A novel optical sensing lab-on-a-disc platform for chromium speciation

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Introduction

The determination chromium speciation in the field is a significant analytical challenge. While chromium exists in oxidation states from 0 to VI, it is predominantly found in the (III) and (VI) states [1]. Industry effluent (e.g. textile/electroplating) is a common source of chromium pollution in the environment. Due to corrosion inhibitors used in pipes, and contamination leaching from sanitary landfills, drinking water supplies can become contaminated also [2]. The bioavailability and toxicity of chromium is largely dependent the oxidation state of the element [2]. Consumption of Cr (III) is an essential component in human diet, as it is responsible for maintaining glucose, lipid and protein metabolism [3]. In contrast, Cr (VI) is strongly oxidizing, exhibiting high toxicity, with carcinogenic and mutagenic properties [4]. It is recommended by the World Health Organisation (WHO) that the maximum allowable concentration of chromium (VI) in drinking water is 0.05 mg L^{-1} [5]. Handheld colourimeters for on-site measurements are a convenient option for frequent water monitoring; however the limit of detection (LOD) of these devices is typically higher than the recommended limit. Microfluidic 'lab-on-a-disc' technologies were used in the development of an optical sensor for chromium speciation in water. The principal behind these devices is to minimize laboratory processes onto a microfluidic system that can be brought to the sampling site for rapid sample-to-answer analyses. The objective for this device was to design and fabricate a fully integrated optical sensor for on-site measurement of both trivalent and hexavalent chromium in freshwater. A strong focus was placed on maximizing sensitivity in order to achieve a low LOD.

The Centrifugal microfluidic system

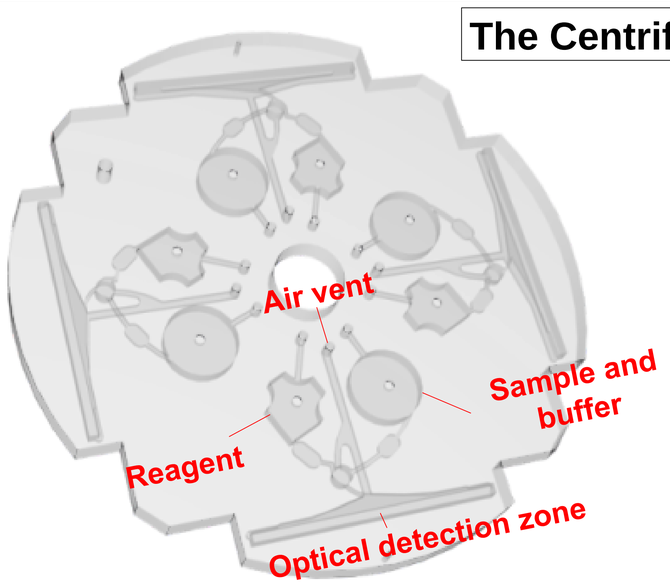


Fig.1 The microfluidic disc was designed to facilitates efficient mixing of sample and reagent, and enables the use of long optical path lengths while minimising reagent use and waste production.

