Research Article

Application of Pneumatic Flow Injection-Tandem Spectrometer System for Chromium Speciation

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In this approach, a pneumatic flow injection-tandem spectrometer system, without a delivery pump, has been developed to study chromium speciation. In this system, suction force of pneumatic nebulizer of a flame atomic absorption spectrometer has been used for solution delivery through the manifold. Cr(VI) and total Cr concentrations were determined using UV-Vis and FAAS spectrometers, respectively. The Cr(III) was determined by difference. The calibration curves were linear up to $10\,\mu g\,mL^{-1}$ and $20\,\mu g\,mL^{-1}$ for Cr(VI) and total Cr with detection limit of $0.12\,\mu g\,mL^{-1}$ and $0.07\,\mu g\,mL^{-1}$ for Cr(VI) and Cr(III), respectively. The midrange precision and accuracy are less than 1.98% and $\pm 2.50\%$ for two species, respectively, at a sampling rate of $100\,h^{-1}$. This system was applied for the determination of the chromium species in spiked and natural waters as well as industrial waters.

1. INTRODUCTION

The demand for fast, reliable analytical methods for determining different species of an element in environmental samples has rapidly increased, because in most cases the different biological, nutritional, or toxicological properties depend critically on chemical form or oxidation state [1, 2]. Chromium is a naturally occurring element, mainly found in minerals, rocks, plants, soil, and water in volcano dust and gases. Although, chromium is known to exist in all oxidation states from Cr(0) to Cr(VI), the Cr(III) and Cr(VI) species are the most widespread in the nature. Trivalent Cr(III) and hexavalent Cr(VI) enter the environment as a result of effluent discharge, electroplating, tanning industries and oxidative dyeing [3]. Chromium(III) is considered as an essential micronutrient for humans playing a role in the maintenance of normal glucose, cholesterol, and fatty acid metabolism, whereas Cr(VI) is highly toxic than Cr(III). Its acute toxic effects include immediate cardiovascular shock, with later effects on kidney, liver, and blood-forming organs. The toxic nature of the Cr(VI) ions is attributed to their high oxidation potential and their relatively small size, which enables them to penetrate through biological cell membranes [4]. Hence, the speciation of chromium has special importance in several fields of life.

Up to now, several methods for speciation of chromium(VI) and chromium(III) have been investigated and published in different journals such as catalytic cathodic stripping voltammetry (CCSV) [5], X-ray absorption near-edge structure (XANES) spectroscopy [6], the separation or preconcentration methods using capillary electrophoresis [7], sorption [8, 9], liquid-liquid extraction [10, 11], extraction using ion-pair formation [12, 13], coprecipitation [14], extraction using supported liquid membranes (SLM) [15], solid phase extraction [16, 17, 19], ion exchange [18], cloud point extraction [20] followed by instrumental analysis such as UV-Vis [7, 13], energy dispersive X-ray fluorescence spectrometry [9], GFAAS [10, 11, 15–17], FAAS [14, 19], ion chromatography [18], and high-performance liquid chromatography (HPLC) [20]. The flow injection methods with conjunction by several detection techniques were also applied for the chromium speciation [3, 4, 21–28]. However, there are several disadvantages of using these methods such as using complicated chemical systems and techniques, expensive reagents and instruments such as ICP and ICP/MS, low sample frequency, and also two determination needs for each sample; first determining one of the species, followed by reduction/oxidation of the corresponding redox form and quantification of the total amounts of chromium or other species.

