



Colorimetric sensing of anions in water using ratiometric indicator-displacement assay

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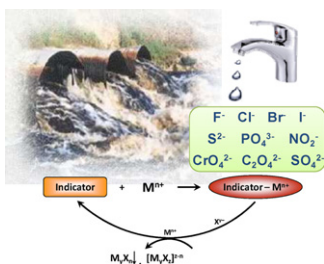
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HIGHLIGHTS

- ▶ The RIDA array was developed to sense ten anions in aqueous solution.
- ▶ No complicated molecular synthesis is needed.
- ▶ The collected images were digitized for the semi-quantitative discriminations.
- ▶ Array technologies and pattern-recognition were combined.
- ▶ The transparency scan unit was used to avoid the light reflection.

GRAPHICAL ABSTRACT

A colorimetric indicator-displacement assay (IDA) array has been developed for the determination of ten anions in water. The color changes in IDA array provide facile identification of these anions with no misclassification.



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ABSTRACT

The analysis of anions in water presents a difficult challenge due to their low charge-to-radius ratio, and the ability to discriminate among similar anions often remains problematic. The use of a 3×6 ratiometric indicator-displacement assay (RIDA) array for the colorimetric detection and identification of ten anions in water is reported. The sensor array consists of different combinations of colorimetric indicators and metal cations. The colorimetric indicators chelate with metal cations, forming the color changes. Upon the addition of anions, anions compete with the indicator ligands according to solubility product constants (K_{sp}). The indicator–metal chelate compound changes color back dramatically when the competition of anions wins. The color changes of the RIDA array were used as a digital representation of the array response and analyzed with standard statistical methods, including principal component analysis and hierarchical clustering analysis. No confusion or errors in classification by hierarchical clustering analysis were observed in 44 trials. The limit of detection was calculated approximately, and most limits of detections of anions are well below μM level using our RIDA array. The pH effect, temperature influence, interfering anions were also investigated, and the RIDA array shows the feasibility of real sample testing.

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1. Introduction

Common anions, such as halide ions (fluoride, chloride, bromide, and iodide), sulphide, sulphate, chromate, phosphate, oxalate, and

nitrite, play vital roles in the environment, industry and biology [1]. Some of these common anions are essential for our life [2,3]. For example, chloride maintains the cellular osmotic balance and regulates the pH of body fluids. Phosphate is the major source of calcium phosphate, which is a crucial material of bone and teeth. Other anions are, however, toxic in excessive amounts [4–6]. For instance, oxalate anions combine with metallic cations to form kidney stones that can obstruct the kidney tubules. Chromate

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is moderately strong oxidizing agents and may be carcinogenic. Nitrites are used for the curing of meat, but react with degradation products of amino acids, forming nitrosamines, which are known carcinogens.

Numerous conventional methods have been developed for the determination of anions [7–11], including ion chromatography, coulometric titration, ion-selective electrode, flow injection, etc. In recent years, anions sensing and recognition have also experienced an exponential growth [12–15]. Gorski et al. reported that zirconium(IV)-salophens exhibit very high fluoride selectivity over most lipophilic anions including perchlorate [16]. Ortuno et al. explored tris(2-aminoethyl)amine as an ionophore for the recognition of nitrate in ISEs [17]. Akkaya et al. expanded bodipy dyes to anion sensing [18]. Yoon et al. developed the optical sensor for the cyanide ion detection [19–21].

The evaluation and discrimination of anions, however, still remains an important challenge to chemical analysis, especially in water. This is largely because that the anions are usually larger than isoelectric cations resulting in lower charge-to-radius ratio, a feature which makes the electrostatic binding of anions to the receptors less effective [22,23]. More importantly, the anions have a relatively high free energy of solvation, which indicates that the receptors have to compete with the medium efficiently. This effect is particularly significant in water [24]. Therefore, there is a clear need to develop new methods for the determination of these anions, not only for monitoring industrial wastewater discharge, but also from the human health perspective.

In recent years, indicator-displacement assay (IDA) has been widely investigated [25–28]. This method is largely derived from the color change of colorimetric or fluorescent ligands, which compete with analytes for binding to the receptors. A number of colorimetric indicator-displacement assays have been proposed for the determination of catecholamines, malate, nitric oxide, glucose oxidase activity, etc. [29–32].

