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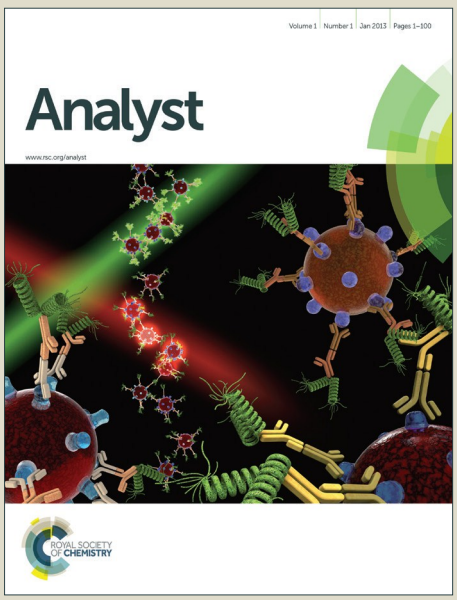

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ARTICLE

Detection of Water Contamination from Hydraulic Fracturing Wastewater: a μPAD for Bromide Analysis in Natural Waters

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Due to the rapid expansion in hydraulic fracturing (fracking), there is a need for robust, portable and specific water analysis techniques. Early detection of contamination is crucial for the prevention of lasting environmental damage. Bromide can potentially function as an early indicator of water contamination by fracking waste, because there is a high concentration of bromide ions in fracking wastewaters. To facilitate this, a microfluidic paper-based analytical device (μPAD) has been developed and optimized for the quantitative colorimetric detection of bromide in water using a smartphone. A paper microfluidic platform offers the advantages of inexpensive fabrication, elimination of unstable wet reagents, portability and high adaptability for widespread distribution. These features make this assay an attractive option for a new field test for on-site determination of bromide.

Introduction

While hydraulic fracturing (fracking) has made shale gas accessible and economical, large quantities of wastewater are produced over the lifespan of a well. For example, to drill and fracture a typical well in the Marcellus shale region approximately 14,000 to 17,000 cubic meters of water are required.[1] Within one year of well completion, 10 to 25% of the water returns to the surface as a concentrated brine.[1] Although 55 to 80% of this returned water is reused for fracturing other wells,[1] there is still excess wastewater. These large wastewater volumes have prompted rising concerns about the need for enhanced environmental protections against potential fracking wastewater contaminants, as well as more appropriate wastewater detection and disposal strategies.[1–4]

Unlike wastewater produced from conventional gas extraction, fracking wastewater management and disposal poses a challenge due to the high volumes produced. Fracking relies on high-pressure injection of fracking fluid to expand and prop open fractures in shale.[5] Once the pressure is removed, gas returns to the surface through the fracture network.[5] Fracking fluid formulations are commonly comprised of water and additives like proppants and chemicals that are site-specific to individual drilling locations.[6] Proppants are small particles used to hold shale fractures open in the absence of hydraulic pressure. Chemical additives can be used for scale inhibition, biocides, friction reducers, etc.[5,6] When wastewaters return to the surface, they typically contain constituents from the shale deposit (metals, salts, naturally occurring radioactive materials)[7–9] in addition to components from the original fracking fluid formulation.

Wastewater disposal methods include deep-well injection,[10] reuse[3] and brine treatment (thermal distillation).[6,9,11] Of these methods, deep-well injection and reuse is more common, but it has been suggested that these methods may be the cause of recent seismic activity.[11–13] It has also been suggested that these methods risk contamination of natural water sources through wastewater containment leaks.[14] Wastewater treatment is challenged by the high concentration of halides and total dissolved solids. Fracking wastewater is characterized by high concentrations of bromide, chloride and iodide.[1,6,9] The concentration of bromide in most drinking, surface and groundwater is below 1 ppm,[15,16] but in fracking wastewater there have been reports of bromide concentrations of 56 ppm or higher.[6,9] The high concentration of halides limits the volume of wastewater that can be sent to municipal wastewater treatment plants due to the formation of toxic halogenated disinfection by-products upon treatment.[4,14,17] For these reasons, concerns have been raised about the risk of contamination of water sources near fracking sites.