Flow techniques present several useful analytical features, in particular the possibility to attain high sample throughput, little sample handling, or manipulation and this eliminates many of the stringent clean particles often necessary for
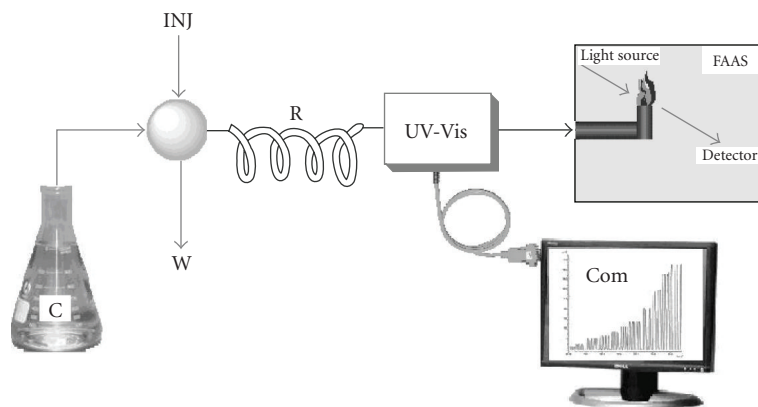
FIGURE 1: Schematic diagram of the PFIA-TS system used for the speciation of chromium. C: carrier; INJ: injector loop valve; R: reactor; UV-Vis: UV-Vis detector; FAAS: flame atomic absorption spectrometer; Com: computer; W: waste.

standard chromium determinations. FI constitutes the most advanced form of solution manipulation available to analytical chemists for mixing and transporting the reagents and products of a chemical reaction to the point of measurement. Four basic sections of an FIA system are as follows pump, injector valve-loop, reactor, and detector. Pump is the heart of an FIA system. Different kinds of pumps such as peristaltic pump, HPLC pump, and syringe pump have been used in all FIA systems [29, 30].

In a flame atomic absorption spectroscopy, an aqueous solution of the sample is nebulized as a fine spray and then mixed with gaseous fuel and oxidant that carry it into a burner. The most commonly used nebulization devices are pneumatic devices in which a jet of compressed gas aspirates and nebulizes the solution. The transport of solution to the nebulizer tip is known as aspiration. With the concentric nebulizer, the nebulization gas flows through an opening that concentrically surrounds the capillary tube, causing a reduced pressure at the tip and thus suction of the sample solution from the container. It is known as Bernoulli effect. In most cases, the flow of solution is laminar, and the aspiration rate is proportional to the pressure drop along the capillary and to the fourth power of the capillary diameter; it is inversely proportional to the viscosity of solution. The solution drawn up by the capillary tube encounters the high velocity of the nebulizing gas, which causes the formation of droplets. The efficiency and the droplet size distribution mostly depend on the diameter and the relative position of the end of the capillary and the nose-piece. The effect of the sample uptake rate on the absorbance has been studied previously [31]. A maximum is obtained between flow rates of 2–6 mL min^{-1} when the efficiency is about 10%.

Here, the authors have designed a simple, cheap, and fast pneumatic flow injection analysis-tandem spectrometer (PFIA-TS) system to work without usual pumps for the speciation of Cr(VI) and Cr(III). The basic element of PFIA-TS is using suction force of a flame atomic absorption spectrometer (FAAS) pneumatic nebulizer for solution delivery (carrier) through the FI manifold. So, usual pumps in FI systems have been eliminated. The potentials of the automated

methodology were evaluated using the spectrophotometric monitoring of chromium as a model of chemistry. The method is suitable for chromium speciation with only one injection and without need to use of an oxidant/reductant in carrier stream. This technique has been designed with the aim to combine the advantages of FIA system and two kinds of spectrometry. In this system, Cr(VI) and total Cr concentrations were determined using UV-Vis spectrometer and FAAS, respectively. The Cr(III) concentration is determined by difference.

2. EXPERIMENTAL

2.1. Reagents

All reagents were prepared from analytical reagent grade chemicals unless specified otherwise and purchased from Merck Company. All aqueous solutions were prepared with double-distilled water (DDW). A Cr(VI) solution stock containing 0.1 g L^{-1} Cr(VI) was prepared by dissolving 0.3735 g pure potassium chromate in 1 L of water. A Cr(III) standard solution was prepared by the dilution of a Titrisol stock solution (0.1 g L^{-1}) Cr as chromium chloride. Working standard solutions of Cr(VI) and Cr(III) used for calibration were prepared by the appropriate dilution of the above solutions. The 0.002 M sym-diphenylcarbazide (sym-DPC) with 0.015% (w/w) KNO$_3$(as ionization suppressor) solution was used as carrier solution in this system. This solution was prepared by dissolving 0.625 g of sym-DPC in 500 mL acetone and 15 g KNO$_3$ diluted to 1000 mL by 0.5 M nitric acid solution. Stock solutions of interfering ions were prepared by dissolving the appropriate salts in water.

