Quantitative Analysis of Cr(III) and Cr(VI) Using Gold Nanoparticles with UV-Vis Spectrometry and Smartphone Colorimetric-Sensing

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ABSTRACT: *Analysis and speciation of chromium ions are important due to the contrasting nature of essential Cr(III) and toxic Cr(VI) ions. Here, the first simultaneous determination of Cr(III) and Cr(VI) ions is introduced using gold nanoparticles (AuNPs) as a colorimetric agent and subsequent detection using an application attached to a smartphone, in addition to the UV-vis spectrometer. A small amount of AuNPs (1 mM) was used as a result of its excellent selectivity and sensitivity toward Cr(III) and Cr(VI) ions. The color change of AuNPs was monitored using a smartphone and validated by a UV-vis spectrometer. The peak absorbance of AuNPs' surface plasmon resonance (520 nm) was red-shifted to 630 nm when Cr(III) was introduced, while it was blue-shifted to 370 nm when Cr(VI) was added to the system. The absorbance shifts of the system produce a color change that is linearly proportional to the Cr concentration. At pH 5.0, a linear relationship of Cr(III) occurred at an absorbance ratio of 630/520 nm in the concentration range of 0.2–1.0 ppm (R^2 = 0.9911), while those of Cr(VI) at an absorbance of 370 nm in the concentration range of 0.05–1.0 ppm (R^2 = 0.9909). The method's detection limit of the UV-Vis spectrometer was found to be 0.051 ppm (0.98 uM) and 0.035 ppm (0.67 uM) for Cr(III) and Cr(VI), respectively. The detection limit of smartphone-digital image colorimetry compared to UV-vis spectrometer was better at about 22%. Finally, the proposed method was tested to analyze Cr concentration in actual samples (drinking and tap water) that give satisfactory accuracy (< 2.0%) and precision (< 5.0%).*

KEYWORDS: *Cr speciation; Trivalent chromium; Hexavalent chromium; Gold nanoparticles; Digital image colorimetry; DIC; Smartphone.*

INTRODUCTION

Chromium is an element with contrast health-effect to the human body, distinguished by its valence. Trivalent chromium or Cr(III) has a key role in metabolizing proteins, carbohydrates, and lipids, and thus it is an essential dietary nutrient needed at concentrations of 50–200 µg per day [1], [2]. In contrast, hexavalent chromium or Cr(VI) is highly toxic. The Cr(VI) damages blood cells by causing oxidation reactions when it enters

the bloodstream, inducing hemotoxic, genotoxic, and carcinogenic [3], [4]. The maximum allowable concentration of Cr(VI) in drinking water is 0.05 ppm, and total Cr concentrations should be less than 0.1 ppm (~2 μmol/L) [1, 2]. These two oxidation states of chromium, i.e., Cr(III) and Cr(VI) species, are the most stable forms in environments [3, 5]. Chromium is found in rocks, volcanic dust and gases, soil, plants, and animals. Besides that, chromium is also produced by industrial activities such as dyes and pigments, leather tanning, chrome plating, wood preserving, etc. [6]. Based on this contrasting toxicity to human health and its increasing use in the industry, monitoring and quantitative analysis of chromium in environmental samples are crucial.

The well-known quantitative analytical methods to determine chromium include Inductively Coupled Plasma–Mass Spectroscopy (ICP-MS) [7], Atomic Absorption Spectroscopy (AAS) [7, 8], Raman spectroscopy [9], electrochemical analysis [10–12], and UV-Vis spectrometry [13]. Most of these methods have excellent sensitivity, but there is a need for alternatives that provide a simple, inexpensive and portable method. In recent years, colorimetric combined with smartphone detection have emerged as a valuable method for qualitative and quantitative analysis of chemicals, such as the detection of organic [14–16] and inorganic [17–20] compounds. On the other hand, ubiquitous smartphones are equipped with decent cameras and sophisticated software. The resolution of the smartphone camera has been improved and it can be used as a mobile detector. Meanwhile, the smartphone`s application acts as a miniature computer for processing the raw data obtained from the built-in camera. We use colorimetry that utilizes visible color, i.e., Red Green Blue, to seek a linear relationship between color change and chemical concentration change [20–22]. Therefore, the coupled between colorimetry and smartphone gives various advantages over conventional instrumental methods, i.e., simple, low-cost, portable, greener, and robust [21, 23, 24].

