A pump-less discrete opto-fluidic chemical spectrophotometry system (DOCSS) for online *in situ* monitoring of dissolved contaminants in aqueous media

Justus C. Ndukaife, A. G. Agwu Nnanna, Shadi Salman and Magloire C. Fandohan

ABSTRACT

This paper presents the fabrication of a discrete chemical analyzer system for online monitoring of dissolved ions in water using UV-VIS absorption spectrophotometry. The device is composed of three main components: fluidic, optical, and control. The test cell was designed to also function as a non-invasive volume sensor, and the volume sensing principle was based on light scattering by entrapped water droplets. This design eliminates the need for expensive high-precision syringe pumps for sample introduction into the test cell. The discrete opto-fluidic chemical spectrophotometry system device can be interrogated remotely over the internet, and the performance was evaluated using the spectrophotometric analysis of chromium (VI) with di-phenylcarbazide as model chemistry. The results showed very good stability in the optical absorbance measurements, a method detection limit of 6.38 ppb, and good precision of 3.04% RSD (relative standard deviation) at 50 ppb chromium (VI). Also a linear calibration range of 25 to 1,250 ppb was obtained, and the response was reversible.

Key words | discrete chemical analyzer, heavy metals, online monitoring, water quality

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INTRODUCTION

The traditional analytical techniques used in the water industry for detection of chemical pollutants in water include inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption and flame emission spectroscopy, atomic fluorescence spectroscopy and high performance liquid chromatography (Scully 1998). These techniques albeit highly sensitive to target analytes and capable of detecting sub-ppb concentrations of the analytes take a long time to perform an assay (usually several hours), as several preparation steps such as digestion, extraction, and dilution are required before results are produced (Benkhedda *et al*. 2002). Furthermore, the standard analytical instruments are not applicable for *in-situ* analysis, and collection of the sample from the site could change the source conditions. For example, exposing the sample to ambient light and atmospheric temperature may alter the temperature-dependent reaction kinetics of the sample (Lai *et al*. 1993). These limitations, coupled with the ever-increasing demand for analysis in environmental, industrial, clinical, and agricultural environments has triggered research in the development of instruments for *in situ* and automated analysis, including continuous flow and discrete chemical analyzers (Rui *et al*. 2002; Carmen *et al*. 2004; Leal *et al*. 2006; Cleary *et al*. 2008; Zhiwei *et al*. 2009).

Continuous flow-based instruments such as the flow-injection analysis (FIA) instrument are arguably the most widely accepted automated chemical analysis devices. First introduced by Ruzicka & Hansen (1975), FIA involves injecting test samples into a continuously flowing reagent carrier stream. The sample stream mixes with the reagent stream through the process of dispersion, to produce a compound which flows into a detector zone to yield an analytical readout. The flow-rate, channel volume, and channel geometry determines the extent of mixing and duration of reaction

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between the reagent and analyte. The FIA technique can enable several sample preparation steps such as preconcentration, dilution, and extraction, prior to spectrophotometric analysis, and has been applied for analysis of environmental samples such as mercury (Andac *et al*. 2003; Asan *et al*. 2003; Kozaka *et al*. 2011). FIA systems rely on the use of peristaltic pumps for sample and reagent handling. This presents a major challenge in sample handling in continuous flow systems, since peristaltic pumps have highly variable flow-rates (Karlberg & Pacey 1989; Christian 1992; Rui *et al*. 2002). The peristaltic pumps normally employed also suffer from several problems, such as wearing and tearing of tubings, and the need for frequent replacement. The variations in flow-rate affect the result of an assay, thus requiring frequent monitoring of the baseline signal. Another challenge with use of continuous flow instruments is the possibility of contamination from sample carryover in the continuously flowing sample carrier stream.

Discrete chemical analyzers (Steige & Jones 1980; Joseph *et al*. 2011), on the other hand, add sample and reagent to a small cell, i.e., cuvette, and measure the reaction product with the chemical reaction product in the cell or transferred to a flow cell. Samples are processed in batches. Compared to FIA, discrete analyzers consume less reagent, since only the required reagent for reacting with the analyte is dispensed into the cell. Thus, microliter volumes of reagents can be utilized. However, the current discrete analyzer systems use expensive high precision pumps and are mostly used for laboratory analysis.

