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Determination of nanomolar chromate in drinking water with solid phase extraction and a portable spectrophotometer

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ABSTRACT

Determination of chromate at low concentration levels in drinking water is an important analytical objective for both human health and environmental science. Here we report the use of solid phase extraction (SPE) in combination with a custom-made portable light-emitting diode (LED) spectrophotometer to achieve detection of chromate in the field at nanomolar levels. The measurement chemistry is based on a highly selective reaction between 1,5-diphenylcarbazide (DPC) and chromate under acidic conditions. The Cr–DPC complex formed in the reaction can be extracted on a commercial C18 SPE cartridge. Concentrated Cr–DPC is subsequently eluted with methanol and detected by spectrophotometry. Optimization of analytical conditions involved investigation of reagent compositions and concentrations, eluent type, flow rate (sample loading), sample volume, and stability of the SPE cartridge. Under optimized conditions, detection limits are on the order of 3 nM. Only 50 mL of sample is required for an analysis, and total analysis time is around 10 min. The targeted analytical range of 0–500 nM can be easily extended by changing the sample volume. Compared to previous SPE-based spectrophotometric methods, this analytical procedure offers the benefits of improved sensitivity, reduced sample consumption, shorter analysis time, greater operational convenience, and lower cost.

1. Introduction

Chromium is widely distributed in the earth's crust as chromite ($FeCr_2O_4$) and can be found in waste water from a variety of sources including metal smelting, electroplating and tanning, metallurgy, and dyestuff industries. In aqueous systems, chromium occurs principally in oxidation states III and VI [1]. Unlike Cr(III), an essential micronutrient that combines with various enzymes in the body to transform sugar, protein, and fat [2], Cr(VI), on the basis of experimental and epidemiological evidence [3], is recognized as a highly toxic elemental species. As such, it is classified as a group I human carcinogen by the International Agency of Research on Cancer (IARC) [4]. Costa [5] analyzed the potential hazards of Cr(VI) (chromate) in drinking water not only from human and animal studies but also from a mechanistic point of view. The provisional guideline value for total chromium set by the World Health Organization (WHO) is 50 μg/L (~0.96 μM) [6], and the maximum contaminant level (MCL) for total chromium set by the US Environmental Protection Agency (EPA) is 100 μg/L (~1.92 μM) [7]. This EPA standard was established two decades ago using the toxicology data available at that time. As additional research on Cr(VI) toxicity has become available, EPA has begun to re-evaluate the standard and has recommended enhanced monitoring of chromate in drinking water [7]. California currently uses a 1 μg/L (~20 nM) detection limit for purposes of reporting (DLR) for monitoring chromium 6 in drinking water [8]. The Office of Environmental Health Hazard Assessment (OEHHA) of the California EPA proposed a Public Health Goal (PHG) of 0.02 μg/L (~0.4 nM) for chromate in drinking water in July, 2011 [9], substantially lower than the 0.06 μg/L (~1.1 nM) level established in 2009 [10].

Although numerous methods for chromate determination are available, such thresholds represent substantial challenges for making chromate measurements. Published methods cover a wide array of modern instrumental analysis. For example, in *Standard Methods for the Examination of Water and Wastewater* [11], atomic absorption, inductively coupled plasma, colorimetric, and ion chromatographic methods are all cited as useful analytical techniques. Reviews of methods for determining chromium concentrations and speciation [1,12–15] indicate that most published methods suffer from shortcomings such as a reliance on laborious and time-consuming procedures, inherently challenging instrumentation (consider, e.g., electrode instability in potentiometric analyses), or expensive and bulky laboratory systems that require experienced analysts. For quick, sensitive, and low-cost chromate measurements, spectrophotometric methods appear to offer an efficacious alternative. Among potentially useful chromogenic reagents, 1,5-diphenylcarbazide (DPC) is widely used for either direct detection or as a post-column reagent after ion chromatographic separation

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[11]. The principle of the method is chromate-induced oxidation of DPC to diphenylcarbadiazone, the enol form of which then reacts with the Cr(III) formed in the reaction to yield a red-purple product. The DPC-based method is highly selective for hexavalent chromium in the presence of other metals [16].