Although these risks are being reviewed and assessed,[1,11] current methods for evaluating contamination were not designed for the detection of contamination specifically arising from fracking

activity. Therefore, there is a need for rapid, efficient methods that are sensitive to fracking-specific contaminants. Due to the high concentration of bromide ions in wastewaters, an increase in bromide concentration can potentially be used as an indicator of wastewater leaks into water sources destined for human use.

Current bromide detection methods include the use of chemiluminescence,[18] ion selective electrodes,[19,20] ion chromatography[21] and colorimetric microwell methods[22]. All of these are wet chemistry methods, which limits their applicability for widely distributed, on-site use. The ability to detect bromide concentrations on-site would allow for rapid, real-time analysis—an ideal characteristic for the detection of water source contamination. Therefore, the aim of this work was to develop a microfluidic paper-based analytical device (μPAD) colorimetric assay specific for quantification of bromide in water samples. To our knowledge, this is the first time a bromide-specific colorimetric flow-through μPAD has been developed for this purpose.

Quantification of bromide in water was achieved by applying a water sample to a μPAD which contained a bromide-specific colorimetric chemistry.[23] In the presence of bromide, a yellow-to-blue color change occurred. Quantitation was achieved by measuring the extent of color change with a handheld color detector that wirelessly connected to a smartphone. This method can serve as a field tool for early detection of water contamination from fracking wastewater leaks. This flow-through μPAD assay offers the advantages of portability, ease of use, low fabrication cost and smartphone-enabled data collection. Therefore, this assay can be easily adapted as a field test for commercial distribution.

Materials and Methods

Reagents. All solutions were prepared using 18MΩ cm, deionized water (obtained from a Milli-Q® Advantage A10). The pH 4.60 buffer was prepared using sodium acetate (Mallinckrodt; Paris, Kentucky, USA), ammonium acetate (Sigma; St. Louis, MO, USA) and glacial acetic acid (Fisher Chemical; Fair Lawn, New Jersey, USA). The final reagent concentrations were: 0.5 mol L^{-1} NaOAc, 12.32 mmol L^{-1} NH_4OAc and 0.5 mol L^{-1} glacial acetic acid. A 1.63 mmol L^{-1} stock solution of phenol red was prepared with phenol red sodium salt (Sigma Aldrich; St. Louis, MO, USA). Chloramine T trihydrate (Sigma Aldrich; St. Louis, MO, USA) was used to prepare a 4.90 mmol L^{-1} stock solution. A stock solution of 1000 ppm bromide was prepared from potassium bromide (J.T.Baker; Phillipsburg, NJ, USA). Stock solutions of 1000 ppm chloride (from potassium chloride; Mallinckrodt; Paris, Kentucky, USA) and 500 ppm iodide (from potassium iodide; Mallinckrodt; Phillipsburg, NJ, USA) were also prepared. Whatman 1 Qualitative Filter Paper (Little Chalfont, Buckinghamshire, UK) was used as the paper substrate.

General flow-through assay fabrication. To prepare the flow-through μPAD assay, 3 μL aliquots of reagents (pH 4.60 buffer, 1.63mM phenol red and 4.90mM chloramine T) were deposited onto separate circles of Whatman 1 qualitative filter paper (diameter: 6mm). These reagent layers were dried at 25°C under vacuum for 30 minutes. Reagent layers were then stacked vertically onto each other in the following order (top to bottom): pH 4.60 buffer, phenol red and chloramine T (Figure 1). A 15 μL sample was subsequently applied to the top of the assay. Color measurements were made from the bottom layer of the assay.

Colorimeter measurements. All reference color measurements were obtained using a Konica Minolta CM-5 Spectrophotometer (Singapore, Asia). The colorimeter was only capable of collecting color measurements in *Lab* (*L* represents lightness, *+a* represents red color, –a represents green, *+b* represents yellow and –b represents blue[24]) colorspace. Color measurements made via a portable color detector were obtained with a wireless sensor platform, NODE+ with a chroma color sensor module (Node Chroma). Both the wireless platform and the sensor were purchased from Variable (Chattanooga, TN, USA). The Node Chroma was capable of simultaneously collecting color measurements in both RGB (Red, Green and Blue) and *Lab* colorspace. For both detectors, color measurements of the bottom layer of the μPAD assay were collected through the 3mm aperture of a custom-built sample holder (Figure S3).