The determination of chromium ions using colorimetry and smartphone detection is described in this paper. Due to their remarkable selectivity and sensitivity for various heavy metals, gold nanoparticles (AuNPs) were utilized as a colorimetric agent for the detection of mercury [25], lead [26], cadmium [27], and other heavy metals. AuNPs are sophisticated materials with an extremely small size,

ranging from 10-100 nm, as compared to bulk gold. As a result, AuNPs exhibit a distinctive Surface Plasmon Resonance (SPR) feature at wavelengths about 520 nm that is sensitive to size changes. Because of analyte-triggered aggregation, which enlarges the particle size of initial AuNPs, most AuNP-based colorimetric sensing relies on the color shift of AuNPs from red to blue. The color change of AuNPs is proportional to the change in analyte concentration [26]. For the first time, we use these unique features of AuNPs for chromium speciation and colorimetric sensing in our study. Smartphones are utilized as detectors because they are ubiquitous and convenient, making them ideal for analyzing Cr ions in the field with low resources.

EXPERIMENTAL SECTION
Reagents and instruments

All chemical reagents were of the highest purity available and used as received without further refinement (analytical grade). Chloroauric acid (HAuCl$_4$), citric acid (C$_6$H$_8$O$_7$), chromium (III) nitrate (Cr(NO$_3$)$_3$), potassium chromate (K$_2$CrO$_4$), salts of ions for the test of selectivity and other reagents were purchased from Merck Ltd. (Darmstadt, Germany). All aqueous solutions were prepared with deionized water. All glassware was cleaned with detergent (5%), 4M HCl and deionized water prior to use. Absorption spectra of the AuNPs were measured using a Genesys 150 UV-vis Spectrometer (Thermo Scientific, U.S.). A smartphone camera (Xiaomi Redmi Note 8, China) with wide lenses of 48 MP sensor, phase detection focusing, f/1.8 aperture, and Light-Emitting Diode (LED) flash was used to record pictures as digital images and processing the quantitative data using attached Android apps.

Synthesis of AuNPs

Gold nanoparticles (AuNPs) were synthesized following the Turkevich method [28] with some modifications. In brief, 35 mL aqueous solution of precursor HAuCl$_4$ 0.25 mM was stirred in a flask and preheated to 100°C on a hotplate. After that, 35 mL aqueous solution of citric acid 2.5 mM was added to the boiling HAuCl$_4$ that acted as reductant. After keeping stirred and boiled for 15 minutes, the solution's color changed from colorless to ruby-red, which shows the formation of AuNPs. AuNPs in this experiment were freshly prepared. All experiments were carried out

in triplicates. The synthesized AuNPs were characterized using a UV-vis spectrometer.

Colorimetric smartphone detection

The software of Android Studio (Google, U.S.) was adopted to construct the Apps, called QAnalytics, for in smartphone digital-image cropping, RGB color-value extraction, and data calculation. The Red-Green-Blue (RGB) color channel was used in this research as an additive color model in which RGB light is added together in various ways to reproduce a broad array of colors. All samples solution was poured into cuvettes, and the images were captured directly as a photograph in a home-made photo studio and computed by the smartphone application. Thus, the concentration of metal ions in the samples can be analyzed instantly by the smartphone. To prevent the error from a different camera and external light sources, the analyte's digital image were always captured together with the standards in one file, as previously described [24].