The molar absorptivity of the detected Cr species ($\sim$40,000 cm^{-1} M^{-1}) is high relative to many colorimetric methods [11], but direct measurements using pathlengths on the order of 10 cm do not provide suitable sensitivity for nM levels of chromium. Effective techniques for enhancing spectrophotometric detection [17] include (a) extending the detection cell pathlength and (b) concentrating the analyte. Liquid core waveguide (LCW) spectrometry has been used to increase pathlength and thereby greatly increase sensitivity for chromate measurements [18,19], achieving detection limits as low as 0.2 nM [18]. However, with a cost per gram that is several times that of gold, the expense of LCW material (Telfon AF) [20] can limit the application of this approach in developing countries or other places where budget constraints are severe.

Alternatively, solid phase extraction (SPE) techniques are particularly attractive for sample preconcentration because of their simplicity, the wide variety of available sorbents, and their low consumption of organic solvents [21–23]. Several absorber materials, such as Amverlite XAD-4 resin [24], mixed bed adsorbent acid-activated montmorillonite (AAM)–silica gel [25], alumina [26], and Ambersorb 563 resin [27] have been utilized for concentrating the Cr–DPC complex. The Cr–DPC that is concentrated on absorbents is removed with various eluents and quantified with visible spectrophotometry. However, these procedures typically require large sample volumes (250–5000 mL) and long analysis times (60–1000 min). Furthermore, custom-made columns with special absorbents can typically be used only 5–10 times, thus limiting their application in routine assays. Although a commercial SPE (Sep-Pak C18) [28] has been utilized for Cr–DPC preconcentration, producing an enrichment factor of 10, the 150 nM detection limit for the analysis is high relative to typical drinking water standards.

To establish a simple, low-cost, and sensitive method for nanomolar chromate analysis of drinking water, this study began with a detailed assessment of Cr–DPC reaction parameter optimization. Although the colorimetric reaction of chromate and DPC in acid conditions is well known, there are discrepancies in previous characterizations of reaction parameters, even including those given in official standard measurement protocols. The reaction kinetics of Cr(VI) with DPC does not appear to have been systematically investigated at different reagent concentrations. The present study includes systematic optimization of SPE parameters—e.g., eluent type, flow rate (sample loading), and sample volume. Toward the objective of minimizing analytical costs, the stability of SPE cartridges was also assessed to establish cartridge longevity after repeated use. To facilitate Cr measurements in the field, light-emitting diodes (LEDs) were selected as the source of light for our portable spectrophotometric system. LEDs are particularly useful because of their energy efficiency, negligible warm-up time, and low cost [29]. The optimized measurement system is well suited for both lab assays and field analyses of trace chromate in drinking water.

2. Experimental

A series of laboratory analyses was first conducted with standard solutions of known chromate concentration to quantitatively assess the effects of various analytical parameters and identify a suite of conditions appropriate for measuring chromate at levels characteristic of drinking waters. Once an optimal parameter suite was determined, the method was applied to spectrophotometrically measure chromate in a variety of bottled and tap waters in the laboratory. A portable field kit that included a custom spectrophotometer was also used to measure chromate in drinking waters at selected field sites. All experiments and analyses were conducted at room temperature ($\sim$20 °C).

2.1. Reagents

All chemicals used were reagent grade or better, purchased from Baker (mallbaker.com) or Sigma (sigmaaldrich.com) and were used without further purification. Milli-Q water (millipore.com), 18.2 MΩ cm, was used throughout. Stock chromate solution (1 mM) was prepared by dissolving K_2CrO_4 in water. Working standards were prepared daily by stepwise dilution of the stock solution with Milli-Q water. Ultrapure grade sulfuric acid was used to prepare 2.5 M H_2SO_4 for sample acidification. A 0.5% (m/v) DPC stock solution was prepared by dissolving 0.25 g of 1,5-diphenylcarbazide in 50 mL of acetone, which was stored in a brown glass bottle at 4 °C.