In this work, gravity-driven flow was employed for injection of analyte-sensitive reagents from reagent containers into a flow cell, by triggering the corresponding electrically actuated solenoid valve. This eliminates the need for multichannel peristaltic or high-precision syringe pumps for reagent introduction. This was made possible because the test-cell acts as a non-invasive volume sensor. Thus any simple flow system with ill-defined flow-rate could be utilized for introducing sample into the cell. The non-invasive discrete liquid level/volume detection mechanism is based on light scattering by entrapped liquid droplets, and is used for detecting when a critical volume of sample has been introduced into the cell, after which, sample introduction can be stopped. The fabrication, description and evaluation of the device performance are presented subsequently.

DESIGN OF THE PUMPLESS DISCRETE OPTO-FLUIDIC CHEMICAL SPECTROPHOTOMETRY SYSTEM (DOCSS) SYSTEM

The schematic of the proposed DOCSS sampling system is depicted in Figure 1. It consists of three major components: fluid (reagent) dispensing, optics, and control. The fluid-dispensing device is oriented vertically such that the dispensing of reagents and rinsing of flow cell using de-ionized water is gravity-driven. The fluid dispensing system consists of miniaturized chemical resistant electrically actuated

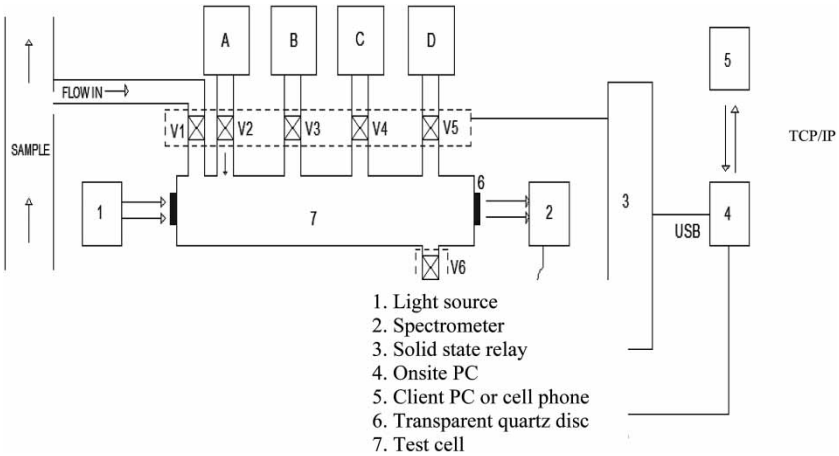

Figure 1 | Components of proposed discrete analyzer (not drawn to scale). A, B, C, and D are for reagent, standard, and deionized water.

solenoid valves V1–V6 (Mcmaster Carr, Chicago, IL, USA), which are connected to ultra-chemical resistant tygon tubes 1.5 mm i.d. (VWR, USA). The solenoid valves are actuated using a solid state relay module USB 6525 (National Instruments, USA), which is interfaced to a computer via a USB cable. The reagent tubings are linked to a reaction test cell to enable the dispensing of sensing reagents into the test cell. Introduction of test sample into the test cell is achieved by triggering valve V1, while reagents, deionized water and standard can be dispensed by triggering valves V2–V5. The minute wastes generated are expelled by triggering valve V6.

The optical detection system is composed of a light source (DH-BAL 2000, Ocean Optics, FL, USA), a specially designed 2.5 cm optical path-length test cell, and a spectrometer (HR-4000 Ocean Optics). The test cell is fabricated from Teflon material, which is chemical resistant and possesses inlet and exit ports as well as two transparent side windows. Transparent quartz discs are installed on the side windows to permit light propagation from the light source through the cell to the spectrometer.