2.2. Apparatus

A scheme of the single-line PFIA-TS system is presented in Figure 1. In this system, suction force of a Philips FAAS (Model PU 9110X) pneumatic nebulizer with an N$_2$O-acetyle flame has been used for solution delivery (carrier) through the manifold. A six-way injection valve (Rheodyne,

Model 7125, USA) allowed the sample to be loaded directly into a 400 μL loop, and subsequently injected into the carrier stream. Manifold lines consisted of 0.8 mm i.d. polyethylene tubing. The injection valve was kept at the loading position for each first 5 seconds of every run to load the sample. After that it was switched to the injection position to inject the sample to the carrier stream. The valve was kept in the injection position for further 30 seconds to ensure that the entire sample was flushed out of the sample loop. Next, the valve was again switched to the loading position to fill the sample loop for the next run. The generated products in reactor were channeled to the 10 mm in-length optical flow cell, a variable wavelength UV-Vis spectrophotometer detector (Knauer, Germany) at 548 nm, then an FAAS with a 5 cm optical path-length (burner). The carrier flow rate in this manifold was 2.4 mL min^{-1}. The signals from UV-Vis detector were performed with computer via the Chromstar software (Bruker, Germany). The light source for FAAS was a Cr hollow cathode lamp. The wavelength was set to 357.9 nm with a spectral slit-width of 0.5 nm and a lamp current of 12 mA.

3. RESULTS AND DISCUSSION

3.1. Optimization of the experimental condition

The performance of the proposed flow injection system depended on the efficiency of the reaction occurring between sym-DPC and chromium(VI) in the reactor, as well as on the reactor length, reactor diameter (reactor i.d.), and the loop volume.

The reactor length (with i.d. 0.8 mm) was varied between 20 cm and 160 cm. The optimizations for two detectors are shown in Figure 2. The analytical signal for UV-Vis detector significantly increases for lengths ranging between 20 cm and 100 cm and remains nearly constant afterwards. The response for FAAS detector decreases slightly for lengths ranging between 20 and 100 and then decreased with increasing in reactor length. The best results were obtained at the length of 100 cm.

The influences of reactors i.d. were studied in range 0.2–1.2 mm. The results for two detectors are shown in Figure 3. In reactors having an i.d. smaller than 0.8 mm, the interactions between the sample and the DPC were weak and the peak height decreases for UV-Vis detector signal. The response of the FAAS increases from 0.2 mm i.d. to an i.d. of 0.8 mm, remaining nearly constant afterwards. Also, the carrier flow rate decreases with decreasing of reactors i.d. An i.d. larger than 0.8 mm led to increase dispersion coefficients. A 0.8 mm i.d. was chosen as the optimum diameter.

The response of the system was also studied for various sample volumes injected (loop volume): 20, 80, 100, 150, 220, 300, 400, 500, 1000, and 2000 μL. These optimizations are shown in Figure 4. The analytical signal increased with an increase of the volume. Larger volumes resulted in higher, yet broader peaks. Consequently, the sampling frequency and the peak capacity sharply decreased. A 400 μL volume was selected as the loop volume.

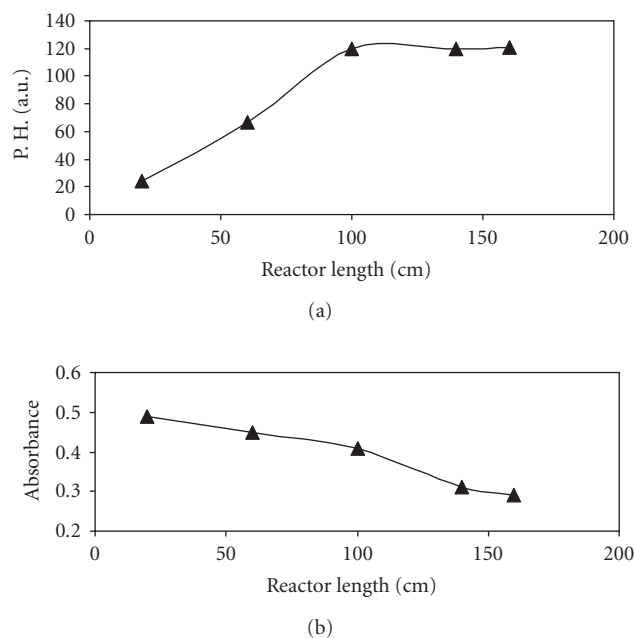FIGURE 2: Influence of the reactor length on analytical signal: (a) UV-Vis detector, [Cr(VI)] = 5.00 μg mL^{-1}, reactor i.d. = 0.8 mm, and loop volume = 400 μL and (b) FAAS detector, [Cr] = 10.00 μg mL^{-1}, reactor i.d. = 0.8 mm, and loop volume = 400 μL.