2.2. Instrumentation and measurement of absorbance

For most of the laboratory analyses, the spectrophotometric system utilized a tungsten lamp (avantes.com) driven at 5 V as the light source and a USB 4000 miniature fiber optic CCD spectrometer (oceanoptics.com) as the detector; the sample cuvette pathlength was 1 cm. For examination of the influence of reagent concentrations, a benchtop spectrophotometer (HP 8453) with a 10 cm pathlength quartz optical cell was used. Cr–DPC absorbances were measured at 542 nm; absorbances at 700 nm were used for baseline drift corrections. Detector output (counts, I) was acquired on a laptop PC. Detector counts at 542 nm and 700 nm were converted to absorbance (A) via the following relationship [30,31].

$$A = \log \frac{I_0 - I_{dark}}{I - I_{dark}}$$

where I_0 is the light intensity (counts) recorded when the cuvette is filled with pure ethanol, I_{dark} is the light intensity (counts) recorded when the lamp is off, and I is the intensity of light recorded while the eluted sample is in the cuvette.

For chromate analyses in the field, a custom LED-based portable spectrophotometer was designed and constructed [32]. A 16 MHz microcontroller (arduino.cc) was used to direct instrument functions and data processing. This microcontroller, which was programmed using the manufacturer's programming language, had a 10-bit analog-to-digital (A/D) converter, 32KB of flash memory, 2KB RAM, and 1KB EEPROM; it was powered through a USB port (in laboratory testing) or by battery (in field applications). The light source consisted of two LEDs: 530 nm (liteonit.com) and 700 nm (lumex.com); the detector consisted of a TAOS TSL257 (taosinc.com) light-to-voltage integrated circuit. During each suite of measurements, the LEDs were activated alternately and the detected signals were processed with a simple 1 s RC filter. The processed voltage signal was sent to the A/D converter, converted to absorbance, and displayed on a 16 × 2 character liquid crystal display (LCD) plate (huijinglcd.com). The spectrophotometer dimensions are 16 cm × 8.5 cm × 6.5 cm; without batteries, the instrument weighs 280 g.

2.3. Complexation and preconcentration procedure

For the laboratory investigations relevant to method development, solutions of known chromate concentration were used: 1 mL of 2.5 M H_2SO_4 was added to 50 mL of standard chromate solution, followed by a 1 mL addition of the 0.5% (m/v) DPC solution. This combined solution was mixed thoroughly for 2 min, and then