The actuation of the sample-inlet, reagent, and waste-exit valves were realized using a Lab-VIEW control program, which was installed on the on-site computer. The on-site computer was also used for acquisition of optical absorbance measurements using the spectra-suite spectroscopy software (Ocean Optics). Remote instrumental control was performed using remote desktop control utility software (Microsoft Inc.). By this means, a cell phone or client PC can be used to control the whole system remotely over the internet, by taking control of the site computer.

A key question is how a user would determine when sufficient volume of test sample has been introduced into the test cell after triggering V1, in order to prevent overflow of the test cell. We addressed this question through the development of a non-invasive volume sensing mechanism based on the concept of light scattering by entrapped liquid droplets.

Non-intrusive volume sensing mechanism to detect volume of test sample

To analyze a sample spectrophotometrically, the sample has to be introduced into a test cell, which serves as the cuvette. Perhaps the most straightforward way of dispensing into the test cell without overflowing for a discrete analyzer is to use a timed high-precision pump with well-defined flow-rate. This approach will not provide information on the state of the cell (whether empty or full) and so for remote monitoring application, it will be necessary to keep logs of each sample introduction and cell rinsing events to note when the cell is empty and available for sample introduction, which would be problematic and could introduce error. This is so because a timed pump would require injection of precise volume by actuating the pump for a set period of time and shutting it off afterwards. With this approach, any variation of the pump flow-rate would affect the volume of test sample dispensed. Here, we propelled the sample into the test cell and detected the volume of test sample introduced non-invasively. Thus when a certain critical volume of test sample has been introduced and detected, the sample introduction can then be stopped.

Several volume/level sensors have been reported in open literature (Vazquez *et al.* 2004; Lomer *et al.* 2007; Ting & Wang 2009; Binu *et al.* 2010; Syed Azer & Nabeel 2010; Fu *et al.* 2011), but none of these can be easily adapted for detecting volume of sample in a small volume test cell measuring a few milliliters. The volume sensor reported here exploits the concept of light scattering by entrapped liquid droplets and is unique in that the same optical instruments such as light source, and spectrometer used for spectrophotometric analysis are employed for volume sensing as well. In a nutshell, the test cell is also a volume sensor, and the working principle is explained in the following text.

Consider a flow cell with transparent quartz glass windows aligned directly on the external sides as shown in Figure 2. Cylindrical-shaped cavities are fabricated on the

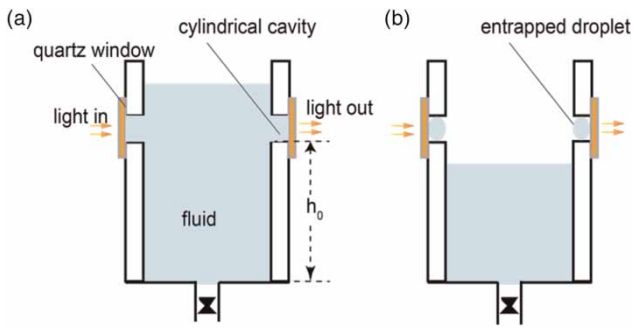

Figure 2 | As the cell is being filled, the liquid also occupies the cavities. On emptying the cell, liquid droplets are entrapped in the cavities.

sides and bounded by quartz glass windows. Assume that initially the cell is filled with some optically transparent liquid such as water, as Figure 2(a) shows, part of the liquid would flow into and fill the cylindrical cavities on the sides. Let the cell be gradually emptied as shown in Figure 2(b), by turning ON an exit valve at the base of the cell.

As the level falls below the position of the cylindrical cavities (specifically below h_0), some of the liquid occupying the cavities will be entrapped within the two cavities due to interfacial tension forces as shown in Figure 2(b).

Thus the cell can be in either of two states: trapped state or untrapped state. After droplets have been entrapped in the cavities, the cell always remains in the trapped state whenever the level of test sample introduced is below h_0. When the position becomes greater than $h_0 + d_0$ (with d_0 being the diameter of the cavities) the cell enters the untrapped state.

