# Supplementary Information

# Droplet detector for continuous flow luminol-hydrogen peroxide chemiluminescence system

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## Analytical application of the droplet detector of continuous flow chemiluminescence

In order to identify which kinds of metal ions this droplet detector of continuous CL of luminol-$H_2O_2$ system can determine, the kinetic curves of 20 other metal ions using the static injection system were obtained. The results are shown in Table S1 which indicate that the luminol-$H_2O_2$ system not only can determine transition metal ions as the traditional flow injection CL,[1,2] but also some other kinds of metal ions. The maximum CL intensity is reached within 0.1 s and the CL signal declined to baseline after 10 s. We can conclude that CL reactions of the luminol-$H_2O_2$-metal ions system are very rapid. This droplet detector is vital to monitor such fast CL reactions. Conventional flow cell detectors are not able to determine metal ions at low concentrations with good sensitivity and accuracy using the luminol-$H_2O_2$ CL system. In this work, the detector can possibly be applied to determine Sn(II), Cu(II), and Co(II). The linearity range, linear regression equation and detection limit ($S/N$ = 3) is displayed in Table S2.

## References

1 H. Kubo and A. Toriba, *Anal. Chim. Acta*, 1997, **353**, 345.
2 M. Derbyshire, A. Lamberty and P. H. E. Gardiner, *Anal. Chem.*, 1999**, 71**, 4203.

**Table S1.** Kinetic study of CL-time curve for luminol-$H_2O_2$-metal ions using the static injection system

| Metal ion[a] | $CL_{max}$ [b] | $CL_{5s}$ [c] | $CL_{5s}$/ $CL_{max}$ | $T_{max}$ [d] (s) | $T_{1/2}$ [e] (s) |
|---|---|---|---|---|---|
| Co(II) | 6734 | 33 | 0.0049 | 1.1 | 0.0356 |
| Fe(III) | 2068 | 32 | 0.01547 | 1.1 | 0.0340 |
| Ni(III) | 27638 | 18 | 0.000651 | 1.1 | 0.0477 |
| Hg(II) | 25225 | 52 | 0.00206 | 1.1 | 0.0703 |
| Fe(II) | 1816 | 56 | 0.0308 | 1.1 | 0.0863 |
| Cr(III) | 10349 | 35 | 0.00338 | 1.15 | 0.0457 |
| Al(III) | 337 | 13 | 0.05485 | 1.1 | 0.0445 |
| Ba(II) | 8802 | 22 | 0.0025 | 1.15 | 0.0356 |
| Mn(II) | 3939 | 17 | 0.00432 | 1.05 | 0.0703 |
| Ag(I) | 1989 | 10 | 0.00503 | 1.1 | 0.0356 |
| Cu(II) | 332 | 36 | 0.10843 | 1.05 | 0.2764 |
| Au(III) | 3603 | 38 | 0.01055 | 1.05 | 0.0776 |
| Zn(II) | 8844 | 8 | 0.000905 | 1.1 | 0.0397 |
| Sr(II) | 10377 | 19 | 0.00183 | 1.05 | 0.0381 |
| Pb(II) | 8972 | 60 | 0.00669 | 1.1 | 0.0945 |
| Cd(II) | 16863 | 72 | 0.00427 | 1.1 | 0.0880 |
| Ca(II) | 2348 | 30 | 0.01278 | 1.1 | 0.0348 |
| Mg(II) | 1467 | 37 | 0.02522 | 1.1 | 0.0429 |
| La(III) | 9118 | 37 | 0.00406 | 1.05 | 0.0840 |
| Sn(II) | 8678 | 57 | 0.00657 | 1.1 | 0.0832 |

[a] The concentration of metal ions was fixed at 0.10 μmol $dm^{-3}$.

[b] The maximum CL intensity.

[c] The CL intensity after 5 s of sample injection.

[d] Time obtained at the maximum CL intensity.

[e] Half-life of the CL intensity.

**Table S2.** Linear regression equation and detection limit of various metal ions using Configuration 3

| Metal ion | Sn(II)[a] | Cu(II)[a] | Co(II)[b] |
|---|---|---|---|
| **Linearity range** | 0.01–0.10 μmol $dm^{-3}$ | 0.1–1.0 μmol $dm^{-3}$ | 0.1–1.0 nmol $dm^{-3}$ |
| **Linear regression equation** | $I = 75.10\ C + 1146$ | $I = 117.3\ C + 90.48$ | $\Delta I = 1898\ C + 2706$ |
| **Detection limit** | 2.29 nmol $dm^{-3}$ | 93.2 nmol $dm^{-3}$ | 3.74 fmol $dm^{-3}$ |
| ***r*** | 0.9953 | 0.9929 | 0.9963 |

[a] $C$ is in μmol $dm^{-3}$.

[b] $C$ is in nmol $dm^{-3}$.