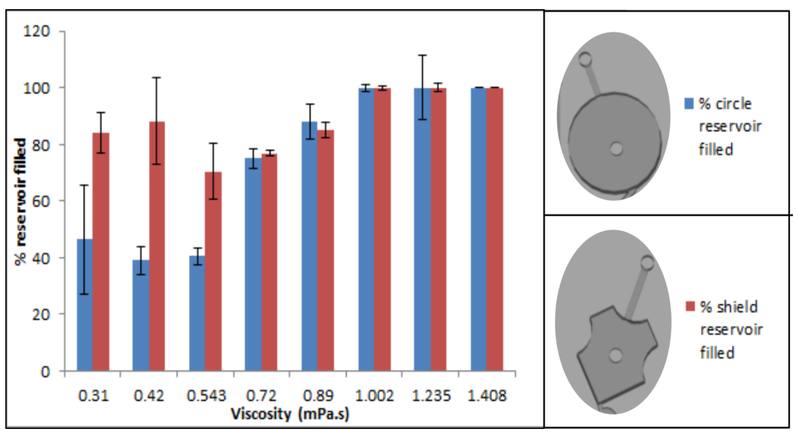
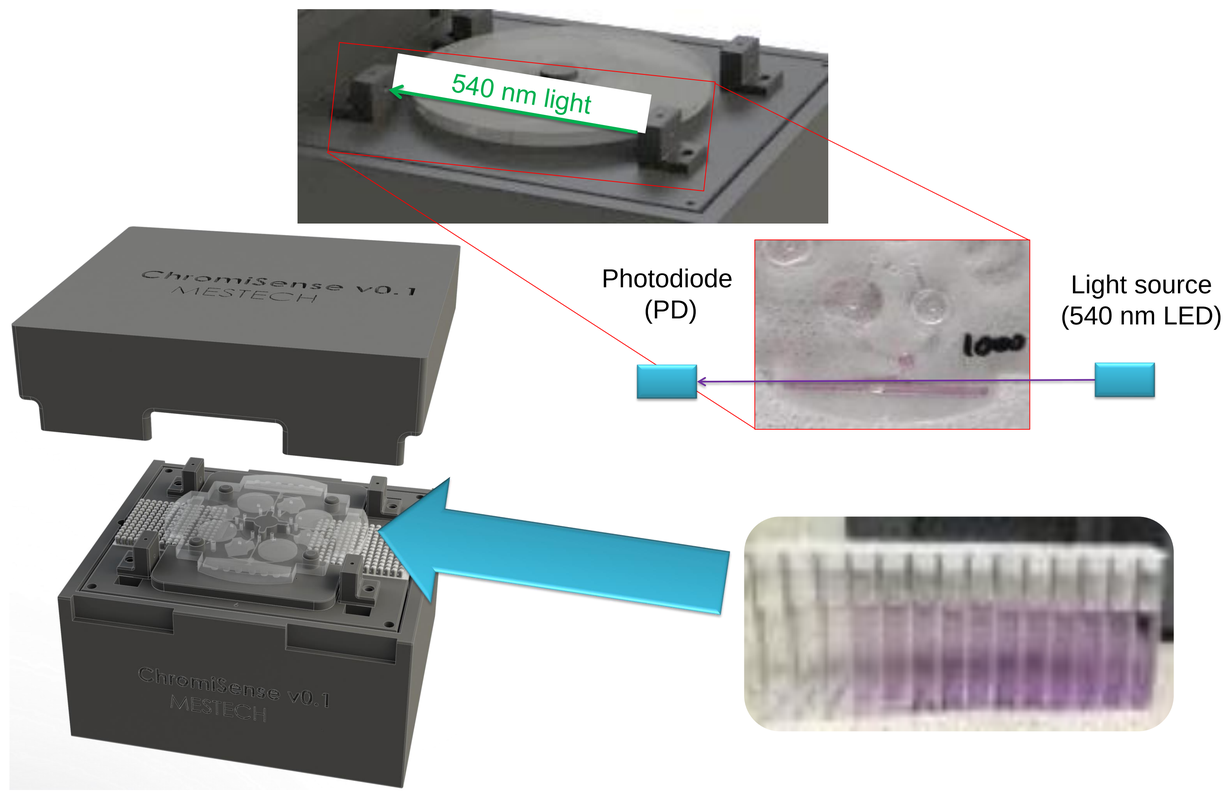


Fig. 2 The shape of the reagent reservoir was optimised to enable insertion of low viscosity fluids. The shield shape reservoir and a circle shaped reservoir were compared.