If light is normally incident on a quartz disc window (which is transparent) from the left, the fate of the light transmitted through the cell is different for when the cell is in the trapped and untrapped states. For the untrapped state, light will be essentially propagating through multiple dielectric media, namely from air to quartz glass disc, to the liquid, to another quartz glass and then to air before reaching the receiving optics as modeled in Section 2 of Ndukaife (2012). On the other hand, for the trapped state, normally incident light would experience scattering by the entrapped droplets before the scattered light reaches a detector. With the detector positioned in the forward direction (scattering angle $\theta \approx 0$), then only the forward scattered light would be received at the detector.

Of interest is to compare the received light intensity through the cell for the two cases when the cell is in the trapped and untrapped states. Theoretical estimates of light transmitted through the cell in the trapped and untrapped states have been carried out in Ndukaife (2012). The results show that in the untrapped state, optical transmittance in the forward direction can be up to 93%, while for the trapped state the value was about 2.6%. We present an experimental validation of how this test cell design concept could provide vital information for detecting critical volume of sample introduced in the following.

Experiment to validate the proposed optical volume sensing mechanism

A 30 cm long Teflon block with cross section of 2.5×3.0 cm was cut to give a length of 2.5 cm. A rectangular groove of about 1.5 mL volume was made in the Teflon block to hold liquid. A hole of 0.5 cm diameter was drilled through two opposite ends of the block, and two 0.16 cm thick quartz glass discs with 1.9 cm diameter were fixed at the two ends to enable light transmission through the cell.

Teflon material was used for fabricating the test cell for two reasons. First, it has very good chemical resistance properties. Second, Teflon has very low critical surface tension, which is about 18 mN/m and as a result, most liquids, such as water, do not wet Teflon (Carey 1992). This low wettability property is necessary to ensure the entrapment of the droplets in the cavities. The optical path length of the cell is 3 cm.

We subsequently demonstrate experimentally that the proposed liquid volume sensing technique can provide an accurate and very effective means for ascertaining when a critical volume of sample has been introduced into the sample cell even if the entrance flow-rate of sample into the cell is ill-defined.

When water was introduced into the cell, the intensity spectrum was recorded after being filled up. Actuation of the exit valve causes the cell to be emptied and in the process, water droplets are trapped in the two cavities bounded by the quartz glass discs. Propagation of light through the entrapped droplets causes light scattering and the scattered light intensity in the forward direction is collected by the receiving optics and recorded on a spectrometer. More water was introduced into the cell, to take the cell from the trapped state to untrapped state and the intensity recorded as the cell entered the untrapped state.

Figure 3 shows the results of experiments for the non-intrusive volume sensor. According to Figure 3, when the cell is in the untrapped state (i.e., when test sample has been introduced to a level above the position of the cavities), light is propagating through multiple dielectric media and the received intensity spectrum is large, as predicted theoretically. The received light intensity for when the cell enters the trapped state (for example, when the cell is

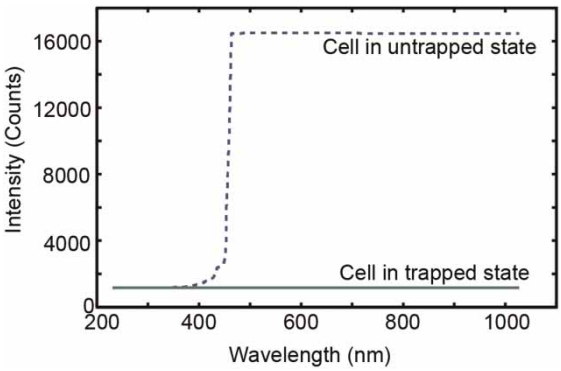

Figure 3 | Received light intensity spectrum (counts) for when the cell is in the 'trapped' and 'untrapped' states.

emptied) is as though light is blocked from reaching the spectrometer, due to scattering by the entrapped droplet, and this agrees with the result predicted theoretically in Ndukaife (2012). Thus by observing the optical intensity spectrum, it is easy to determine when a critical volume of test sample has been introduced into the cell, and likewise when the cell is empty. The critical volume is defined here as the volume at which the level of sample introduced into the cell just crosses the position of the cavities, where the initially entrapped droplets cease to exist. In other words, this is the volume corresponding to when the level of sample in the cell just exceeds $h_0 + d_0$, as depicted in Figure 2. Also during sample introduction, as much sample may be introduced until the cell moves from trapped to untrapped state, after which the sample inlet valve V1 may be turned OFF. Thus, this way no high precision pumps are required for metering the test sample.