Method validation. To perform a direct comparison between the benchtop colorimeter and Node Chroma, color surrogates were printed to eliminate experimental variation in the samples. The color surrogates were designed to mimic the final assay colors of bromide concentrations in the linear range of the calibration curve (0-10 ppm). *Lab* color values for the surrogates were obtained from actual assays. These color values were entered into colorpicker† software to generate color surrogates, which were then printed on a color printer (RICOH Aficio MP C4500, Malvern, PA, USA). *Lab* color measurements of these color surrogates were then collected with the benchtop colorimeter and the Node Chroma.

Because the Node Chroma can simultaneously collect measurements in RGB and *Lab* colorspace, a direct comparison of colorspaces was performed. In this case, actual assay samples (0-10 ppm bromide) were used instead of color surrogates; both colorspace readings were collected simultaneously (five replicate readings were obtained). Each color channel (R, G, B, *L*, *a* and *b*) was plotted against bromide concentration, and each curve was evaluated for sensitivity and linearity.

Assay specificity. To evaluate the bromide-specificity of the μPAD assay, the assay was tested in the presence of a wide, relevant range of concentrations of chloride and iodide. Color measurements were collected for solutions containing only bromide, only chloride and only iodide. Only the bromide-containing solutions produced a yellow-to-blue color change (data not shown). Color measurements from solutions containing

bromide, chloride and iodide were compared to color measurements from solutions containing only bromide. This experiment was repeated for 3 concentrations of chloride and iodide that were selected to represent environmental samples. Five replicate readings were collected per assay.

Assay stability. To evaluate the stability of the µPAD assay over time, assays were prepared and stored under various conditions for 7 days. Every 24 hours, three assays were removed from their storage conditions and were treated with a 10 ppm bromide solution; color measurements were then collected. The concentration 10 ppm bromide was chosen because it is within the environmentally-relevant linear range of the calibration curve and produces a yellow-to-blue color change. An increase in measured red color values in the stored assays over time indicated a decline in assay activity, suggesting that the assays have a limited shelf life. This decline in assay activity is visually observed as a yellow-pink discoloration, which can also provide means of declaring an assay to be expired.

The following four storage conditions were tested: oxygen, light, moisture and temperature. Control assays were prepared and stored on the under ambient conditions. To test the effects of oxygen on the shelf life of the assay, assays were prepared and vacuum-sealed using a vacuum food sealer (SealAMeal, Model FSSMSL0160-000, Boca Raton, FL, USA). To test the effects of light on the shelf life of the assay, assays were prepared and protected from light using reflective foil or exposed to ambient lighting. To test the effects of moisture, assays were sealed in the presence of activated desiccant or left exposed to the environment. To test the effects of temperature, assays were stored at -20°C and at ambient temperature (23°C).

Data analysis. In all figures, results and error bars were reported as the mean ± standard deviation (SD). In some figures, error bars were too small to see. To evaluate assay specificity, a two-tailed t-test (α=0.05) was used to compare assay color measurements from solutions containing bromide, chloride and iodide with color measurements from solutions containing only bromide. Assays were also stored under various conditions (oxygen-free, moisture-free, and low temperature) with or without light exposure to assess stability over time. A three-way ANOVA with Tukey's HSD was used to compare each assay storage condition individually, with storage condition (vs. storage on the bench top), light exposure, and time as the independent variables, and red color value as the dependent variable. A two-way ANOVA with Tukey's HSD was used to compare ambient and moisture-free storage conditions separately, with light exposure and time as the independent variables, and red color value as the dependent variable. Linear regression was used to explore the effects of time separately on assays stored under moisture-free conditions in the dark and in the light.

Results and Discussion

Preparation of the flow-through assay. To adapt the assay from a wet chemistry platform to a dry, paper-based platform, the reagents were spotted onto separate paper substrates and allowed to dry under vacuum at 25°C for 30 minutes. After the reagents dried completely, the individual layers were stacked vertically to create a flow-through µPAD assay. Water sample was applied to the top layer of the assay and flowed through the reagent layers. Depending on the concentration of bromide, a yellow-to-blue color developed in the bottom layer of the assay, from which color measurements were made (Figure 1).