TABLE 1: Optimization of the experimental condition PFIA-TS system for chromium speciation.

Parameter	Study range	Optimum value
Reactor length (cm)	20–160	100
Reactor diameter (mm)	0.2–1.2	0.8
Loop volume (μL)	20–2000	400

The optimization ranges of the experimental conditions and optimum value for PFIA-TS system are summarized in Table 1.

3.2. Sample matrix interference

The effect of potentially interfering ionic species on the determination of Cr(VI) with UV-Vis detector was investigated. The tolerance limit was defined as the concentration of foreign ions resulting in the ±5.0% error in the determination of 5 μg mL^{-1} Cr(VI). It was found that even a 250-fold excess of Ca^{2+}, Mg^{2+}, Cl^-, Br^-, I^-, F^-, 200-fold excess of NO_3^-, Zn^{2+}, Al^{3+}, Mn^{2+}, Ni^{2+}, SO_4^{2-}, 120-fold excess of Cu^{2+}, Co^{2+}, $S_2O_4^{2-}$, $S_2O_8^{2-}$, $S_2O_5^{2-}$, CO_3^{2-}, and 45-fold excess of Fe^{3+}, Cd^{2+}, VO_3^-, 12-fold excess of Hg^{2+}, Pb^{2+}, and CH_3COO^- did not interfere.

3.3. Calibration plot and precision

A typical response of UV-Vis detector in optimum conditions was shown in Figure 5. The results show the stability of the flow rate and repeatability of the proposed system. The
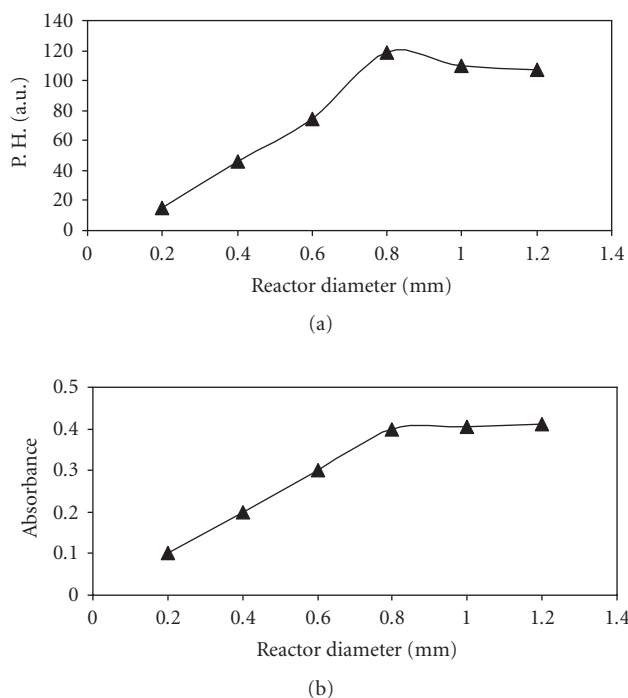
(a)

(b)

FIGURE 3: Influence of the reactor diameter on analytical signal: (a) UV-Vis detector, [Cr(VI)] = $5.00\,\mu\mathrm{g\,mL^{-1}}$, reactor length = 100 cm, and loop volume = $400\,\mu\mathrm{L}$ and (b) FAAS detector, [Cr] = $10.00\,\mu\mathrm{g\,mL^{-1}}$, reactor length = 100 cm, and loop volume = $400\,\mu\mathrm{L}$.

