



ChromiSense: A colourimetric lab-on-a-disc sensor for chromium speciation in water



G. Duffy^a, I. Maguire^a, Brendan Heery^a, Pauline Gers^a, J. Ducreé^b, F. Regan^{a,*}

^a Water Institute, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

^b School of Physical Sciences, Fraunhofer Project Centre at Dublin City University (FPC@DCU), Glasnevin, Dublin 9, Ireland

ARTICLE INFO

Keywords:

Centrifugal
Chromium
Optical
Sensor
Water
Microfluidic

ABSTRACT

The development of a centrifugal device for quantitative analysis of both chromium (III) and (VI) species in water is reported. ChromiSense is a colourimetric sensor system that has been applied to the measurement of chromium in spiked river water samples. For analysis, the sample is loaded into a reservoir on the disposable microfluidic disc, along with reagents. A centrifugal force is created by spinning the disc to pump liquids through microchannels, causing them to mix and react to form a coloured product. The coloured product is then presented to a low-cost optical detection system, where absorbance measurements can be recorded. The optical detection system consists of a light emitting diode (LED) and photodiode (PD) couple. Chromium (III) was measured using 2,6-pyridine dicarboxylic acid as a ligand, forming a complex that was measured at 535 nm and at 335 nm. While measuring at 535 nm allowed for the use of a low cost LED, the sensitivity was improved 2.5 times by measuring at 335 nm. However, 335 nm also yielded a diminished linear range with little improvement in limit of detection (LOD), and required a lengthier manufacturing process due to the need for a UV-transparent material. Chromium (VI) was detected using 1,5-diphenyl carbazide (DPC). This standard analysis method was simplified for automation on-disc, and optimised to achieve a low LOD. 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). While this range is high for Cr(III), incorporation of an off-disc pre-concentration method would make this technology suitable for environmental sample analysis. The device is simple to use, low in cost, and could provide rapid on-site measurements, with results comparable to those obtained using a benchtop spectrophotometer.

1. Introduction

Chromium speciation refers to the quantitative analysis of chromium species. Although chromium exists in oxidation states from 0 to VI, it is primarily found in the (III) and (VI) states [1]. Chromium enters the environment through effluent discharged from industry (e.g. textile/electroplating) and cooling towers. It can enter drinking water supplies through corrosion inhibitors used in pipes or through contamination leaching from sanitary landfill [2].

Changes in the oxidation state of an element can greatly change its bioavailability and toxicity [2]. Cr (III) is an essential micronutrient in the human diet, and is considered essential for maintenance of glucose, lipid and protein metabolism [3]. Cr (VI) is strongly oxidizing, exhibiting high toxicity, with carcinogenic and mutagenic properties [4]. According to the World Health Organisation (WHO), the recommended maximum allowable concentration for chromium (VI) is 0.05 mg L⁻¹ in drinking water [5].

Traditional laboratory-based measurements of chromium in freshwater are time and labour intensive, requiring expensive instrumentation and trained personnel. Commonly used techniques include atomic absorbance or emission spectroscopy, inductively coupled plasma mass spectrometry, ion chromatography, spectrophotometry, potentiometry and capillary electrophoreses. These methods can incorporate sample pre-treatments such as solid or liquid phase extraction, cloud point extraction, adsorbents or ion exchange [2].

Handheld colourimeters for on-site measurements are a more convenient option for frequent monitoring; however the limit of detection (LOD) of these devices is typically higher than laboratory-based methods. A low LOD is essential for a chromium sensor as the recommended Cr (VI) limit is so low.

A centrifugal 'lab-on-a-disc' (LoaD) approach is employed for the development of an optical sensor for chromium speciation in water. This approach was proven successful for a different analyte in a previous publication [6]. By making changes to the sensor and disc design,

* Corresponding author.

E-mail address: Fiona.regan@dcu.ie (F. Regan).

the versatility of the system was demonstrated, and it was successfully applied to chromium speciation. The chromium speciation disc contains microchannels guiding the flow. By rotation of the disc using a simple motor, a centrifugal field is created, which acts from the centre of the disc, radially outwards [7]. This force acts as a fluid pump, pushing fluids through the micro-channels. The philosophy behind these devices is to minimise and automate laboratory processes onto a compact, user-friendly and robust LoAD system that can be brought to the sampling site for simple and rapid analysis. The objective of this work was to design and fabricate an integrated optical sensor prototype that would be capable of simultaneous on-site measurement of both trivalent and hexavalent chromium in water.

A major concern for the minimisation of analytical protocols onto microfluidic analysers is the reduction in the optical path length from a typical 10 mm cuvette to approximately 2–5 mm, depending on the thickness of materials used in fabrication. This leads to a subsequent decrease in sensitivity and increase in detection and quantitation limits. Through using a previously published horizontal optical interrogation of the disc rather than vertical interrogation, this disc design overcomes this obstacle by incorporating an optical path length of 50 mm [6].