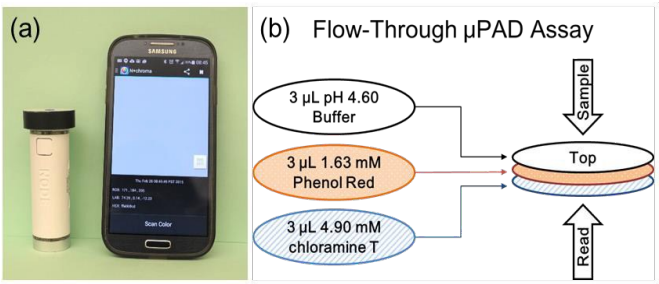

Figure 1. Flow-through assay detection using the portable color detector and assay preparation. (a) A custom-built sample holder for the portable color detector (Node Chroma) which wirelessly connects to a smartphone to deliver color measurements of the bottom layer of (b) the assembled flow-through assay.

Colorimetric analysis with a benchtop colorimeter. To determine if the color development could be linearly correlated with concentration of bromide, *Lab* color readings were obtained with a benchtop colorimeter. A linear relationship between bromide concentration and b color values was established over the 0-10 ppm bromide concentration range (Figure 2). Because 0-10 ppm is the environmentally-relevant concentration range of bromide[15,16,25] in water samples, all other experiments were carried out within this concentration range.

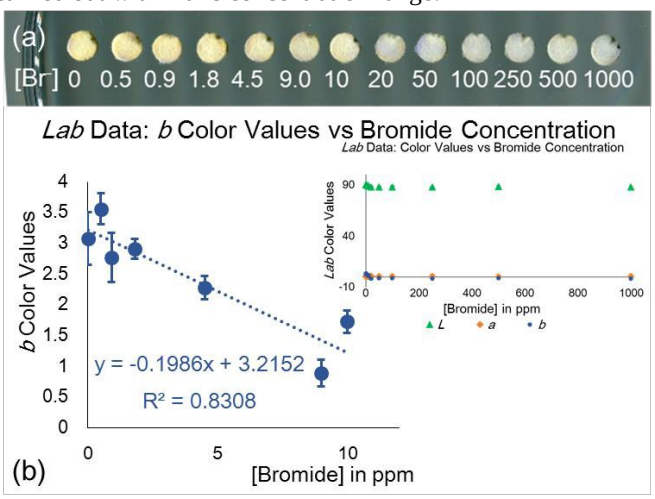

Figure 2. *Lab* colorspace values from a benchtop colorimeter. (a) The color development shows a yellow-to-blue color change. (b) There is a linear relationship between bromide concentration (range 0-10 ppm) and *b* color values. The inset shows all *Lab* color readings for the 0-1000 ppm bromide concentration range. 18MΩ cm, deionized water was applied as a blank (0 ppm). This figure illustrates the usable linear response of *b* color values, but also highlights the importance of the use of red color response from RGB data.

Method validation for a portable color detector. The aim of this project was to design and develop a field assay that could be used for the on-site colorimetric detection of bromide in water samples. The Node Chroma is a portable color detector that connects wirelessly to a smartphone via Bluetooth. To determine if the Node Chroma was an appropriate color detector for on-site bromide determination, a direct comparison between the Node Chroma and the benchtop colorimeter was performed.

To use the Node Chroma as a portable color detector, a sample holder was custom built for the flow-through assay (Figure 1). The holder was designed to fit onto the Node Chroma color detector. The purpose of the holder was to facilitate color measurements from the bottom layer of the assay without the need to invert the assay. Samples were placed on top of a sample holder and color measurements were made from the bottom layer of the assay.

The Node Chroma reads color in two regimes: *Lab* and RGB. To perform a direct comparison between the Node Chroma and colorimeter, color surrogates were made by printing surrogate samples based on the colorimeter *Lab* color readings from the 0-10 ppm bromide range (Figure 2). *Lab* color space measurements were used for this direct comparison because the colorimeter delivered only *Lab* color measurements. The *b* color channel was used specifically because previous experiments showed the greatest sensitivity and linearity with the *b* color channel (Figure 2).

When using the Node Chroma, the *b* color response remained linear over the 0-9 ppm bromide concentration range represented by the color surrogates (Figure 3). When the *b* color measurements from the colorimeter were plotted against the Node Chroma measurements, a linear relationship was observed (Figure 3). These results show that the Node Chroma is a suitable, portable color detector for this work.