As well, the volume sensing mechanism also makes possible rinsing of the test cell remotely, by providing information on the state of the cell whether filled above the critical level or empty, thus eliminating the need to always keep a log of the state of the test cell.

EXPERIMENTAL

Experiments were conducted using the DOCSS device for the spectrophotometric analysis of chromium (VI). The prototype DOCSS system was designed to have five dispensing bottles, for reagents, standards, and deionized water.

Reagent for chromium (VI) based on the diphenylcarzide reaction was prepared and stored in one of the reagent bottles.

Reagents and sample preparation

The reagent was prepared from 1,5-diphenylcarbazide, concentrated tetraoxosulfate (VI) acid and water. A systematic approach for combining all reagents into a single product was developed as follows: 0.5 g of 1,5-diphenylcarbazide was dissolved in 2 mL of 97% tetraoxosulfate (VI) acid. The product was transferred into a beaker containing 200 mL deionized water, which resulted in the formation of white precipitates. The supernatant was filtered and stored as a reagent for chromium (VI). A stock solution of 100 ppm chromium (VI) was prepared. Working standard solutions were prepared by serial dilution of the stock solution.

Procedure for contaminant detection

Deionized water valve is triggered to dispense deionized water into the test cell, until a desired critical volume has been dispensed. Next, the reagent valve for target analyte is triggered to dispense a set volume of sensing reagent into the cell. The dispensed reagent and deionized water produces the reagent blank I_{ref} optical intensity spectrum. The cell is then emptied. The dark spectrum is obtained for when no light is transmitted through the cell. Rather than turning OFF the light source, the dark spectrum was obtained simply by using the spectrum received when the cell is in the trapped state (that is, when the cell is emptied by triggering valve V6). Deionized water is again introduced into the cell, and emptied for rinsing. The test sample is then introduced into the cell and the cell is emptied to rinse out the entrapped droplet (to prevent diluting the sample water with the previously entrapped water droplet). Then the test sample is again introduced into the test cell and chromium (VI) reagent is dispensed to obtain the sample spectrum I_{sample}. The sample is incubated with the reagent for about 5 min.

The absorbance at any given wavelength is obtained as: $A_\lambda = -\log\left(\frac{I_{\text{sample}} - I_{\text{dark}}}{I_{\text{ref}} - I_{\text{dark}}}\right)$, using the Spectra suite software

(Ocean Optics). After detection, the cell is rinsed with deionized water by triggering the deionized water valve. The wastes generated are collected in a receptacle for proper disposal.

RESULTS

The reaction between chromium (VI) and the diphenylcarbazide reagent produces a purple-colored complex, with an absorbance maximum at about 542 nm as shown in Figure 4. Figure 4 shows the absorbance at 25 ppb chromium (VI) was 0.06, while that at 100 ppb was about 0.248, which is approximately 4.1 times the absorbance at 25 ppb. This result is in agreement with the Beer–Lambert law which predicts a linear relation between absorbance and concentration. Subsequent absorbance readings in this study were therefore recorded at a wavelength of 542 nm.

We discuss the absorbance variation at 542 nm wavelength with time of the chromium (VI)–diphenylcarbazide colored complex with time when the reagent is injected into the test cell containing chromium (VI) sample, based on a simple model. We assumed that all chromium (VI) ions react completely with the diphenylcarbazide reagent to form the purple-colored complex. We write the rate equation for the amount of colored complex N formed when the injected reagent reacts with chromium (VI) as

$$\frac{dN}{dt} = k_f(N_t - N)$$

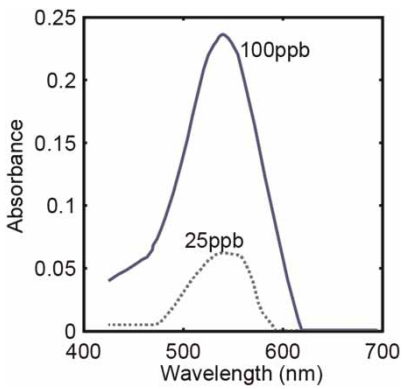

Figure 4 | Measured absorbance at various wavelengths for 25 and 100 ppb chromium (VI) concentrations.