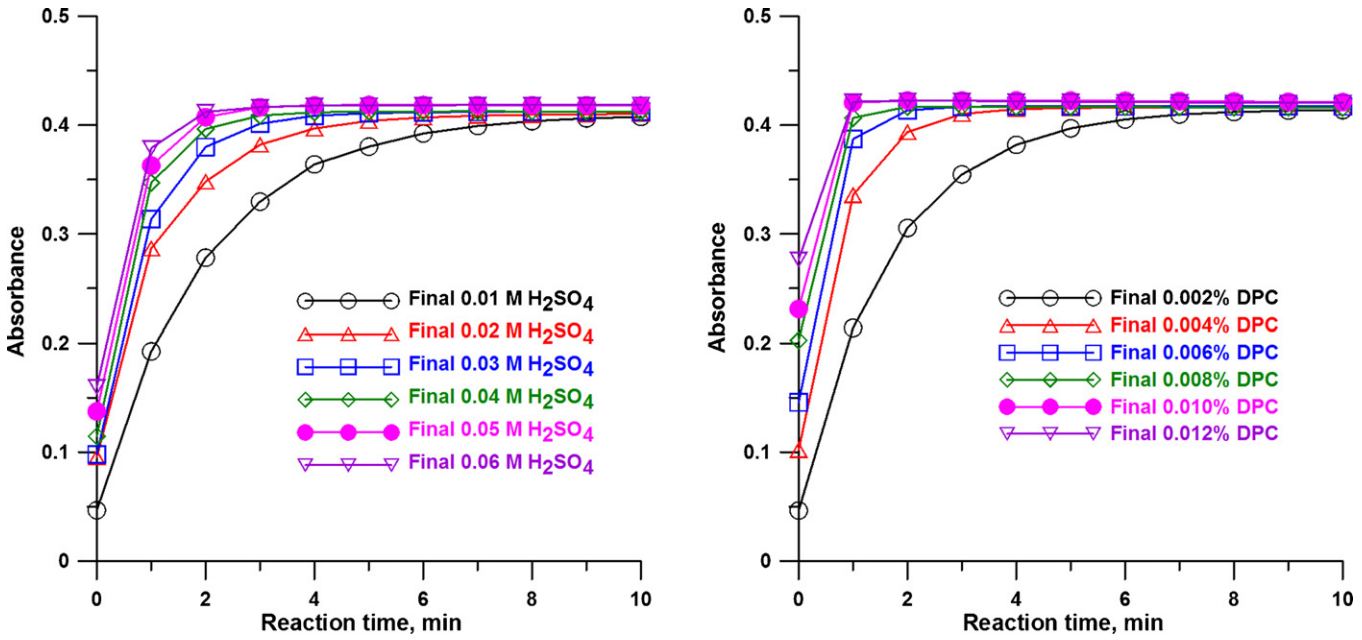

Fig. 1. Development of Cr–DPC absorbances over time for (left panel) a range of H_2SO_4 concentrations (with the DPC concentration equal to 0.005%) and (right panel) a range of DPC concentrations (with the H_2SO_4 concentration equal to 0.05 M).

loaded via a 60 mL syringe onto a preconditioned C18 cartridge (Sep-Pak Plus C18, waters.com) at a flow rate of 20–25 mL/min. (For simplicity, a syringe rather than a mechanical pump was used to load and elute samples.) After loading, the cartridge was cleaned with 2 mL of Milli-Q water to remove residual acid and other ions. The reddish-violet Cr–DPC complex on the cartridge was then eluted into a cuvette with 2 mL of methanol. Finally, the absorbance of the Cr–DPC eluate in methanol was measured as described in Section 2.2. For analysis of drinking water samples, the procedure was the same except that 50 mL of tap or bottled water was substituted for the 50 mL of standard chromate solution.

2.4. Drinking water sample collection and analysis

For the laboratory assays, bottled drinking water samples ($n = 3$) were purchased from local markets; tap water samples ($n = 4$) were collected in the lab or at local residences in St. Petersburg, FL. The samples were stored briefly in clean bottles without addition of reagent; all samples were analyzed within 4 h of collection. For the field analyses, drinking fountain water samples were collected from local parks and university buildings ($n = 4$). These samples were processed and analyzed with the portable field kit immediately after sample collection. Each water sample was first passed through a Sep-Pak Plus Accell CM cartridge, which contains a weak cation exchanger, in order to remove particles and interfering cations (e.g., Fe^{3+}) [11]. The sample (50 mL) was then acidified, complexed, and preconcentrated as described in Section 2.3. Finally, the absorbance of the colored methanol eluent was measured as described in Section 2.2.

3. Results and discussion

The influence of various parameters on chromate measurements (e.g., reagent composition, eluent type, sample-loading flow rate, sample volume) were investigated and optimized via univariate experimental design. A 50 nM chromate standard solution was used throughout the parameter-optimization procedures unless stated otherwise.