Based upon this indicator-displacement assay, we recently developed a semi-quantitative determination of halide anions and obtained a facile identification of chloride, bromide, and iodide anions at a wide concentration range [33]. In this paper, we have significantly improved our colorimetric IDA methodology by the combination of array technologies and pattern-recognition methods. Sensor array technologies [34,35] have been broadly applied for the determination of toxic industrial gases [36–39], heavy metal cations [40–42], nucleic acid and biomolecules [43,44], diols [45], and even for diagnostics [46]. Array-based cross-reactive fluorescence sensor for multianion detection in water has also been developed recently [22,23]. These sensor arrays show tremendous potential for the identification of multiple anions, however, aqueous solution is always problematic for the hydrogen bonding-based recognition, and limited the sensitivity largely. It also either needs complicated synthetic procedures for fluorescence molecules or uses external fluorescence excitation sources. Facing the difficulty of solution imaging, trivial indicator immobilization usually had to be utilized.

Herein, we report a ratiometric indicator-displacement assay (RIDA) array for the colorimetric distinguishing of ten anions at their wastewater discharge standard concentrations or drinking water levels [47,48]. We observe excellent discrimination among ten different anions in water.

2. Experimental

2.1. Materials

Deionized water was used throughout the whole work. The indicators and metal salts used were analytical-reagent grade, obtained

from Shanghai Jingchun Reagent Co., P.R. China, and used without further purification unless otherwise specified. All anion salts (NaF, NaCl, NaBr, NaI, Na₂S, Na₂SO₄, Na₃PO₄, Na₂CrO₄, NaNO₂, NaNO₃, KNO₃ and Na₂C₂O₄) were also purchased from Shanghai Jingchun Reagent Co., P.R. China, and were metal basis (99.99%).

2.2. Instruments

All stock solutions of cations and anions were prepared using deionized water (pH=6.8). No buffer was used in case of cross-contaminations. 180 μ L aqueous (alcohol/water=50%, v/v) solutions of 18 indicators were loaded in a 3 \times 6 home-made (polystyrene) well plate (see [Supplementary Data, Fig. S1](#)). Each well was an individual cylinder with 10 mm tall (the inner diameter=6 mm; the out diameter=8 mm). A film was sealed immediately to prevent the solvent evaporation. The “before” image was acquired. The Epson V200 flatbed scanner with a built-in transparency unit was utilized to collect the full digital images of our RIDA array from the bottom of the home-made 18-well plate. The transparency scan unit was used (usually for negative scan) to avoid the light reflection of solutions, which is a major problem for most solution imaging experiments. By using this technique, uniform images of solutions could be easily obtained. No indicator immobilization was needed. 20 μ L individual corresponding cation stock solutions were added to another 3 \times 6 well plate, in which a PTFE membrane (waterproof and breathable) was used as the bottom of each well. The whole bottom of the plate was sealed except for only one air inlet. Meanwhile, capillary tubes were installed on the top of each well containing cation solutions. Since all indicator and cation solutions were stored separately, they could be stored for weeks at room temperature. After combining these two well plates together, cation solutions were all transferred to the indicator 3 \times 6 well plate at the pressure blown from the air inlet and mixed with respective indicators. The final concentration of 18 indicators (see [Supplementary Data, Fig. S2](#)) and cations at the beginning of mixing are individually listed in the [Supplementary Data, Table S1](#). After the chelating reaction, the poked film was replaced by a new transparent sealing film immediately. The 20 μ L anion stock solution for each individual well was transferred to the mixture solution using the same way. The final concentration of each anion at the beginning of mixing in the mixture solution was its wastewater discharge standard concentration or drinking water level. After 5 min mixing, the “after” image was acquired.

UV-vis spectra were obtained from TU-1901 UV/Vis spectrometer (Beijing Perkinje General Instrument Co., Ltd, P.R. China).

2.3. Data processing

Digitization of the color differences can be performed using Adobe Photoshop software package. Difference maps were obtained by taking the difference of average red, green, and blue (RGB) values from the center ($\varphi = 4$ mm, 80% of the total size) of each individual well from the “before” and “after” images. The chemometric analysis was carried out on the color difference vectors using the Multi-Variate Statistical Package; in all cases, minimum variance (i.e., “Ward’s Method”) was used for hierarchical clustering analysis (HCA), and “Center data” and “Standardize data” were performed in principal component analysis (PCA).

3. Results and discussion

3.1. Methods

As shown in [Scheme 1](#), the colorimetric indicators chelate with metal cations, forming the color changes. Upon the addition of anions, anions compete with the indicator ligands according

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