where N_t is the final amount of colored complex produced after all chromium (VI) and the reagent have reacted. After the reagent is dispensed, it reacts with chromium (VI) ions and N changes until it equals N_t. Also, the magnitude of N is dependent on the concentration of chromium (VI) present since the amount of reagent injected is assumed constant. Using the initial condition: at $t = 0$, $N = 0$, the solution is readily obtained as $N = N_t\left[1 - e^{-k_f t}\right]$. But the absorbance by Beer's law, is absorbance $A = \epsilon lC$, where C is concentration of chromium (VI) that has reacted with reagent, and $C = N/\text{Volume}$. So that in terms of absorbance, absorbance rate equation is

$$A(t) = \frac{\epsilon l N_t}{V}\left[1 - e^{-k_f t}\right] = A(t) = \epsilon l C_t\left[1 - e^{-k_f t}\right]$$

or

$$A(t) = A_{\text{Final}}\left[1 - e^{-k_f t}\right]$$

We conducted experiments to determine the rate of change of absorbance with time using 50, 200, and 500 ppb chromium (VI). Five experiments were conducted for each concentration and the average of the data was plotted as shown in Figure 5. Fitting the data using an exponential association fitting function gives $A(t) = 1.2\left(1 - e^{-0.0683t}\right)$ with a correlation coefficient of 0.997 for 500 ppb. This result shows a good fit of the optical absorbance rate data, even though the DOCSS device does not incorporate a stirrer.

The steady state absorbance is readily obtained as t tends to infinity. After 100 s, $dA(t)/dt \sim 10^{-4}$. Thus steady state could be said to have occurred after 100 s, and subsequent absorbance readings were recorded after this time duration.

An experiment was conducted to determine the stability and reproducibility of absorbance measurements using the DOCSS device. Ten assays were performed using 50 ppb chromium (VI) solutions. The results shown in Figure 6 indicate the readings are very stable.

An RSD (relative standard deviation) of 3.04% was obtained for 50 ppb chromium, thus the DOCSS device has good precision.

A calibration relation for determining chromium (VI) concentration using the DOCSS device was generated. The result in Figure 7 shows a linear relationship over the

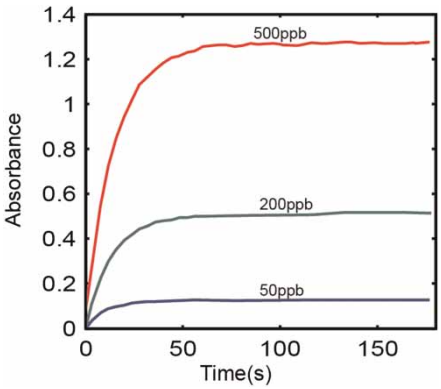

Figure 5 | Time response of reaction between chromium (VI) sample and reagent.

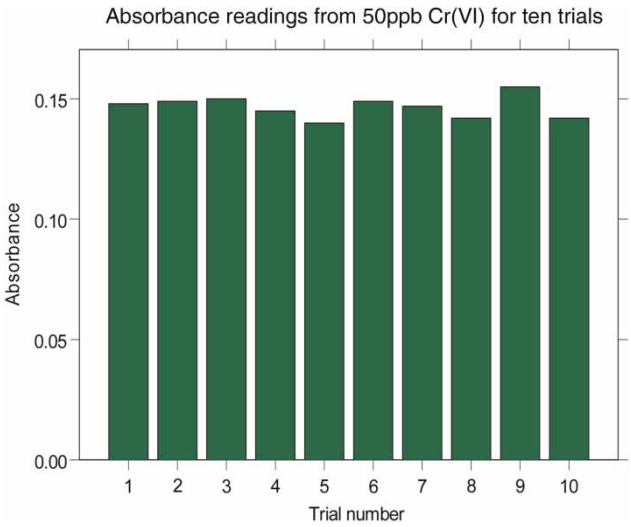

Figure 6 | Measured absorbance for ten tests with 50 ppb chromium (VI).