RESULTS AND DISCUSSION
#### Synthesis of AuNPs and selectivity tests

The precursor of gold nanoparticles used in this study was Au^{3+} from $HAuCl_4$ that has a pale-yellow color. Upon the addition of citric acid as a reductant, the color of Au^{3+} turned to ruby-red that indicates the formation of colloidal gold Au^0 or AuNPs. The UV-vis spectrometer also confirmed this formation of AuNPs with peak absorbance at 520 nm (Fig. 1). The mechanism that occurs in the formation of AuNPs is the reduction of Au^{3+} which has a reduction potential of 1.5 V by citric acid with a reduction potential of 1.1 V [5, 29]. This chemical reduction method of synthesizing AuNPs is known as the bottom-up approach. The reactions that occur in the gold nanoparticles synthesis can be seen in the following equation:

$$2Au^{3+} + 6e^- \rightarrow 2Au^0$$
$$E^o = +1.5\ V$$

$$3C_6H_8O_7 \rightarrow 3C_5H_6O_5 + 3CO_2 + 6H^+ + 6e^-$$
$$E^o = -1.1\ V$$
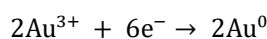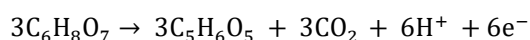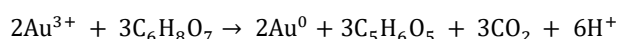
$$2Au^{3+} + 3C_6H_8O_7 \rightarrow 2Au^0 + 3C_5H_6O_5 + 3CO_2 + 6H^+$$
$$E^o = +0.4\ V$$

In this reaction, citric acid acts as an electron donor in the reduction-oxidation of gold nanoparticle formation. This is because the reducing potential of citric acid (+1.1 V)
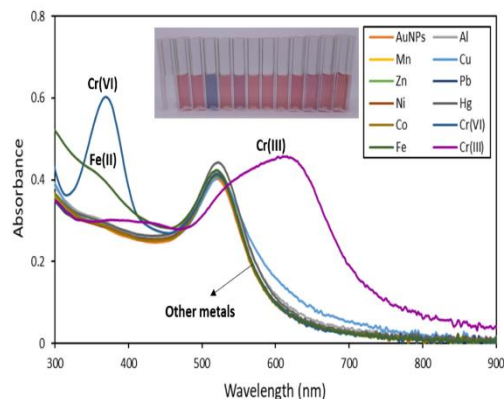

Fig. 1: The response of AuNPs peak absorbance to various metal ions with concentration of 20 ppm. Peak absorbance of AuNPs was red-shifted in the present of Cr(III), while it was blue-shifted in the present of Cr(VI). The other metals have no effect to the AuNPs absorbance. Inset: the digital image of the samples in cuvettes for this selectivity test.

is lower than Au^{3+}, which is +1.5 V. Therefore, citric acid as a reductant tends to undergo oxidation to donate electrons. In contrast, Au^{3+} as an oxidant tends to gain electrons and undergoes reduction. The selectivity of the system was tested to various metals, i.e., Na(I), K(I), Ca(II), Ba(II), Mn(II), Zn(II), Ni(II), Co(II), Fe(II), Al(III), Cu(II), Pb(II), Hg(II), Cr(III), and Cr(VI). The results, as shown in Fig.1, demonstrate that AuNPs were selective only to Cr ions on the optimized condition with pH = 5, incubation time 10 minutes, and temperature 30°C. The peak absorbance of colloidal gold nanoparticles surface plasmon resonance (520 nm) was red-shifted to 620 nm when Cr(III) was introduced, while when Cr(VI) was added to the system, it was blue-shifted to 370 nm. At high concentrations, i.e., > 20 ppm, Fe ions interfere with the analysis, and thus it must be separated from the sample before being added to the system.

