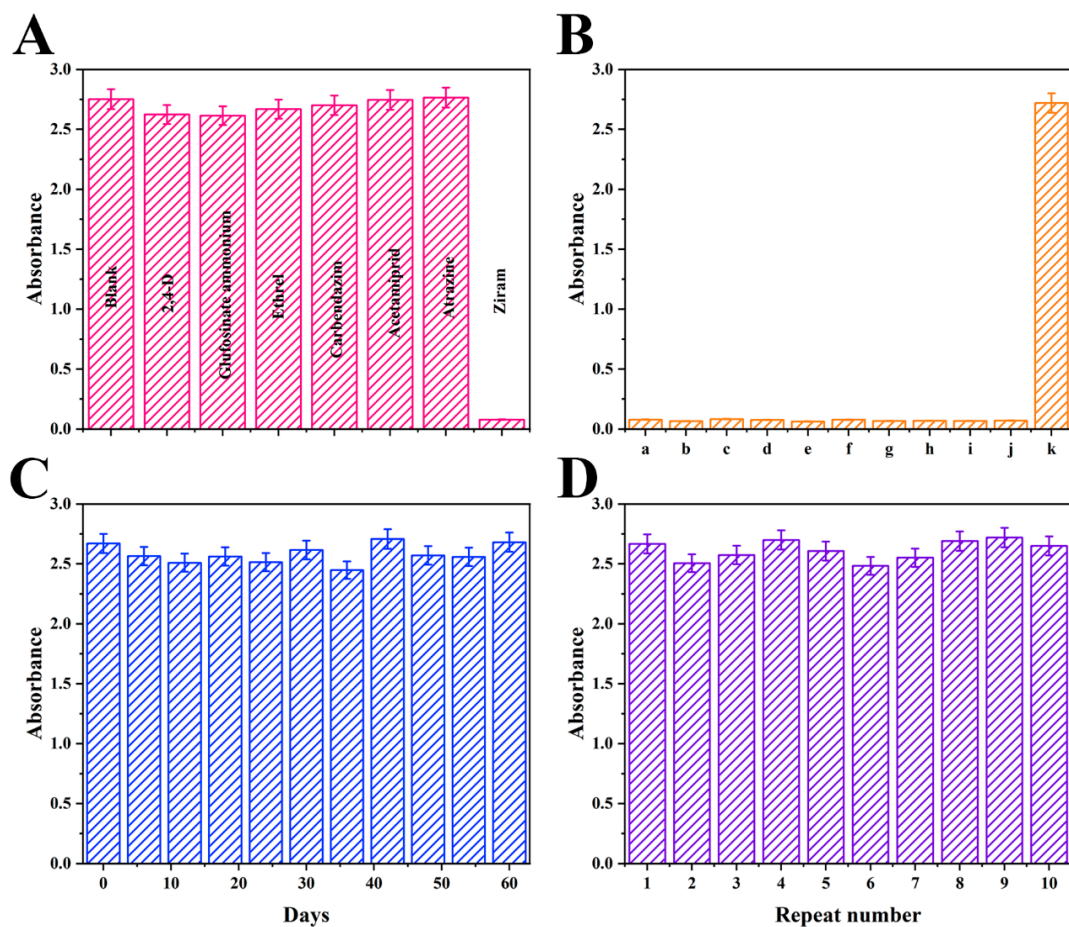


Figure S6. Potential interferences of other substances for the detection of (A) Ziram and (B) Cu<sup>2+</sup> (a: control, b: Na<sup>+</sup>, c: Mn<sup>2+</sup>, d: Mg<sup>2+</sup>, e: Zn<sup>2+</sup>, f: Ca<sup>2+</sup>, g: K<sup>+</sup>, h: Al<sup>3+</sup>, i: Pb<sup>2+</sup>, j: Cd<sup>2+</sup>, h: Cu<sup>2+</sup>); (C) Sensor stability; (D) Reproducibility of our method ( $n=3$ ).