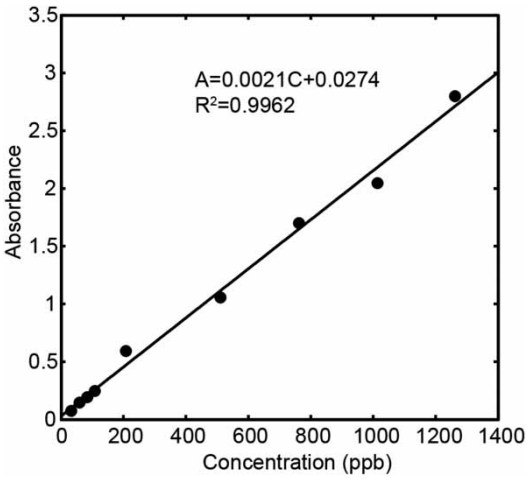

Figure 7 | Chromium (VI) calibration over a range of 25 to 1,250 ppb.

range from 25 to 1,250 ppb with a correlation coefficient of 0.9962. This result shows that the DOCSS device can provide linear response in the measurement of optical absorbance for varying concentrations.

Figure 8 shows the reversibility of the response signals after each testing and cell rinsing events. After testing for 100 ppb chromium (VI), the absorbance response is depicted by section A. Next the cell was rinsed three times. After the first rinsing with deionized water, the absorbance reduced to about 0.025. After the second and third wash periods, the absorbance became 0.006 as depicted by sections C and D, which was the absorbance of di-water with respect to reagent-blank. On subsequently testing for the 100 pbb sample, the absorbance returned to the original value which is about 0.24. This result shows that only two wash periods are required and the response signal is reversible.

Since the DOCSS device is proposed for *in-situ* monitoring of water in remote locations, which may contain water with varying level of quality, experiments were tested using both source and finished water. Two samples were collected from tap water and a well in Crown Pointe, Indiana. The total dissolved solids (TDS) and turbidity levels of the samples were measured using a water quality monitor (Horiba), and turbidimeter (Hach 2100N), respectively, and are shown in Table 1. The samples were spiked with chromium (VI) and analyzed using both the DOCSS and ICP-MS with no further sample preparation steps such as digestion performed. The concentration added for the

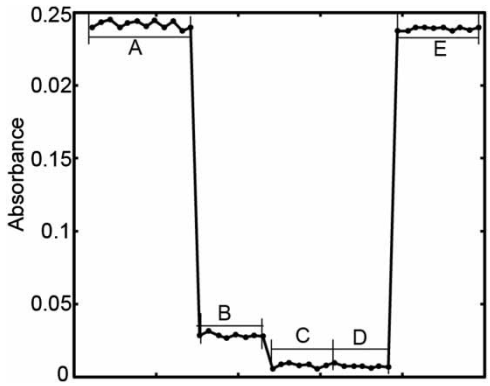

Figure 8 | The reversibility of the signal response after cell rinsing. A is absorbance for 100 ppb chromium (VI), B, C, and D are the absorbance after first, second, and third cell rinsing, respectively. E is the absorbance on subsequent testing of an aliquot of 100 ppb chromium (VI).

Table 1 | Chromium (VI) determination in tap and well water

Sample	TDS (mg/L)	Turbidity (NTU)	Cr (VI) added (ppb)	[a]Result with DOCSS (ppb)	Result with ICP-MS (ppb)
Tap	230	0.4	100	110	111
Well	1,000	40	120	147	151

[a]Result is average of three analyses.

spiked tap water sample compared well with the results obtained from measurements using DOCSS and ICP-MS. For the well sample, there was about 22% deviation between the measured concentration and added concentration, and this is attributed to the high TDS and turbidity levels of the well water sample. We note that the results obtained using DOCSS compares well with those from ICP-MS. Thus the DOCSS device could be utilized for analysis of environmental samples with relatively high TDS and turbidity levels.