Analysis of Cr(III) and Cr(VI) using UV-vis spectrometry

UV-visible spectrometry has been the gold standard for quantitative investigation of chemical compounds that undergo electronic transitions from the ground state to the excited state via absorption of the energy source. Because most metals are colorless in their natural state and at low concentrations, they must be complexed with ligands, organic dyes, or chromophores before UV-visible spectrometry can be used to investigate them. We used a more contemporary technique to colorize metals
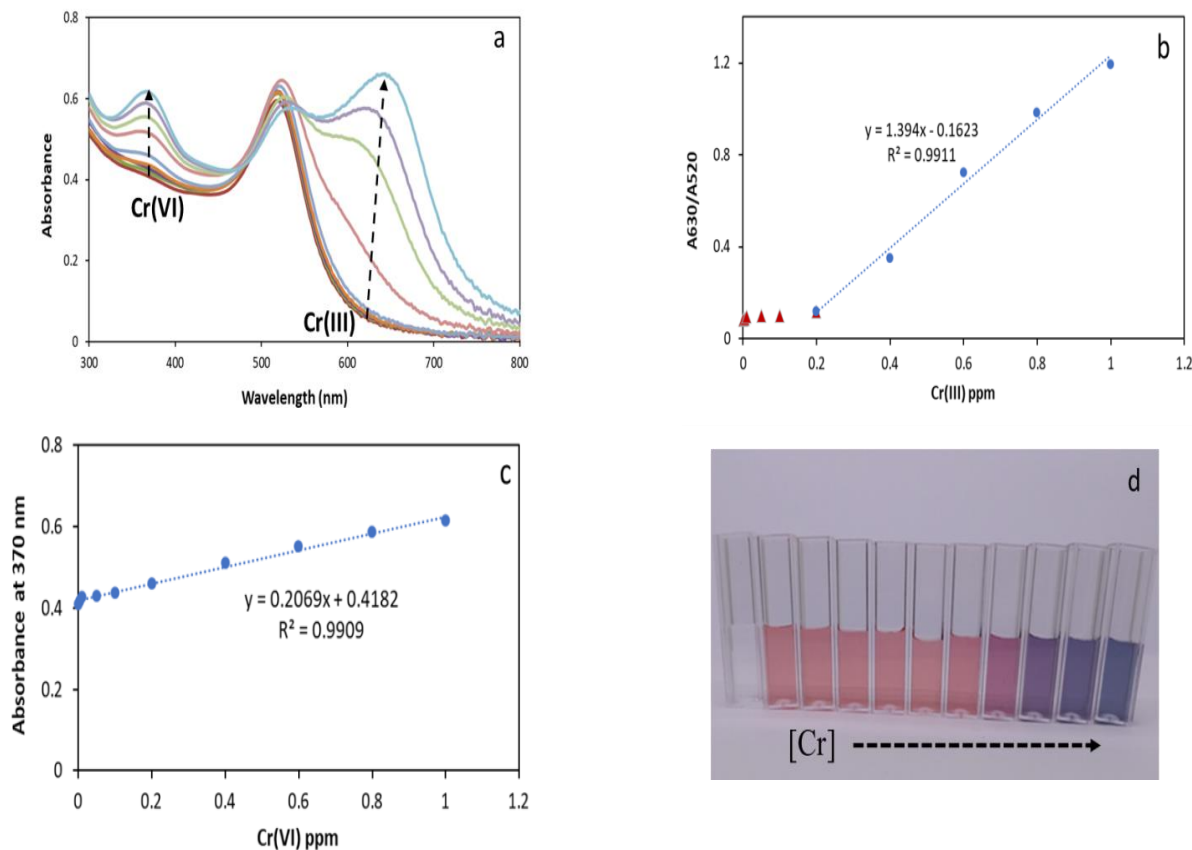
Fig. 2: (a) The change of UV-vis spectra upon addition of various Cr(III) and Cr(VI) concentration (0-1.0 ppm) into AuNPs colloid; (b) The plot of the absorbance 630/520 nm ratio versus Cr(III) concentration; (c) The plot of the absorbance at wavelength 370 nm versus Cr(VI) concentration; (d) Digital image of Cr ions from 0 to 1.0 ppm in AuNPs.