(a)

(b)

FIGURE 4: Influence of the loop volume on analytical signal: (a) UV-Vis detector, [Cr(VI)] = $5.00\,\mu\mathrm{g\,mL^{-1}}$, reactor length = 100 cm, reactor diameter = 0.8 mm and (b) FAAS detector, [Cr] = $10.00\,\mu\mathrm{g\,mL^{-1}}$, reactor length = 100 cm, and reactor diameter = 0.8 mm.

linearity of the response was evaluated for the analyte concentration ranging from 1 to $100\,\mu\mathrm{g\,mL^{-1}}$ under the above experimental conditions. The calibration graphs were linear up to $10\,\mu\mathrm{g\,mL^{-1}}$ and $20\,\mu\mathrm{g\,mL^{-1}}$ for Cr(VI) and total Cr and are described by the following equations:

$$\mathrm{P.\,H.} = 24.138(\mathrm{Cr(VI)}) + 2.3704, \quad n = 11, r = 0.9996,$$

$$\mathrm{Absorbance} = 0.0379(\mathrm{Cr}) + 0.001, \quad n = 11, r = 0.9991,$$

$$\text{(1)}$$

where P. H. is peak height in arbitrary unit (for UV-Vis detector signals), (Cr(VI)) and (Cr) are the chromium(VI) and total chromium concentrations, n is the number of experimental points, and r is the correlation coefficient. The detection limits (DL) were defined as the analytes concentration equal to 3 times the standard deviation of the most diluted standard solution. DL were found to be $0.12\,\mu\mathrm{g\,mL^{-1}}$ and $0.07\,\mu\mathrm{g\,mL^{-1}}$ for Cr(VI) and Cr(III), respectively. Through validation and applications to evaluate the analytical applicability of the method and to check its accuracy and precision, synthetic aqueous mixtures containing Cr(VI) and Cr(III) were analyzed. The precision and accuracy of the method were determined by 7 replicate analyses of standard solutions under optimum conditions. The midrange precision and accuracy are $< 1.98\%$ and $\pm 2.50\%$ for two species, respectively, at a sampling rate of $100\,\mathrm{h^{-1}}$. According to the results presented in Table 2, the concentrations of Cr(VI) and Cr(III)
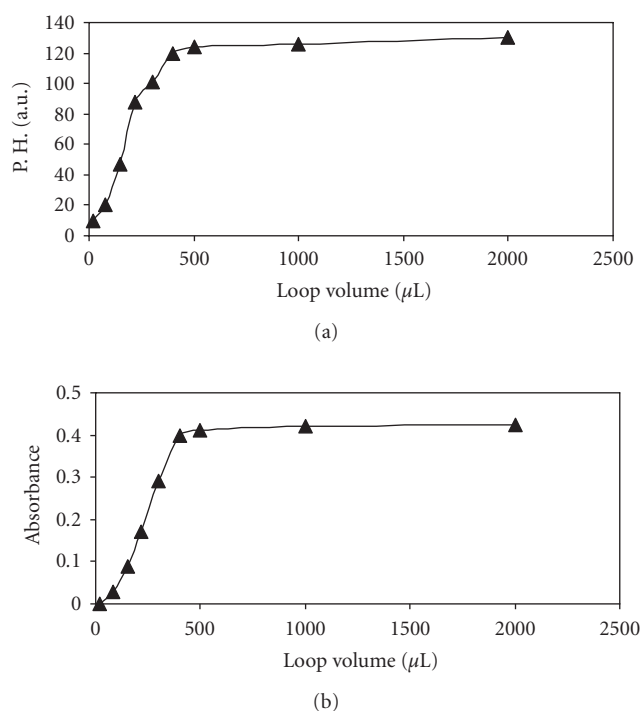
obtained with the proposed method are in good agreement with the expected values.