DISCUSSION AND CONCLUSIONS

A discrete analyzer for online monitoring of heavy metals via spectrophotometric analysis has been developed. The device contains an in-built non-intrusive discrete optical volume sensor for detecting the volume of test sample introduced into the test cell. The volume sensor provides simple and yet accurate measurement of sample volume via opto-digital signals, thus eliminating the need for high-precision pumps for sample handling. The resident time of the droplets in the cavities, defined as the time duration for which the droplets when entrapped can maintain the cell in the trapped state, is found to be greater than 48 hours. Thus there are no problems of 'drying out' of the droplets during an online monitoring event. The device is a 'true' lab-on-a-valve, as no pumps but only valves are used for sample and reagent delivery.

Experimental validation of the performance and practical application of the device was also demonstrated using chromium (VI) as model chemistry. Using the DOCSS device and chromium (VI) reagent, the MDL (method detection limit) was found to be 6.38 ppb, which is well below the EPA specified maximum contaminant level of 100 ppb for total chromium content in drinking water, and the response time was within 150 s. Urone (1955) have performed detailed experiments on stability of diphenylcarbazide reaction reagent for chromium (VI) detection and showed that the reagent could be stable for over 18 months. Thus the diphenylcarbazide reagent represents a good option for long-term remote monitoring of chromium (VI) using the DOCSS device.

While chromium detection with diphenylcarbazide reaction was considered here for illustration, other sensitive and highly selective reagents could also be used in the device for detecting target heavy metal ions in a medium containing other analytes of environmental concern. For example, Hamza *et al.* (2010) introduced a new reagent called 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one for spectrophotometric determination of mercury. The authors reported a detection limit of 26 ppb for mercury. Also, recently, Al-Kady & Abdelmonem (2013) reported a new reagent 2,4,7-triamino-6-phenylpteridine for colorimetric detection of mercury (II). Cadmium, which is another heavy metal of environmental concern could also be detected using reagents described in Ullah & Haque (2011). Thus, with appropriate reagents, several heavy metals could be analyzed with the DOCSS device to enable online monitoring of target contaminants in remote and not so accessible locations.

The issue of fouling is particularly relevant for long-term monitoring especially in the bio-environment. We anticipate a fouling problem in several sections of the device, especially the sample inlet section. For instance, build-up of foulants may cause partial blockage of the inlet zone, causing a reduction in the flux of gravity-driven sample introduction into the cell. This would have constituted a significant problem if sample introduction was carried out by using a timed pump set to dispense for a given time. However, the approach used in DOCSS involves detecting the volume of test sample introduced optically, such that the inlet valve could be turned off after the required critical volume. Thus the DOCSS system would still function well when there is partial blocking of the tubing due to fouling. However, complete blocking of the tubing due to fouling must be prevented. Studies have shown that biofouling could be mitigated by use of copper-based materials (Manov *et al.* 2004). Thus the sample introduction section

could be replaced with copper tubings and pipe in order to mitigate foulant growth. Also, since the injected sample makes contact with the transparent optical windows during testing, fouling of these windows may occur with extended use. Fortunately, several approaches have been proposed for mitigating fouling using transparent adhesive polymers; for example, Chae *et al*. (2007) developed antifouling coating containing phosphorylcholine groups. The polymer coating was found to be optically transparent for wavelengths above 300 nm. Such a transparent antifouling coating may be employed to coat the optical windows to prevent the formation of fouling which would interfere with optical measurements. Future work would focus on exploring the potential effects of biofouling on the performance of DOCSS during long-term use, as well as the most effective means to mitigate any influence of fouling.

In summary, the DOCSS device provides simple and accurate testing of samples using microliter volumes of reagents, while producing small volumes of waste. Integration of the device with existing wireless sensor technology could enable *in situ* and remote monitoring of dissolved water-borne pollutants.

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