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Title: Fluorescent sensing arrays for metal ions and how we can simplify them

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Abstract

A key application of analytical tools is sensing and monitoring water for pollutants that may pose a threat to human and environmental health. For example, heavy metals ions such as Pb^{2+}, Hg^{2+} and Cd^{2+} are extremely toxic, causing adverse effects in children and adults at micromolar levels.[1] Furthermore, biologically-essential transition metal ions, such as Zn^{2+}, Cu^{2+} and Fe^{3+}, are needed in trace quantities to sustain life in all organisms.[2] However, an excess or imbalance of these metal ions in humans can also have toxic effects, resulting in chronic illness or permanent organ damage.[3] As a result, it is important to monitor metal ion levels in water sources, such as drinking water and freshwater bodies of water, to minimise human exposure. At present, metal ion analysis is predominantly conducted in laboratory facilities with expensive equipment, making on-site testing unfeasible.

Optical sensors, such as small molecule fluorescent sensors, have the advantage of requiring less expensive machinery and analytical expertise, while retaining high sensitivity.[4] These probes can be used to selectively detect a single analyte, or by combining them into a cross-reactive sensing array to detect multiple analytes simultaneously. Using arrays, the unique combination of fluorescence responses for all analytes can be analysed by multivariate statistical techniques, allowing them to be distinguished from each other. In sensing arrays, cross-reactivity is desired over selectivity, the sensing elements of arrays are often more structurally simple, lending themselves to simpler synthetic routes. However, in some cases more than ten sensing elements are required for accurate analyte identification,[5] increasing the time needed for data collection and analysis.

Here, we report two strategies to decrease the number of sensing elements required for array-based identification of metal ions. In the first strategy, we use generic metal-chelating receptor groups to decrease the number of sensing elements needed in an array from six to three while retaining 100% accurate classification of nine metal ions.[6] In the second strategy, we use multiple pH environments, rather than using multiple sensors, which allows us to accurately classify 12 metal ions with just a single hydroxycoumarin fluorescent probe. We also demonstrate the versatility of the three-sensor array and single-sensor pH array by analysing metal ions in complex matrices of pond water and tap water respectively.

References

1. Wu, X.; Cobbina, S. J.; Mao, G.; Xu, H.; Zhang, Z.; Yang, L., A review of toxicity and mechanisms of individual and mixtures of heavy metals in the environment. *Environ. Sci. Pollut. R.* **2016,** *23* (9), 8244-8259.
2. Crichton, R. R., Chapter 1 - An overview of the role of metals in biology. In *Practical Approaches to Biological Inorganic Chemistry (Second Edition)*, Crichton, R. R.; Louro, R. O., Eds. Elsevier: 2020; pp 1-16.
3. Crichton, R. R., Chapter 1 Metal Toxicity – An Introduction. In *Metal Chelation in Medicine*, The Royal Society of Chemistry: 2017; pp 1-23.
4. Rasheed, T.; Bilal, M.; Nabeel, F.; Iqbal, H. M. N.; Li, C. L.; Zhou, Y. F., Fluorescent sensor based models for the detection of environmentally-related toxic heavy metals. *Sci. Total Environ.* **2018,** *615*, 476-485.
5. Anzenbacher, P. J.; Lubal, P.; Buček, P.; Palacios, M. A.; Kozelkova, M. E., A practical approach to optical cross-reactive sensor arrays. *Chem. Soc. Rev.* **2010,** *39* (10), 3954-3979.
6. Bowyer, A. A.; Shen, C.; New, E. J., A fluorescent three-sensor array for heavy metals in environmental water sources. *Analyst* **2020,** *145* (4), 1195-1201.