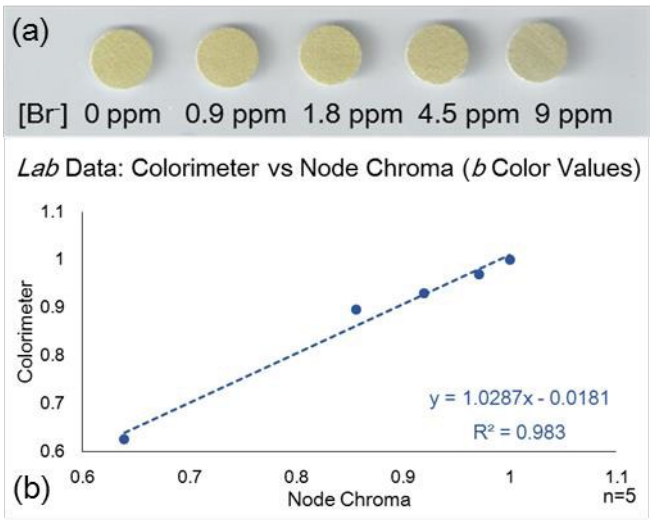

Figure 3. Portable detector validation. A benchtop colorimeter typically provides measurements in the *Lab* colorspace, therefore we made a comparison in *Lab* colorspace. The assay, however, works best in RGB colorspace. After demonstrating that the Node Chroma compares favorably to a benchtop colorimeter for the assay, we proceeded to use the Node Chroma with RGB colorspace because it was most appropriate for the field use of this assay. (a) Color surrogates were printed to represent color development for 0-9 ppm bromide. (b) A direct comparison between the benchtop colorimeter and Node Chroma was performed by plotting the normalized *b* color values from each instrument against each other (n=5). These values were normalized against *b* color values of the 0 ppm color surrogate; in other words, all colorimeter measurements were divided by the colorimeter measurement obtained from the blank and all Node Chroma measurements were divided by the Node Chroma measurement obtained from the blank.

RGB vs *Lab* colorspace comparison. The Node Chroma was used to obtain color measurements for the remaining experiments. After demonstrating that the Node Chroma works well in the *Lab* colorspace, a comparison between the RGB and *Lab* colorspaces was performed to assess which colorspace gave the best sensitivity and linearity for bromide. In the RGB colorspace, the red color signal gave the best sensitivity and linearity. The standard deviation increased in RGB colorspace, however, the RGB colorspace provided more consistency and improved linearity in the red color measurements. A detection limit of 3.218 ppm bromide was observed. Additionally, when compared to the *b* color values from *Lab* colorspace, the red color signal from the RGB colorspace demonstrated higher sensitivity and linearity to bromide concentration determination (Figure 4). It is important to note that the differences in *b* color value calibration equations (Figure 2B and 4B) are attributable to the different calibration protocols for the Node Chroma and benchtop colorimeter as well as the observed variability in *Lab* colorspace. The calibration for each detector is vendor-specific, and the obtained measurements depend on factors including sensitivity, stray light, assay to assay variability, and sample placement. For these reasons, further experiments were carried out using the red color values from the RGB colorspace measurements obtained with the Node Chroma.

