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Notes

Simple Spectrophotometric Flow Injection System with an In-valve Minicolumn for Enhancement during the Determination of Chromium(III) Using EDTA

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A simple spectrophotometric flow injection (FI) procedure for the determination of Cr(III) using ethylenediaminetetraacetic acid (EDTA) was developed. An FI system with a column packed with Amberlite IR-120(H) was employed for sample pretreatment. This leads to the possibility of a single standard calibration. A linear calibration in a range of 10 – 27 μg Cr(III) was obtained with a detection limit of 1 μg Cr(III) and RSD of 2% (18 μg Cr(III), n = 12). The proposed procedure was applied for determination of Cr(III) in leachate and dietary supplement samples. The results agreed with those obtained by the standard methods.

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Introduction

Chromium(III) is a minor essential element for a human body concerning carbohydrate and fat metabolism.[1] Picolinate salt of chromium has served as a dietary supplement for body-weight control. On overdosage, it could be accumulated in the body.

Various chromium determination procedures have been reported. These include for example, titration,[2] visible,[3,4] and luminescent spectrophotometry,[5] AAS (a USP standard method),[6–10] ICP-MS,[7] HPLC,[11] CE[12] and FIA.[13–15] In some procedures, ethylenediaminetetraacetic acid (EDTA) has been employed as a complexing agent for chromium before the final determination step. The slow reaction of Cr(III) with EDTA may be accelerated by employing heating or by using a catalyst.[2,12]

In this work, attempts were made to develop a spectrophotometric chromium determination using a simple spectrophotometric FI system with an on-line pretreatment minicolumn and employing EDTA, a chemical commonly available in a laboratory. Its applications to the assay of chromium picolinate dietary supplement samples and to ore leachate samples were demonstrated.

Experimental

Chemicals and reagents

All chemicals were analytical grade except when otherwise stated. Milli-Q water was always used. A reagent solution (0.06 M EDTA in 2 M NaOH) was prepared by dissolving a portion (22.60 g) of EDTA ($C_{10}N_2H_{14}O_8Na_2$, Merck) in NaOH (2 M) and the volume was made up to 1 L with sodium hydroxide solution (2 M). Chromium(III) standard solutions of appropriate concentrations were prepared from the 1000 ppm Cr(III) standard solution for AAS (Merck).

The FIA manifold

The FIA manifold is schematically depicted in Fig. 1. A mini-column (2 mm i.d. × 20 mm) packed with Amberlite IR 120(H) (BDH) replaced the sample loop of a six-port injection valve (Upchurch, Model V-451).

A standard/sample solution was propelled through the mini-column for a required period. By switching a three-way valve the minicolumn was then washed with water. Through another three-way valve, an eluent solution (2 M HCl), E1 was flowed to fill up the minicolumn (to be ready for the next step of elution by another eluent solution (2 M HCl), E2: this is to prevent the Schlieren effect). By switching the six-port valve, one caused the E2-eluent (in Fig. 1) to elute the sorbed Cr(III) from the minicolumn. The Cr(III) stream would merge with the reagent (0.06 M EDTA in 2 M NaOH) before passing through a 50 cm heating coil (immersed in a water bath of 80 ± 5°C) and a

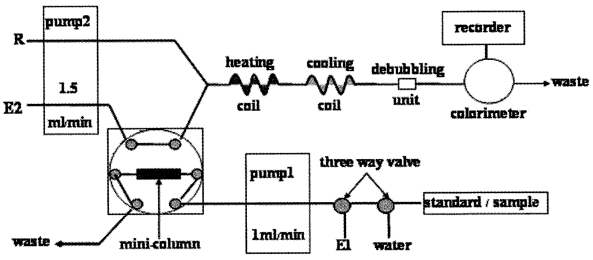

Fig. 1 FIA manifold for Cr(III) determination: wavelength, 530 nm; pH of the final solution, 3 – 6; eluent, E1 and E2 (2 M HCl); reagent, 0.06 M EDTA in 2.0 M NaOH; flow rate of eluent and reagent, 1 ml/min; flow rate of sample 1.5 ml/min; pH of standard/sample solution, 3 – 5; Cr(III) standard solution, 1 mg/l; controlled temperature, 80 ± 5°C and 32 ± 5°C.

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100 cm cooling coil (in a cooling bath of 32 ± 5°C). Any air bubbles would be trapped by a debubbling unit. The colored reaction product was continuously monitored for absorbance change by a colorimeter (Cole Palmer, Model 5565-15) using a filter for 530 nm. A calibration graph was constructed by using a single standard solution approach. Each peak area was plotted as a function of the mass of Cr(III). The amount of Cr(III) in μg was calculated from the relationship: Cr(III) (μg) = concentration of Cr(III) standard (μg/ml) × flow rate (ml/min) × the period that the standard solution passed through the minicolumn (min).