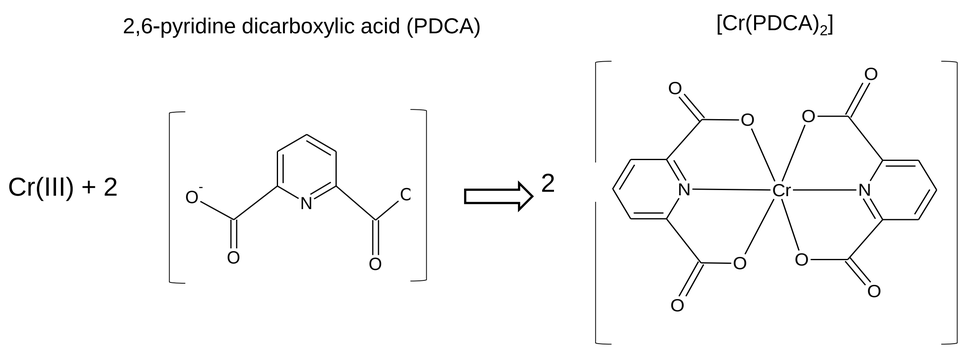
Fig. 3 Rendered image of the fully integrated system, incorporating a motor for rapid disc rotation, a low-cost optical detection system, a precise alignment stage for absorbance measurements, heating elements and a *Wixel* microcontroller for live command capabilities. **(Right)** Alignment of disc with LED-PD detection system for absorbance measurements.



Detection

Chromium (III) determination

Cr(III) was determined using the reaction shown in Eq. 1. The product was determined by measuring its absorbance of UV light at its absorbance maximum of 335 nm. The method was optimised by varying the pH, temperature, heating time, PDCA concentration and solvent.



Eq. 1. (Above) Reaction of Cr(III) with PDCA to form complex $[Cr(PDCA)_2]$. λ = 335 nm.

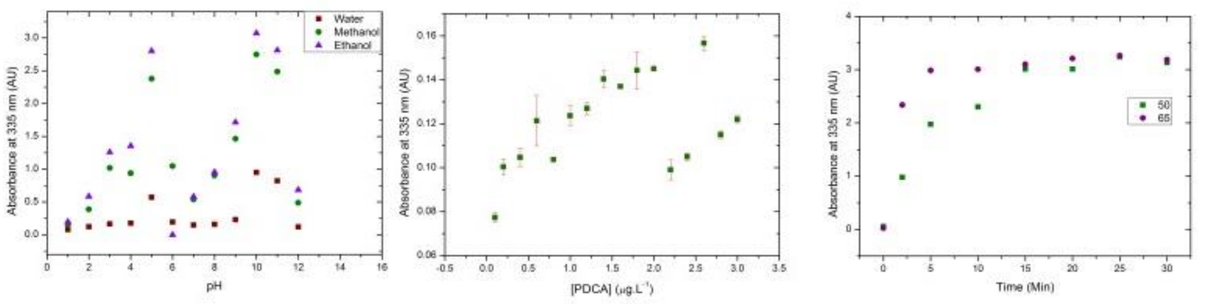
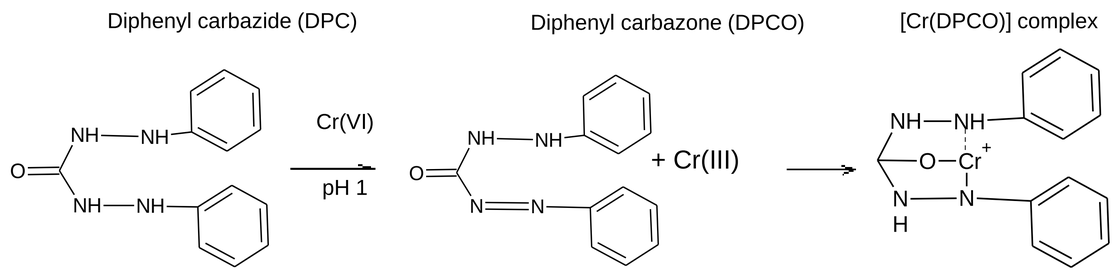


Fig. 4 Selection of optimal pH (10) and PDCA solvent (ethanol) to maximise $[Cr(PDCA)_2]$ formation using 500 mg.L^{-1} Cr(III). **(Centre)** Optimisation of [DPCA] in ethanol at pH10, 65ºC. **(Right)** Increase in speed of complex formation with increased temperature.