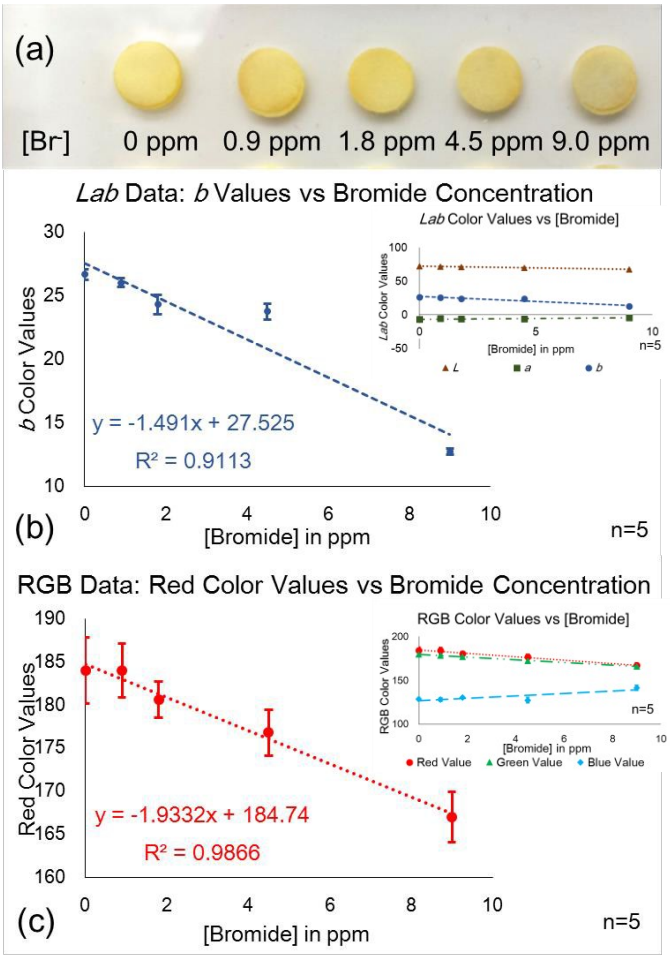

Figure 4. An RGB vs *Lab* colorspace comparison. (a) 0-9 ppm bromide solutions were applied to assays and RGB and *Lab* measurements were collected with the Node Chroma. (b) *b* color measurements plotted against bromide concentration (n=5). Inset shows all *Lab* color values plotted against bromide (n=5). (c) Red color measurements plotted against bromide concentration (n=5). The inset shows all RGB color measurements plotted against bromide concentration (n=5).

Assay specificity. A common problem with bromide detection is interference from other halogens.[22] Chloride and iodide are