Table S1. Comparison of steady-state kinetic parameters for the oxidase-like activity of CoMnO<sub>x</sub> and other nanozymes.

| Nanozyme   | $K_m$ (mM) | $V_{max}$ ( $\mu\text{M}\cdot\text{s}^{-1}$ ) | Reference                             |
|--|------------|---|---------------------------------------|
| Co <sub>3</sub> O <sub>4</sub>                   | 0.0469     | 0.0459  | Error!<br>Reference source not found. |
| Co <sub>3</sub> O <sub>4</sub> NPs               | 0.051      | 0.033   | Error!<br>Reference source not found. |
| Co-Fe LDH  | 0.218      | 0.263   | Error!<br>Reference source not found. |
| Co <sub>3</sub> O <sub>4</sub> /rGO              | 0.19       | 0.1071  | Error!<br>Reference source not found. |
| MnO <sub>2</sub> nanosticks                      | 0.147      | 1.34  | Error!<br>Reference source not found. |
| FO@ZMFO@FM-MOG                                   | 0.291      | 0.149   | Error!<br>Reference source not found. |
| MOF(Co/2Fe)                                      | 0.199      | 0.39  | Error!<br>Reference source not found. |
| Fe <sub>3</sub> O <sub>4</sub> @MnO <sub>2</sub> | 0.12       | —   | Error!<br>Reference source not found. |
| FeCo NPs@PNC                                     | 0.091      | 0.0939  | Error!<br>Reference source not found. |
| CNF/MnCo <sub>2</sub> O <sub>4.5</sub>           | 0.04       | 0.0645  | Error!<br>Reference source not found. |

|                    |        |        |           |
|--------------------|--------|--------|-----------|
| CoMnO <sub>x</sub> | 0.0022 | 0.1809 | This work |
|--------------------|--------|--------|-----------|

Table S2. XPS analysis results of Mn 2p and Co 2p.

| Sample                  | Mn <sup>2+</sup> /Mn <sup>3+</sup> | Co <sup>2+</sup> /Co <sup>3+</sup> |
|-------------------------|------------------------------------|------------------------------------|
| CoMnO <sub>x</sub>      | 1.054                              | 0.407                              |
| CoMnO <sub>x</sub> +TMB | 1.001                              | 0.726                              |

Table S3. XPS analysis results of O 1s.

| Sample                  | Chemisorbed oxygen | Oxygen vacancy | Lattice oxygen |
|-------------------------|--------------------|----------------|----------------|
| CoMnO <sub>x</sub>      | 9.88%              | 17.15%         | 72.97%         |
| CoMnO <sub>x</sub> +TMB | 9.26%              | 26.57%         | 64.17%         |

Table S4. Comparison of different methods for the detection of Ziram.

| Material            | Detection method | Linear range (μM) | LOD (μM) | Reference                             |
|---------------------|------------------|-------------------|----------|---------------------------------------|
| p-AgSAE             | Voltammetry      | 0.5-5             | 0.24     | Error!<br>Reference source not found. |
| Carbon dots         | Fluorometry      | 0-16              | 1.80     | Error!<br>Reference source not found. |
| CsPbBr <sub>3</sub> | Fluorometry      | 0.32-163.49       | 0.28     | Error!                                |



|                                   |                     |            |       |                                       |
|-----------------------------------|---------------------|------------|-------|---------------------------------------|
|                                   |                     |            |       | Reference source not found.<br>Error! |
| Oct/Au@AgNPs                      | SERS <sup>a</sup>   | 0.33-32.70 | 0.050 | Reference source not found.<br>Error! |
| Silver nanoparticles              | Colorimetry         | 0.64-2.4   | 0.49  | Reference source not found.<br>Error! |
| Pt/Co <sub>3</sub> O <sub>4</sub> | Colorimetry         | 5-50       | 3.36  | Reference source not found.<br>Error! |
| Copper foam                       | SEIRAS <sup>b</sup> | 60-1000    | 58.87 | Reference source not found.<br>Error! |
| AuNPs                             | Fluorometry         | 0.052-0.50 | 0.052 | Reference source not found.           |
| CoMnO <sub>x</sub>                | Colorimetry         | 5-280      | 1.475 | This work                             |

a: surface enhanced Raman spectroscopy

b: surface enhanced infrared absorption spectroscopy

Table S5. Comparison of different methods for the detection of Cu<sup>2+</sup>.