The proposed method was applied to the analyses of various water and leather treatment plant samples collected from different locations in Iran . The samples were filtered (Whatman filter no. 1) and determined by the proposed method. Initial concentration of chromium in these samples was determined before spiking. After spiking the samples with the known amounts of Cr(VI) and Cr(III), excellent recoveries were obtained and no matrix interference was observed (Table 3). Recoveries for Cr(VI) and Cr(III) were found to be in the range of $100 \pm 4.0\%$.
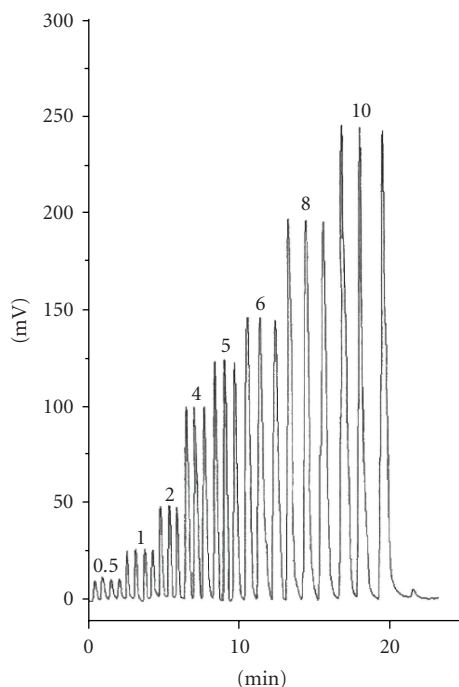
4. CONCLUSIONS

The application of the flow injection analysis-tandem spectrometer to the speciation analysis of trace Cr(VI) and Cr(III) in water samples has been demonstrated. In the proposed system, the pump from usual FIA manifold has been eliminated and suction force of a flame atomic absorption spectrometry (FAAS) pneumatic nebulizer has been used for solution delivery through the manifold. In this system, Cr(VI) and the total Cr concentrations were determined using UV-Vis and flame atomic absorption spectrometers, respectively. The method is very simple, rapid, accurate, and has good sensitivity and selectivity. It requires only small sample volumes ($400\,\mu\mathrm{L}$). It provides good reproducibility of the results (% RSD < 1.98) which is superior to other

TABLE 2: Determination results for Cr(VI) and Cr(III) in synthetic aqueous mixtures.

Added/μg mL^{-1}		Total found/μg mL^{-1}	Cr^{6+}/μg mL^{-1}			Cr^{3+}/μg mL^{-1}		
Cr^{6+}	Cr^{3+}		Found	RSD (%)	RE (%)	Found	RSD (%)	RE (%)
0.5	4.00	4.39	0.49	1.98	−2.00	3.90	1.47	−2.50
3.00	3.00	5.98	3.05	1.51	1.66	2.93	1.69	−2.33
5.00	6.00	11.00	4.90	1.73	−2.00	6.10	0.98	1.66
7.00	2.00	8.95	6.91	1.67	−1.28	2.04	1.33	2.00

TABLE 3: Determination results and recoveries for Cr(VI) and Cr(II) speciations in water and west water samples collected at different locations in Iran.

Sample	Added/μg mL^{-1}		Cr(III) found/μg mL^{-1}	Recovery (%)	Cr(VI) found/μg mL^{-1}	Recovery (%)
	Cr(III)	Cr(VI)	($n = 5$)		($n = 5$)	
Drinking water Zahedan city	0.00	0.00	0.00	—	0.00	—
	2.00	3.00	1.98	99.0	3.04	101.3
	0.00	0.00	0.00	—	0.00	—
Well water	3.00	3.00	2.97	99.0	3.02	100.7
	4.00	4.00	3.94	98.5	4.05	101.3
Lether treatment plant 1	0.00	0.00	1.33	—	0.00	—
	4.00	2.00	5.40	101.8	1.96	98.0
	2.00	3.00	3.39	103.0	2.90	96.7
Lether treatment plant 2	0.00	0.00	3.71	—	0.00	—
	3.00	2.00	6.65	98.0	2.05	102.5
	1.00	5.00	4.75	104.0	4.90	98.0
Caspian sea	0.00	0.00	0.00	—	0.00	—
	3.00	5.00	3.04	101.3	4.89	97.8
	5.00	2.00	4.95	99.0	1.97	98.5

FIGURE 5: Typical analytical signals of UV-Vis detector for determination of Cr(VI) with PFIA-TS system. Values above peaks are concentrations of Cr(VI) in μg mL^{-1}.

speciation methods already described in the literature. The PFIA-TS is inexpensive, stable, and available in every laboratory.

ACKNOWLEDGMENT

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