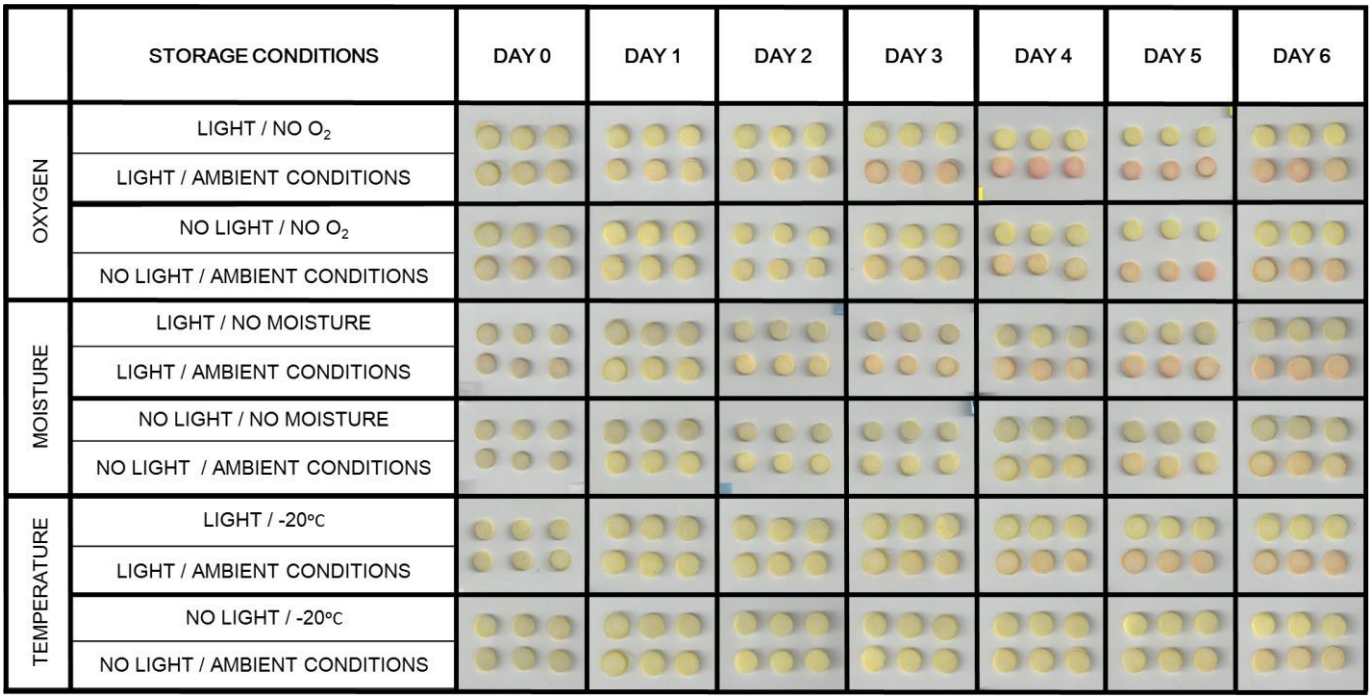

Figure 6. Assay stability under 4 conditions. In each image, the top row shows assays stored under oxygen- or moisture-free or low temperature conditions. The bottom row shows assays stored under ambient conditions as a control. Pink discoloration indicated assay expiration. For the oxygen storage tests, assays were vacuum-sealed. For the moisture tests, assays were stored in the presence of desiccant. For the temperature tests, assays were stored at -20°C. For the light tests, assays were stored under dark conditions. Readings were collected every 24 hours (n=3).

halogens commonly found in water, so these are the halogens most likely to cause interference with bromide detection. Because on-site sample pre-treatment options are limited for field tests, an ideal bromide quantification method would be specific for bromide in the presence of both chloride and iodide.

The specificity for bromide was tested over a range of environmentally-relevant concentrations of chloride and iodide. Concentrations of these ions vary over geographic locations, so concentrations were chosen to represent high, mid and low levels of chloride and iodide (Table 1). Selection of these concentrations was based on values reported in the literature. [25,26] Bromide samples ranging from 0-9 ppm were spiked with high, mid and low concentrations of chloride and iodide. Red color values collected from assays with spiked samples were compared to values collected from bromide-only samples. Chloride and iodide did not significantly affect the sensitivity and linearity of bromide detection (Figure 5). Mid-level and low-level concentrations of chloride and iodide are reported in Figure S1.

	Chloride	Iodide
High-Level Concentration	50 ppm	10 ppb
Mid-Level Concentration	25 ppm	5 ppb
Low-Level Concentration	2 ppm	0.5 ppb

Table 1. Environmentally-relevant concentrations of chloride[25] and iodide[26] were selected based on values reported in the literature.

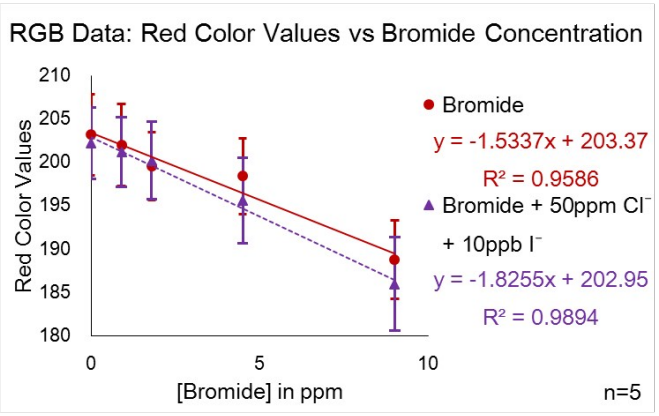

Figure 5. Bromide samples (0-9 ppm) were compared to samples spiked with high levels of chloride and iodide (50 ppm chloride and 10 ppb iodide). The presence of chloride and iodide does not drastically affect the linearity and sensitivity of bromide detection (p=0.7376).

Assay stability. To determine what storage conditions would prolong assay shelf life, the lifetime of the assay was monitored for 7 days. The following storage conditions were investigated and compared to control assays stored under ambient room conditions: oxygen, light, moisture and temperature. Every 24 hours, an assay was removed from storage and a 0 ppm bromide sample was applied. Red color measurements were collected and compared to red color measurements collected on Day 0 (after 0 hours of storage) (Figure 6). Note that assays stored under

ambient conditions displayed over time a yellow-to-pink color change upon sample application rather than the expected yellow-to-blue color change. It is hypothesized that this discoloration is caused by prolonged exposure to atmospheric humidity during μPAD assay preparation. This hypothesis is supported by the results from the moisture conditions experiment (Figures 6 and 7), which showed that assays protected from moisture produced the expected yellow-to-blue color change. The pink discoloration can be used as a tool for visual confirmation of assay expiration or improper (compromised) storage.