Chromium (III) is quantified by absorbance measurement following reaction with 2,6-pyridine dicarboxylic acid, which forms a $[\text{Cr}(\text{PDCA})_2]$ complex, as shown in Fig. 1. PDCA was selected due to its high selectivity for Cr(III) compared to other common ligands [8]. It has been used for Cr(III) for both pre- and post-column derivatisation to obtain a UV detectable complex [8,9]. Other ligands used for Cr(III) include EDTA for suppressed IC-ICP-MS, 2-hydroxybenzaldiminoglycine for colourimetric detection and Mo(VI) for UV detection after separation of Cr(III) and (VI) using CE [10–12]. The low molar extinction coefficient of this complex leads to poor sensitivity. Despite efforts to optimise the method and improve this sensitivity, the method does not reach environmentally relevant concentrations. This limits the applicability of the sensor to industrial run off or extracted samples from food [2]. The same DPC ligand as was used for Cr(VI) could be used to determine Cr (III), however this reaction is inhibited by water, making its automation on a centrifugal system for water analysis challenging [13].

Chromium (VI) is quantified using a modified version of the standard 1,5-diphenyl carbazide (DPC) protocol [14]. In this reaction, DPC is oxidised by chromium (VI) to form diphenyl carbazone (DPCO), with subsequent reduction of chromium (VI) to chromium (III). A Cr(III)-DPCO complex then forms, which absorbs strongly at 535 nm. The positive charge on $[\text{Cr}(\text{DPCO})]$ is uncertain, and is written as $(3-n)^+$, where n is the unknown number of protons released in the complex formation [15] Fig. 2.

Incorporation of a pre-concentration step for Cr (III), on- or off- disc, for subsequent complexation with PDCA would be a more straightforward approach to the issue. Pre-concentration has been achieved on microfluidic LoAD by incorporation of stationary phases such as C_{18} , porous carbon monoliths and ion exchange monoliths [18–20]. In 2009, LaFleur et al. demonstrated a disc that carried out SPE for heavy metal pre-concentration. It was capable of running 8 low volume samples on one disc, taking a total of 20 min. This type of pre-concentration could

be done on-site, making it compatible with the ChromiSense system [20]. One example of a LoAD system with absorbance based detection for Cr(VI) in water was published by LaCroix-Fralish et al. in 2009 [21].

2. Experimental

2.1. Materials and methods

2.1.1. Reagents

All solutions were prepared using ultra-pure water (Elga Maxima®, 18.2 MΩ) and ACS grade reagents purchased from Sigma Aldrich, Ireland, unless otherwise stated. Working standards were prepared by dilution of stock solutions prepared from potassium dichromate and chromium (III) nitrate nonahydrate, respectively.

Chromium (VI) was quantified using a 0.02 M solution of 1,5-diphenyl carbazide (DPC) dissolved in HPLC grade methanol. The results from this were compared to the same concentration of DPC in acetone (ACS grade), which is the solvent used in the standard method [5]. A pH 1 ± 0.3 buffer was made by mixing 25 mL of 0.2 M KCl and 67 mL of 0.2 M HCl.

Chromium (III) was quantified using a 0.05 M solution of 2,6-pyridinedicarboxylic acid (PDCA) in methanol. A pH 10 buffer was made by mixing 50 mL of 0.05 M sodium tetraborate decahydrate and 18.3 mL 0.2 M sodium hydroxide.

For optimisation of reservoir filling capacity for low viscosity fluids, solutions covering a range of viscosities were prepared using ACS grade acetone, HPLC grade methanol and ACS grade glycerol. The kinematic viscosity of each two liquid mixture was estimated using Gambill's method [22].

Two river water samples were spiked with Cr(III) and Cr(VI). The first was made with 100 mg L^{-1} Cr(III) and $200 \text{ } \mu\text{g L}^{-1}$ Cr(VI). The second was made with 800 mg L^{-1} Cr(III) and $800 \text{ } \mu\text{g L}^{-1}$ Cr(VI). These were measured on ChromiSense, with reference measurements on the spectrophotometer.

2.2. Instrumentation

Reference measurements for the samples and sensor calibrations were obtained using a Shimadzu mini 1240 spectrometer with the same colourimetric methods as used on-disc using a 10 mm glass cuvette. Samples were run in parallel with the device for assessment of performance. Glass cuvettes with a variety of different path lengths were used (purchased from Spectro Service Ltd., UK).

Spectra were obtained using a VWR UV-1600PC UV-vis spectrophotometer (VWR, Ireland).

2.3. Disc design and fabrication

The centrifugal disc was fabricated from polymethyl methacrylate (PMMA) sheets (Radionics Ltd., Ireland) and pressure sensitive adhesive (PSA), (Adhesives Research Inc., Ireland). The 5 layer design is shown in Fig. 3. The three PMMA layers (Fig. 3, shown in purple) contain the larger reservoir features. They were cut using an Epilog

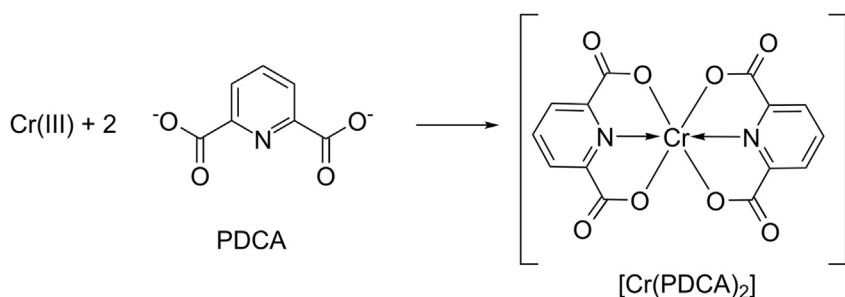


Fig. 1. Reaction of Cr (III) with 2 molecules of PDCA to form $[\text{Cr}(\text{PDCA})_2]$ [16].

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