3.1. Influence of H_2SO_4 and DPC concentrations

The influence of the concentrations of the acidifying agent, H_2SO_4, and the complexing agent, DPC, on Cr–DPC absorbance values was evaluated using a 1 μM chromate solution. For a wide range of reagent concentrations, no significant absorbance differences were observed (Fig. 1) after reaction completion. At H_2SO_4 concentrations ≥0.05 M and DPC concentrations ≥0.010%, the reaction was complete within approximately 2 min. Therefore, solutions of these higher concentrations were used for all subsequent experiments.

3.2. Effect of eluent identity

Three organic solvents were tested to elute the extracted Cr–DPC from the cartridge. As shown in Fig. 2, methanol, acetone, and ethanol all exhibited similar elution abilities. Because 50 mL of the 50 nM sample was concentrated to 2 mL, the final Cr–DPC concentration in the eluent should be ~1.25 μM. Therefore, the spectrum of 1.25 μM Cr–DPC in water is also shown for comparison. The insignificant absorbance differences between the water and eluent spectra indicate that satisfactory recovery was achieved during the sample loading and elution procedure. Methanol was used as the eluent in all subsequent work because of its better equilibration/conditioning ability with the C18 SPE cartridge [33].

3.3. Influence of flow rate

The influence of flow rate on sample loading was investigated over a range of rates between ~12 and 43 mL/min. Flow rate was calculated as the total volume of the sample divided by the time required to pass the entire sample through the cartridge. No significant differences were found for flow rates between ~12 and 32 mL/min. At higher flow rates (~43 mL/min), a 10% reduction in signal was observed. This was likely due to insufficient contact time between the sample solution and C18. A flow rate of 20–25 mL/min was chosen to achieve a balance between cartridge extraction efficiency, convenience of sample loading, and analysis time (less than 3 min for a 50 mL sample).

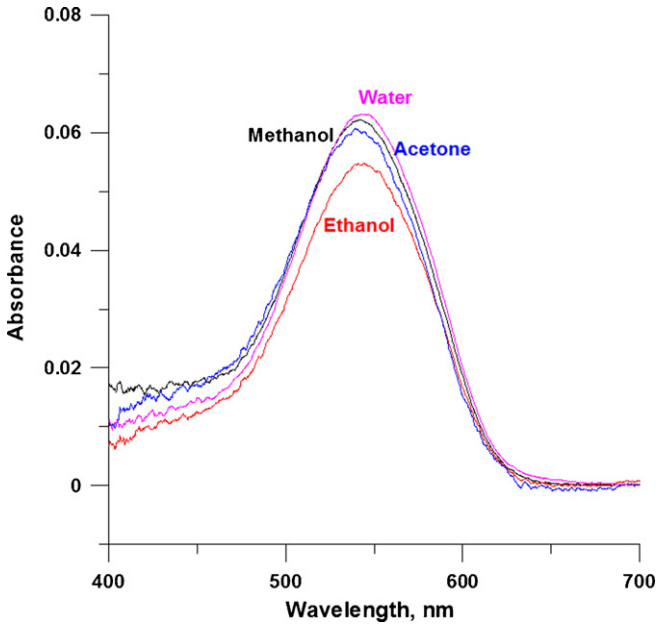

Fig. 2. Absorbance spectra of concentrated Cr–DPC in various eluents (50 mL of 50 nM sample concentrated to 2 mL eluent). For comparison, the absorbance spectrum of 1.25 μM Cr–DPC in water (formulated without use of the concentration and elution procedure) is also shown.