Chromium (VI) determination

Cr(VI) was determined using the reaction shown in Eq. 2. The product was determined by measuring its absorbance of visible light at its absorbance maximum of 540 nm. The method was optimised by varying the volumes of buffer and reagent used.



Eq. 2 (Above) Reaction of Cr(VI) with DPC to form a [Cr(DPCO)] complex. λ = 540 nm, ε = 4.3x104 L mol^{-1} cm^{-1}.

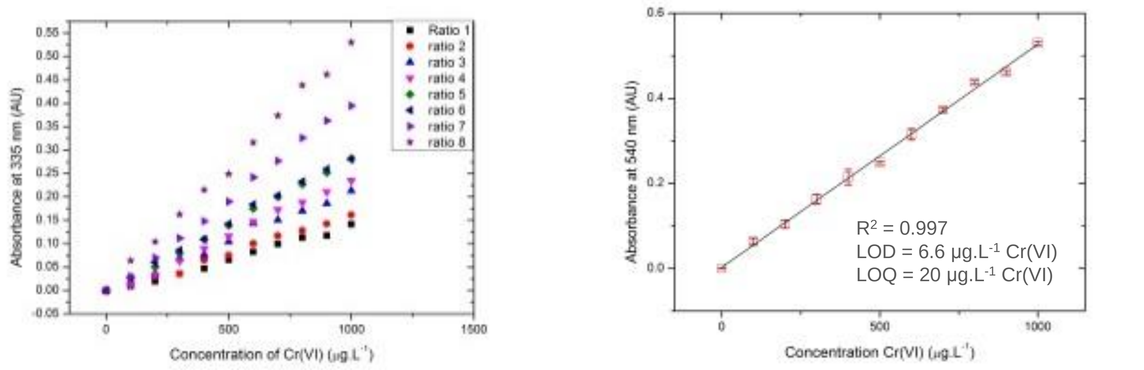


Fig. 5 (Left) Decreasing of buffer to sample ratio resulted in increased sensitivity. **(Right)** Calibration curve for Cr(VI) on UV-vis after method optimisation.

Conclusion

Herein, describes the development of a centrifugal-based microfluidic device (CMD) optimised for the quantitative analysis of both chromium (III) and (VI) species in water. The CMD platform is inclusive of a centrifugally-driven lab-on-a-disc (LOAD) cartridge with a complementary 3d printed colourimetric sensor system with heating and results read-out capabilities. For analysis, the sample is loaded into a reservoir on a disposable microfluidic disc, along with reagents. Due to the low viscosity of the reagents, a microfluidic 'shield-shaped' reservoir was designed for the prevention of premature liquid flow. A centrifugal force is achieved through the spinning of the disc, for liquid pumping through microchannels, causing them to mix and react to form a coloured product into the optical-pathway detection zone, as previously reported [6]. In the case of the chromium speciation system however, as two analytes were being assessed, a preferred path length of 50 mm was selected to allow both samples to be measured in duplicate. The optical detection system consists of a light emitting diode (LED) and photodiode (PD) couple. Chromium (III) and (VI) are measured using 2,6-pyridine dicarboxylic acid and 1,5-diphenyl carbazide (DPC) respectively, forming complexes that were measured at 535 nm. The LOD for trivalent and hexavalent chromium using this device were 21 mg L^{-1} and 4 µg L^{-1}, respectively. The linear range for quantitative analysis was found to be 69–1000 mg L^{-1} for Cr(III) and 14–1000 µg L^{-1} for Cr (VI). The optical sensing device is simple to use with the potential for rapid on-site measurements comparable with standard benchtop spectrophotometers.

Acknowledgments

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References

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