| Material                             | Detection method | Linear range (μM) | LOD (μM) | Reference                                       |
|--------------------------------------|------------------|-------------------|----------|---|
| Chol-RN                              | Fluorometry      | 5-40              | 1.12     | Error!<br>Reference source not found.<br>Error! |
| Rhodamine-based derivative           | Fluorometry      | 10-300            | 3.42     | Reference source not found.<br>Error!           |
| Furfuraldehyde fluorescein hydrazone | Colorimetry      | 6.6-330           | 6.6      | Reference source not                            |

|  |             |            |        |                                   |
|--|-------------|------------|--------|-----------------------------------|
|  | Fluorometry |            |        | found.<br>Error!                  |
| Rhodamine B hydrazone                    |             | 2.63-200   | 2.63   | Reference<br>source not<br>found. |
|  | Fluorometry |            |        | Error!                            |
| Cu <sub>2</sub> (BDC) <sub>2</sub> (BPY) |             | 50-250     | 0.005  | Reference<br>source not<br>found. |
|  | Fluorometry |            |        | Error!                            |
| Ferrocene benzobisimidazole              |             | 0-10       | 1.6    | Reference<br>source not<br>found. |
|  |             |            |        | Error!                            |
| Rhodamine-based fluorescent<br>probe     | Fluorometry | 2-20       | 0.1    | Reference<br>source not<br>found. |
|  |             |            |        | Error!                            |
| Flu@Mea-CdS                              | Fluorometry | 4-14       | 0.17   | Reference<br>source not<br>found. |
|  |             |            |        | Error!                            |
| Cu <sup>2+</sup> -triethylamine          | Colorimetry | 0.0625-8.0 | 0.0625 | Reference<br>source not<br>found. |
|  |             |            |        | Error!                            |
| CoMnO <sub>x</sub>                       | Colorimetry | 80-360     | 3.906  | This work                         |

Table S6. Assay results of Ziram in soil and water samples ( $n=3$ ).

| Sample | Add (μM) | Determined (μM) | RSD (%) | Recovery (%) |
|--------|----------|-----------------|---------|--------------|
| Soil   | 0        | 0.87            | 1.04    | —            |
|        | 60       | 59.28           | 2.23    | 98.81        |
|        | 90       | 91.03           | 2.70    | 101.14       |
|        | 120      | 122.61          | 3.46    | 102.18       |

|       |     |        |      |        |
|-------|-----|--------|------|--------|
|       | 0   | 0.87   | 1.04 | —      |
| Water | 50  | 48.72  | 3.67 | 97.44  |
|       | 100 | 100.84 | 1.60 | 100.84 |
|       | 150 | 144.92 | 2.85 | 96.60  |

Table S7. Assay results of Cu<sup>2+</sup> in soil and water samples (*n*=3).

| Sample | Add (μM) | Determined (μM) | RSD (%) | Recovery (%) |
|--------|----------|-----------------|---------|--------------|
|        | 0        | 0.94            | 1.21    | —            |
| Soil   | 60       | 59.61           | 0.57    | 99.35        |
|        | 90       | 89.33           | 2.16    | 99.25        |
|        | 120      | 118.48          | 4.69    | 98.73        |
|        | 0        | 0.94            | 1.21    | —            |
| Water  | 50       | 49.95           | 0.52    | 99.90        |
|        | 100      | 100.42          | 1.42    | 100.42       |
|        | 150      | 150.26          | 2.11    | 100.18       |