in this study, which involved employing gold nanoparticles (AuNPs) as a color carrier due to their surface plasmon resonance characteristic. To match the target analyte, AuNPs can be functionalized with a variety of chemical substances. Fig. 2 demonstrates how the absorbance of AuNPs colloid changes when different Cr(III) and Cr(VI) concentrations are added. The changes of Cr(III) concentration had a linear relationship with $R^2 = 0.9911$ at an absorbance ratio of 630/520 nm in the concentration range of 0.2–1.0 ppm, while Cr(VI) had $R^2 = 0.9909$ at an absorbance of 370 nm in the concentration range of 0.0–51.0 ppm. The lowest concentration (0–0.2 ppm for Cr(III)) can't be detected accurately due to overlapping absorbance bands.

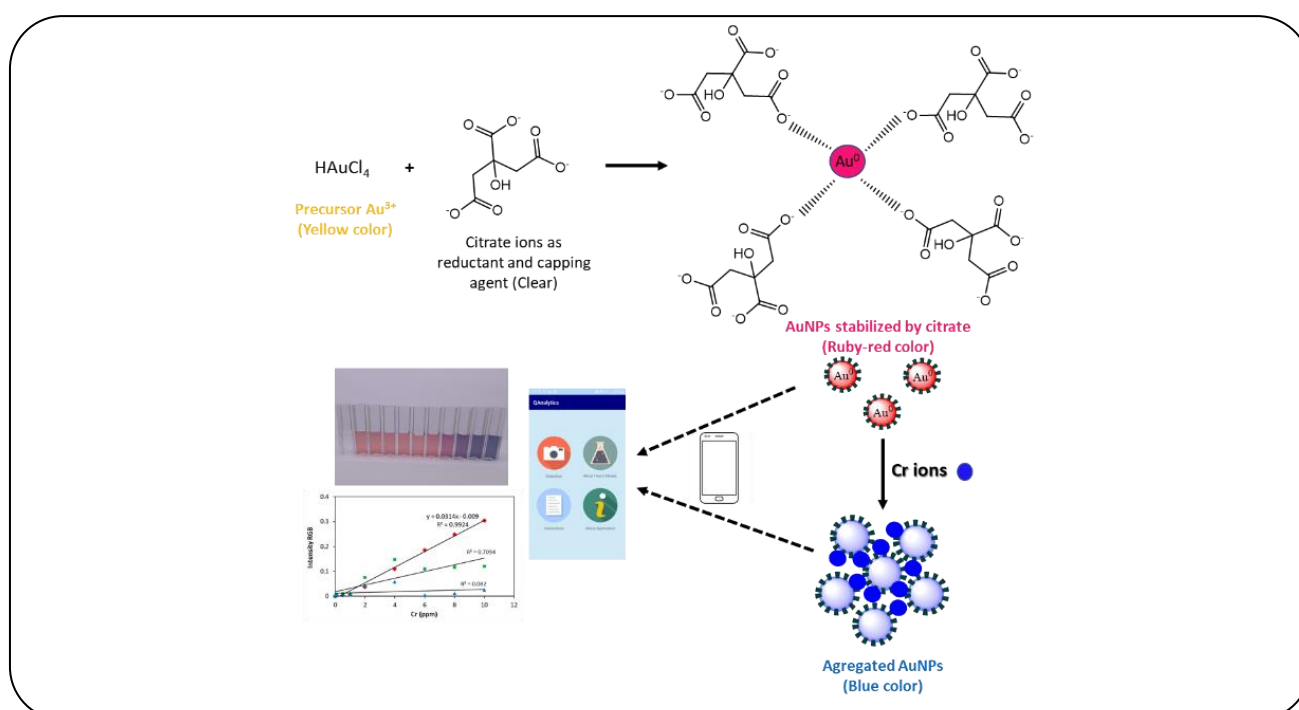### Digital image colorimetry coupled with smartphone detection

To improve the portability and ease of use, in addition to the UV-vis spectrometer, we used the digital image-based colorimetry tandem with smartphone detection for chromium ions analysis, as shown in Fig. 3. The smartphone serves as a digital image recorder which at the same time also acts as a detector that calculates the analyte concentration in the sample based on the calibration curve method. Since the Cr(VI) peak absorbance is in the UV region (i.e., 370 nm), we only detect the Cr(III) for the DIC-smartphone method. Nevertheless, total chromium concentration, after reduction of Cr(VI) to Cr(III) can also be done using the DIC-smartphone method.