Of the conditions tested, only assays stored under moisture-free conditions appeared visually to maintain activity (the expected yellow-to-blue color change) upon application of bromide over the seven-day testing period (oxygen and temperature results were reported in Figure S2). Assays stored under moisture-free conditions exhibited only minimal changes in red color values after 7 days of storage (Figure 7), suggesting that assay shelf life can be preserved by packaging (storing) under moisture-free conditions. In a 3-way ANOVA with storage condition (moisture vs. no moisture), light exposure (light vs. no light), and time (stored assays measured on days 0 – 6) as the independent variables and red color value as the dependent variable, storage conditions ($p<0.0001$), light exposure ($p=0.0062$), and time ($p<0.0001$) were all significant. Additionally, the interactions of storage and light ($p=0.0045$), storage and time ($p<0.0001$), and light and time ($p<0.0001$) were significant. However, in a 2-way ANOVA using only red color values generated from samples stored under moisture-free conditions, the effects of light exposure were not significant (light was significant ($p=0.0003$) in a 2-way ANOVA for samples stored under ambient conditions). Time was still shown to be significant ($p=0.0141$) in this analysis. However, the line of best fit generated by a linear regression using red color values from samples kept in the dark under moisture-free conditions had a slope of 0.0357, $R^2=0.00197$ (moisture-free samples stored in the light showed a slope of 0.4643; $R^2=0.10735$). This suggests that there is no linear relationship between red color value and time (for both moisture-free samples stored in the light and in the dark, measurements taken on day 0 were not significantly different from measures taken on day 6, as determined using a two-tailed t-test). Alternatively, the sample variability described above could have been the result of unknown sample preparation inconsistencies, and the enhanced accuracy of assays stored under moisture-free conditions in the dark will be further explored in future work. These results show that the assay can be prepared in advance and stored appropriately for later use.

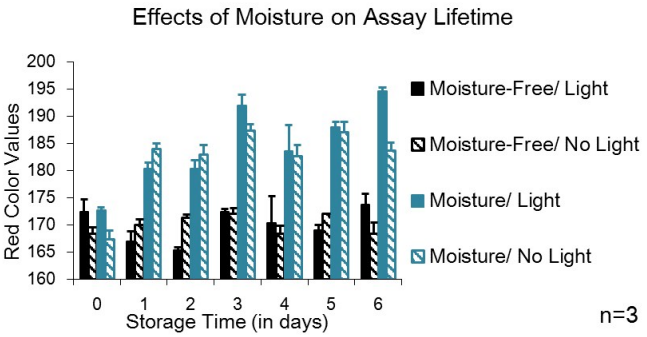

Figure 7. Assay lifetime under moisture-free conditions. Red color values were obtained from 3 replicate assays. Assays stored under moisture-free conditions exhibited less noticeable red color change over time. The control assays (stored under ambient conditions) showed increasing red color values over the duration of the experiment. Increasing red color values indicate that the assay is no longer working because the yellow to blue color change no longer occurs.

Conclusions

Successful quantification of bromide in water samples. The aim of this project was to demonstrate the feasibility of using a flow-through μPAD assay for colorimetric bromide determination from water samples. The described assay successfully produces linear calibration curves over an environmentally relevant range of bromide concentrations. A detection limit of 3.218 ppm bromide was observed, and future work will focus on improving this detection limit (a multi-parametric calibration curve will be investigated). The presented work demonstrates that this assay is specific for bromide, even in the presence of high concentrations of chloride and iodide.

Portability and practicality for on-site analysis. Importantly, the assay demonstrates features that are advantageous for on-site use, including an inexpensive fabrication method that allows for one-time disposable use, a stable chemistry that is easy to use in the field without the need for wet reagents and compatibility with portable detection methods. Calibration reproducibility could potentially be improved by decreasing batch-to-batch variability. This can be achieved by producing the assays under conditions that are idealized for manufacturing, by better controlling humidity, temperature, and light exposure, among other variables. As demonstrated, the assay can detect bromide concentration with a handheld color detector that wirelessly connects to a smartphone. This color detector can be used on-site and supplants a traditional benchtop colorimeter. While the detector used in this study works well and offers the convenience of portability and functionality (specifications are provided in Table S1), a benefit of this assay is the flexibility of detector choice. For example, the smartphone's built-in camera could potentially be used as an alternative detection platform. Furthermore, the assay is robust and stable when stored under moisture-free conditions. This feature allows for advanced preparation and storage, which are important properties for commercialization and distribution.

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Notes and references

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† Colorpicker software used to print color surrogates based on entered *Lab* color values (http://davidjohnstone.net/pages/lch-lab-colour-gradient-picker)

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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