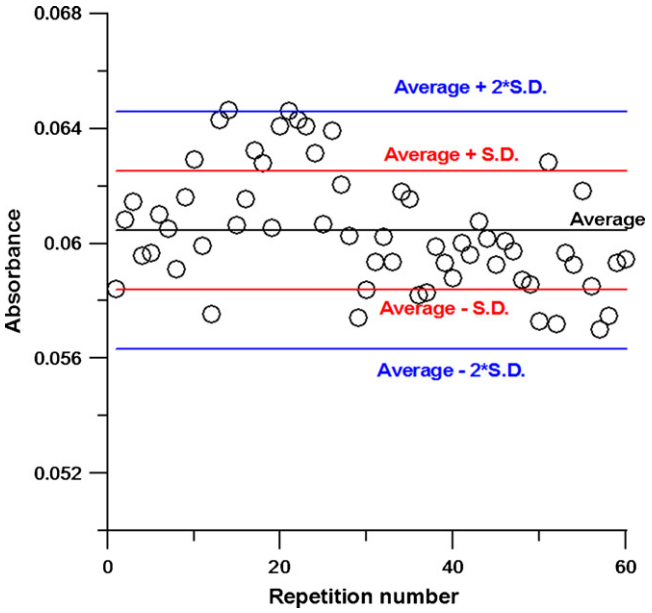

Fig. 4. Cr–DPC absorbance values measured for 60 consecutive extractions/elutions through a single SPE cartridge.

3.4. Influence of sample loading volume

For samples with a fixed concentration, the maximum sample loading volume depends on both the cartridge loading capacity and the breakthrough volume [22,34,35]. The influence of sample loading volume on Cr–DPC absorbance was then investigated over the range of 10–150 mL. As illustrated in Fig. 3 (circle symbols), absorbance increased linearly with increasing sample volume for volumes between 10 and 100 mL, indicating complete extraction of Cr–DPC in this range. In contrast, for sample volumes ≥125 mL, absorbances deviated from that linear trend. This departure indicates that a portion of the Cr–DPC passing through the cartridge had not been extracted onto the resin. To substantiate this interpretation, samples that had already passed once through the cartridge were then re-extracted, eluted, and measured again as described in Section 2.3. The results in Fig. 3 (square symbols) show that Cr–DPC absorbances for the eluates of the second extraction were essentially zero for loading volumes below 100 mL and became increasingly large for greater volumes. Therefore, the maximum sample loading volume for the selected SPE C18 cartridge was taken as 100 mL, providing an enrichment factor of 50.

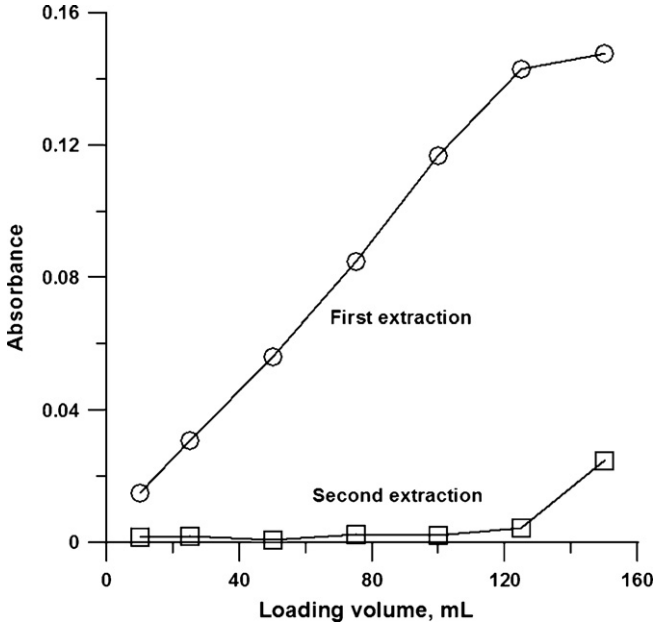

Fig. 3. Cr–DPC absorbance as a function of sample loading volume.