Table 1 and Fig. 4 show the results of digital image colorimetry tandem with smartphone analysis. For this DIC-smartphone method, the chromium ions concentration was calculated from red color intensity by applying the Lambert-Beer equation, complying with the method in our published papers [20], [24]. The color of the red channel gave the highest slope and correlation coefficient compared to blue and green channels; thus, we used this red color for the rest of the experiments. Digital image colorimetry used reflectance instead of absorbance

Table 1: The value and intensity of RGB color from the smartphone digital-image colorimetry.

Cr (ppm)	Color Value			Color Intensity		
	Red	Green	Blue	Red	Green	Blue
0	163.9	110.5	124.2	0	0	0
0.005	162.8	108.4	122.2	0.003	0.009	0.006
0.01	162.3	108.4	123.1	0.004	0.009	0.004
0.05	162.3	107.9	122.8	0.004	0.010	0.005
0.1	160.7	108.5	121.9	0.009	0.008	0.008
0.2	150.6	92.9	112.3	0.037	0.075	0.044
0.4	127.5	78.7	108.6	0.109	0.147	0.058
0.6	107.1	85.8	122.7	0.185	0.110	0.005
0.8	92.4	84.4	120.6	0.249	0.117	0.013
1.0	81.3	83.7	117.2	0.304	0.121	0.025

Fig. 3: The illustration of chromium ions detection using AuNPs as colorimetric agent and subsequent digital image colorimetry detection using smartphone. The smartphone Apps, called QAnalytics, was pre-installed in the smartphone.

in the spectrometer. Therefore, in DIC-smartphone, the actual color of the sample gives the highest color intensity. This result is opposites with the sample's complementary color that offers the highest absorbance in UV-vis spectrometry.

The next step is to determine the Limit of Detection (LOD) picked from 3σ (three times of standard deviation) of ten replicates of blank measurements and divided by the slope of the calibration curve at the ppm level [24, 30, 31]. The Cr(III) ions detection limit of DIC-smartphone was found to be 0.027 ppm (0.52 uM). This LOD of the DIC-smartphone method is better compared to UV-vis spectrometer for about 22%, namely 0.051 ppm (0.98 uM) and 0.035 ppm (0.67 uM) for Cr(III) and Cr(VI), respectively. Compared to other UV-vis spectrometry methods, as shown in Table 2, the DIC-smartphone method gives a broader linear range and better detection limit. This result is most likely due to a broader dynamic range of digital images, namely from 0 to 255 color values compared to 0 to 2.0 absorbance value in UV-Vis

Table 2: Present work compared to other reported methods for Cr determination.

Methods	Linear range		Detection limit		Ref.
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
ICP-MS*,**	NA		0.15 ng/mL		[7]
AAS*	0.003−50 ug/L		0.05−0.2 ug/L		[2], [8]
Raman scattering	NA	1.71-171 nM	NA	1.01 nM	[34]
Raman spectroscopy	0.07−0.40 uM	0.01−0.25 uM	0.05 uM	0.005 uM	[35]
Electrochemical	NA	0.5−180 μM	NA	0.3 uM	[10]
Electrochemical	NA	0.5−378 uM	NA	0.026 uM	[11]
UV-vis spectrometry	5−65 uM	NA	1.4 uM	NA	[36]
UV-vis spectrometry	NA	0.05 nM	NA	2-100 nM	[37]
UV-vis spectrometry**	0.05−1.45 ug/L	NA	8 ng/L	NA	[13]
Smartphone- colorimetry	0−80 uM	NA	11 uM	NA	[38]
AuNPs and UV-vis spectrometry	0.2−1.0 ppm (3.8−19 uM)	0.05−1.0 ppm (0.96−19 uM)	0.051 ppm (0.98 uM)	0.035 ppm (0.67 uM)	This work
AuNPs and DIC-Smartphone	0−1.0 ppm (0−19 uM)	NA	0.027 ppm (0.52 uM)	NA	