Results and Discussion

Preliminary spectral characteristics study

A mixture solution (1:1 mol ratio) of Cr(III) and EDTA was boiled before being adjusted to a pH value 3 – 11 by using HNO_3 (1 M) or NaOH (1 M). Spectra of the solutions were recorded using a UV-visible spectrophotometer, Shimadzu UV-265. The results indicate two absorption maxima at 540 ± 10 nm and 580 ± 10 nm. The first was from the red-violet solutions with pHs of 3 – 6, while the latter was from the blue solutions having pHs of 8 – 11.

Optimization for conditions of the FIA system

Various parameters were investigated. For the eluent, the concentrations of 1, 1.5, 2 and 2.5 M HCl were studied. Use of 2 or 2.5 M resulted in calibration graphs of lower slope values than those of 1 or 1.5 M HCl but yielding better peak shapes, better baseline signal, and also with shorter periods for the elution of Cr(III) from the column. 2 M HCl was then chosen. The effect of reagent (EDTA) concentration was examined in the range of 0.02 – 0.08 M. Signals obtained were found to be constant when the concentration was 0.05 M or higher. An EDTA concentration of 0.06 M was then selected. As in the preliminary studies, a solution of the Cr-EDTA complex product should be monitored in a solution of a pH in the range of 3 – 6. The EDTA solution should be prepared in a NaOH solution having the same concentration (2 M) as the eluent (HCl) concentration so that it would be neutralized in the stream of FIA manifold.

Flow rates of 1 ml/min for eluent and reagent streams were found to be satisfactory, while a flow rate of a loading step for the minicolumn should not exceed 1.5 ml/min. A higher flow rate led to a smaller peak. The set of conditions selected for the FIA procedure is summarized in Fig. 1.

Analytical characteristics

Under the conditions, for a single standard calibration using 1 ppm Cr(III) standard solution, a linear calibration: $y = 4.6x - 26.6$, $r^2 = 0.9964$ was found in the range of 10 – 27 μg, with a detection limit (3σ)[16] of 1 μg. A sample thoughput of 10 h^{-1} was achieved. RSD was 2% (18 μg Cr(III); 12 min loading period).

Applications

Leachate samples. Using the selected conditions, we studied leachate samples obtained from leaching the solid waste in ore dressing. The solid waste was treated with HNO_3 (1×10^{-4} M) by the acid volume to the weight of 1:25 to 50, with 24 h shaking. The leachate solution was analyzed for Cr(III). The results (Table 1) agreed with that obtained by using ICP-OES.

Dietary supplement samples. Dietary supplement samples containing chromium picolinate were obtained from local drug stores. A portion of ground sample containing 250 μg Cr was accurately weighed. To it were added 50 ml water and 10 ml conc. HNO_3 and the mixture was boiled for 1 h. To the filtrate from the mixture was added 5 ml conc. HNO_3 before further boiling until the solution became clear. The pH of the solution was adjusted to be 3 – 5 with 2 M NaOH before making the volume 250 ml with water. The final solution was analyzed for Cr(III) using the proposed FIA procedure. The results (Table 2) agreed well with those obtained by the USP method.[6]

Table 1 Determination of Cr(III) in leachate samples

Sample	Chromium(III)/μg ml^{-1}	
	FIA	ICP-OES[b]
1	0.48	0.51
2	0.57	0.62
3	0.68	0.75
4	0.94	0.90
5	0.87	0.85

a. Mean of triplicate results.
b. Determined by the Office of Primary Industries and Mines Region 3, Department of Primary Industries and Mines, Ministry of Industry.

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Table 2 Assay of dietary supplement for Cr(III) (triplicate)

Sample	Labeled amount/μg		FIA			USP method (Ref.)		
			Amount found/μg			Amount found/μg		
	Chromium picolinate form	Chromium(III) form	Chromium picolinate form[A]	Chromium(III) form[B]	Labeled amount, %	Chromium picolinate form[A]	Chromium(III) form[B]	Labeled amount, %
1[a]	1038	130	1038	130	100	1022	128	98
2[b]	480	60	469	59	98	485	61	102
3	1609	200	1641	204	102	1609	200	100
4[c]	1609	200	1633	203	102	1585	197	98

A was calculated from B. a. Containing: ZnO, 12.447 mg, $MnSO_4$, 9.621 mg, selenium yeast, 16.667 μg, vitamin B6, 2 mg; soil bean protein, 500 mg. b. Containing: apple vinegar powder, 400 mg, lecitin, 100 mg, grape fruit juice powder, 20 mg, kelp extract, 7.5 mg; vitamin B6, 1 mg. c. Containing: lecitin, 500 mg.

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