3.5. Stability of the SPE cartridge

The stability of the SPE cartridge was investigated by repetitive analysis of 50 mL of a 50 nM standard solution. As shown in Fig. 4, no significant differences were observed for 60 consecutive Cr–DPC extractions and elutions. The average absorbance and standard deviation (2σ) for the 60 samples were 0.0601 (±0.0041). The stability of this cartridge is superior to that reported for custom-packed columns used in previous publications [24–27]. Results obtained using different cartridges ($n = 5$) from the same manufacturer's batch showed good reproducibility: for a 50 nM standard solution, the average absorbance and standard deviation (1σ) were 0.0608 (±0.0025).

3.6. Analytical figures of merit

For 50 mL samples, the optimization evaluation led to the following selected protocol: the volumes of reagent additions were 1 mL of 2.5 M H_2SO_4 and 1 mL of 0.5% DPC solution, the reaction time was 2 min, the sample-loading flow rate was 20–25 mL/min, and the eluent (methanol) volume was 2 mL. A calibration curve over a range of Cr(VI) between 0 and 500 nM is shown in Fig. 5. The range of linear absorbance can be easily broadened by decreasing the sample loading volume. The Fig. 5 inset shows absorbance spectra for samples with low (≤125 nM) chromate concentrations. The total analysis time for each sample is ~10 min, including 2 min for the reduction/complexation reaction, ~3 min for sample loading, and 5 min for other procedures.

The detection limit, calculated as three times the standard deviation for measurements of blank samples ($n = 9$) divided by the calibration curve slope, was 3.0 nM (equivalent to an absorbance of

Table 1
Drinking water samples: chromate concentrations, spike additions, and recoveries.

Sample	Added, nM	Found, nM	Added, nM	Found, nM	Recovery, %	Added, nM	Found, nM	Recovery, %
Tap water—1	0	9.6	50	58.0	96.8	100	108.5	98.9
Tap water—2	0	9.0	50	60.0	102.0	100	109.8	101.0
Tap water—3	0	25.8	50	76.6	101.7	100	121.8	96.1
Tap water—4	0	34.3	50	83.5	98.5	100	130.7	96.4
Bottled spring water—1	0	14.9	50	64.7	99.6	100	112.3	97.5
Bottled spring water—2	0	29.7	50	78.2	97.0	100	126.4	96.8
Bottled purified water	0	Not detected	50	50.1	100.1	100	100.3	100.3
Fountain drinking water	0	17.7	50	67.1	98.8	100	116.2	98.4

Table 2
Comparison of Cr–DPC extraction methods.

SPE material	Eluent	Enrichment factor	Sample volume, mL	Detection limit, nM	Reusable times of SPE	Analysis time, min	Linear range, nM	RSD, %	Reference
Amverlite XAD-4 resin	Acetone–H_2SO_4	27	400	115	7	>100[a]	N.D.[b]	3.6	[24]
Mixed-bed adsorbent	Polyethylene glycol–H_2SO_4	25	250	115	10	>62[a]	0–19,000	4.0	[25]
Alumina	H_2SO_4	125	5000	77	5	>1000[a]	0–19,000	2.5	[26]
Ambersorb 563 resin	Acetone	30	150	65	N.D.[b]	>75[a]	0–4800	<6.0	[27]
C18	Acetone–H_2SO_4	10	50	16	N.D.[b]	>20[a]	0–23,000	2.5	[28]
C18	Methanol	25	50	3	60	10	0–500	3.4	This work

[a] Calculated from the reported sample loading volume and maximum flow rate.
[b] No data.

0.0029). The relative standard deviation of 3.42% (n = 60) for repetitive determinations of 50 nM chromate is quite good for a fully manual procedure.

3.7. Applications

The SPE method with CCD spectrophotometric detection was used to assess chromate in drinking water as described in Sections 2.3 and 2.4. The results of the analyses are tabulated in Table 1. With the exception of bottled purified water, the various investigated tap, bottled (spring), and fountain waters had Cr(VI) concentrations between 9.0 and 34.3 nM. Spiked sample recoveries ranged from 96.1% to 102%, indicating insignificant analyte loss during sample pre-treatment (i.e., filtration through the cation-exchange cartridge) and low interference from other ions in the drinking water matrix.