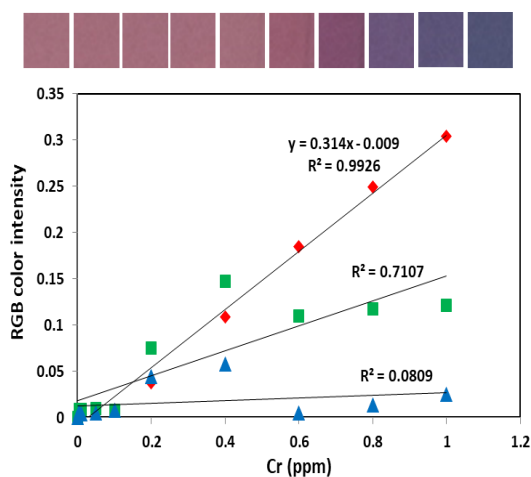**Value for total chromium   **After preconcentration step   NA: Not available*

Fig. 4: The cropped digital image of standard solutions containing 0 to 1.0 ppm chromium ions, plotted together with its calibration curve. Red color, which has the highest slope and linearity, was used for further calculation.

spectrometry. Since the U.S. Environmental Protection Agency (EPA) has a drinking water standard of 0.1 ppm for total chromium [1], the developed DIC-smartphone is applicable for quantifying this Cr ions concentration in drinking water. These results is in accordance with previous report of meso-2,3-dimercaptosuccinic acid (DMSA) functionalized gold nanoparticles performance for chromium detection [32], [33].

Experiments on recovery and analysis of real samples

We performed recovery tests using the addition or spiking approach to validate the developed analytical method. After that, the accuracy was compared to that of UV-vis spectrometry, which was used as a reference method (Table 3). Furthermore, the suggested method was used to determine Cr concentration in real-world samples (drinking and tap water), yielding acceptable accuracy (2.0%) and precision (5%). Following references [20], [32], the precision was measured as the percent relative standard deviation (RSD) from three replicate analyses, while the accuracy was calculated as the percent error of the proposed DIC-smartphone approach compared to UV-Vis spectrometry.

CONCLUSIONS

In summary, we have successfully developed a simple analytical method to analyze chromium ions concentration in aqueous samples using gold nanoparticles. The visible color change was linearly proportional to the change of chromium concentration. By using the optimized condition, we can achieve the detection limit of 0.027 ppm. This detection limit is better than the maximum allowable level of Cr(VI) in drinking water set by U.S. EPA, which is 0.1 ppm. The protocol was tested to analyze chromium in actual samples with satisfactory accuracy and precision, with quantitative recovery. By coupling the Digital Image

Table 3: Accuracy and precision test using recovery experiments of spiked samples (n = 3).

Samples	Added (ppm)	UV-vis spectrometry (ppm)	Smartphone-based colorimetry	
			Found (ppm)	Recovery (%)
Drinking water	0	0	0	-
	0.05	0.051±0.002	0.052±0.002	104
	0.10	0.104±0.003	0.098±0.004	98
Tap water	0	0	0	-
	0.10	0.101±0.001	0.101±0.003	101
	0.20	0.197±0.002	0.197±0.003	99

Colorimetry (DIC) with a smartphone as a detector, this method has better portability than any bulk instrument. The offered protocol provides a real-time, simple, low-cost, and on-site analytical method for chromium ions speciation that can be used in a remote area with limited resources.

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