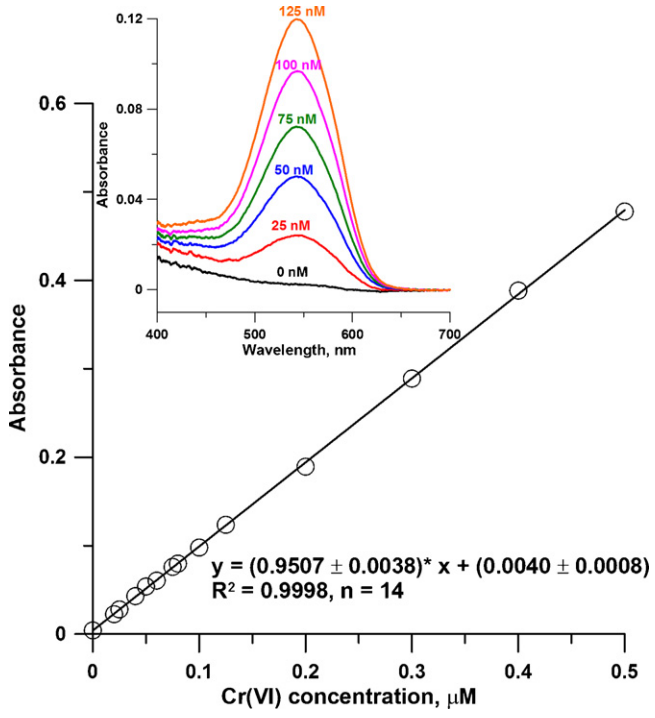

Fig. 5. Calibration curve obtained using the optimized parameters. The inset figure shows the Cr–DPC absorbance spectra of low-chromate samples in methanol eluent.

Using the portable field kit with an LED-based spectrophotometer, our measurement protocol was also applied to analysis of chromate in the field. Measured Cr(VI) concentrations for four different drinking-fountain water samples were 6.6 (±0.7), 24.6 (±1.4), 31.8 (±1.4), and 19.8 (±0.7) nM, n = 3. These results were in good agreement with those obtained through direct long-path LCW measurements [18] of the same samples: the corresponding concentrations of Cr(VI) measured by this second method were 7.1 (±0.4), 21.8 (±0.5), 35.0 (±1.1), and 18.7 (±0.6) nM, n = 3. Based on the one-tail t-test at the 95% confidence level, differences between the results from the two measurement protocols were not statistically significant (t-calculated is 0.05, lower than t-critical 2.35).

4. Conclusions

Commercial SPE cartridges combined with a custom-made spectrophotometer provide a very sensitive, simple, and low-cost approach for both routine laboratory assays and field analyses of trace chromate in drinking water. As summarized in Table 2, relative to other protocols [24–28] that utilize SPE and spectrophotometric procedures for chromate analysis, the method developed in this work exhibits improved sensitivity, reduced sample consumption, shorter analysis time, and easier operational processing. Most importantly, utilization of a highly stable commercial SPE cartridge that can be used for at least 60 analyses makes the analytical protocol highly reproducible (i.e., custom synthesis of SPE materials and columns is not required). Through repetitive use of a single cartridge, the column cost per analysis is reduced from 5 US dollars to less than 10 cents, making this chromate measurement method suitable even for developing countries or other entities operating under severe budget constraints. A portable field kit that included an LED-based spectrophotometer was shown to be suitable for field applications, further demonstrating the analytical simplicity of the measurement protocol. In view of proposals to establish or lower concentration thresholds for chromate in drinking water [e.g., 9,10], increasing the sensitivity of this method—for example, through the use of larger sample volumes or longer pathlength

cells—is a reasonable focus for future methodological improvement. The general protocol described here is amenable to such adjustment.

Acknowledgments

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