Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Chromatography A, 1118 (2006) 62–67
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Ultrafast concentration and speciation of chromium(III) and (VI)

Steven A. Steiner [a], Marc D. Porter [b], James S. Fritz [b,*]

[a] *Department of Chemistry and Engineering Physics, University of Wisconsin-Platteville, Platteville, WI 53818, USA*
[b] *Institute for Combinatorial Discovery, Ames Laboratory-US Department of Energy, Iowa State University, Ames, IA 50011, USA*

Available online 14 February 2006

Abstract

There is an increasing need to know the concentrations of chromium(III) and (VI) separately rather than only the total chromium content. A method is described for accomplishing this very quickly using only low-cost, portable equipment. Two small, resin-loaded extraction disks are placed one on top of the other in a plastic holder. Then a syringe containing the aqueous sample is attached to the holder and the sample is pushed through the disks. In a matter of seconds, all of the chromium(VI) is retained on the top anion-exchange disk and chromium(III) is extracted by the second cation-exchange disk. The concentrations on each disk are several hundredfold higher than they were in the original sample. The amounts of chromium(III) and (VI) extracted are measured directly on the surface of the respective disks by diffuse reflectance spectroscopy (DRS). Despite the low molar absorptivity of chromium(III) in aqueous solution, the concentration on the upper most layer on the extraction disk is high enough to permit the determination of chromium(III) in samples at the low mg/L range. Chromium(VI) can also be determined at low to sub-mg/L concentrations. A study of the cation-exchange disks was undertaken to compare the performance characteristics of disks containing sulfonated resins and those with iminodiacetate functionality. In addition, data are presented to show the effects of heating the iminodiacetate disks after the initial extraction. The disks were heated in hot water for 15–30 min to complete the slow complexation reaction on the surface.

Keywords: Chromium; Speciation; Colorimetric solid-phase extraction (CSPE); Diffuse reflectance spectroscopy

1. Introduction

Speciation of chromium(III) and (VI) has been a long-standing analytical challenge. The selective determination of chromium(VI) is of particular importance because of its toxicity. Analytical techniques such as atomic spectroscopy [1–3], spectrophotometry [4,5], fluorometry [6], and chemilluminescence [7] have been used for the quantitative determination of the chromium species after their separation or preconcentration. However, the reliable analyses of such samples can be problematic because of integrity compromises due to storage and transport and the affects of additives on the distribution of the two species used in sample preservation [8–10]. As is evident, there is a need for preconcentration methods that can be used under dynamic conditions with minimum sample manipulation.

Reddy and co-workers [11] described a simple method for selective preconcentration and determination of chromium(VI) using a flat sheet polymer sorbent. The polymer sheet was immersed in the aqueous sample, stirred for 1–8 h, and then the sheet was reacted with 1,5-diphenylcarbazide for 10 min to form a more intense color. Frenzel [12] proposed a highly sensitive field test in which chromium(VI) was retained on a small Empore anion extraction disk. The disk was subsequently dipped into a 1,5-diphenylcarbazide solution to form a highly colored oxidation product. Visual comparison with colored standards gave, however, a poor relative precision of 30–80%. An Empore anion-exchange disk has also been used to preconcentrate chromium(VI) prior to determination by atomic absorption [13].

Our research group has developed a fast and accurate method called colorimetric solid-phase extraction (CSPE) for concentrating and measuring selected analytes in aqueous samples. Specific methods using this technique have been designed for measuring low concentrations of iodine and iodide [14], silver [15], nickel [16,17] and pH [18] in drinking water samples from spacecraft and elsewhere. Only simple portable equipment is employed in CSPE and the analyses can be performed on-site. Typically, a measured 10 mL water sample in a syringe is injected through an extraction disk that is impregnated with a selective colorimetric reagent and mounted in a plastic holder. The selected analyte is extracted and concentrated onto the disk surface as a colored complex. The next step measures the diffuse reflectance of the analyte directly on the disk by a portable

* Corresponding author. Tel.: +1 515 294 5987; fax: +1 515 294 3578.
E-mail address: kniss@ameslab.gov (J.S. Fritz).

0021-9673/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2006.01.117

reflectance spectrometer, with the amount then calculated from a calibration plot prepared with known standards. The SPE and data acquisition steps require a total time of about 1 min.

A CSPE method is now described for speciation of chromium(III) and (VI) in aqueous samples. Chromium(VI) is preconcentrated onto an anion-exchange disk and chromium(III) is simultaneously retained by a second cation-exchange disk, which is mounted in series after the anion-exchange disk. Chromium(VI) is determined with excellent selectivity in the approximate range of 0.1–10 mg/L in the original sample and chromium(III) is measured in the 1–50 mg/L range.

2. Experimental

2.1. Chemical reagents and solutions

All chemicals were analytical-reagent grade from one of the following sources: J.T. Baker (Phillipsburg, NJ, USA); Fisher (Fair Lawn, NJ, USA); or Aldrich (Milwaukee, WI, USA). Standard solutions of Cr(III) and Cr(VI) were prepared from $Cr(NO_3)_3{\cdot}9H_2O$ and Na_2CrO_4, respectively, in 1.0 mM HCl made with purified water obtained from a Nanopure II water purification system (Barnstead, Dubuque, IA, USA). Separate standard solutions of Cr(III) and Cr(VI) were used to produce the calibration plots needed for quantitation. Sample solutions containing both chromium species were prepared by dilution of more concentrated standards with 1.0 mM HCl solution.

2.2. Instrumentation

The diffuse reflectance spectrometer (DRS) consisted an FO-6000 fiber optic light source (World Precision Instruments, Sarasota, FL, USA) connected via a 1.0 mm diameter fiber optic cable to a standard SMA connector port on an ICZ Integrating Cube (StellarNet, Tampa, FL, USA) The visible light output from the fiber optic source is directed onto the 15 mm aperture opening of the integrating sphere and illuminates the surface of the membrane during the analysis. The diffuse reflected light from the sample surface is collected by 1.0 m length fiber optic cable having a 1.0 mm diameter connected into a second standard SMA connector on the integrating sphere which is angled away from the aperture opening of the integrating sphere. The diffuse reflected light from the sample membrane is transferred through the fiber optic cable to a StellarNet EPP2000C fiber optic spectrometer controlled by the SpectraWiz software operating on a Gateway Solo 5300 laptop computer. The spectral data collected by the SpectraWiz software is transferred to MS-Excel for calculation of the Kubelka–Munk function and for all data plotting.

The Kubelka–Munk function, $F(R)$, is defined as:

$$F(R) = \frac{(1-R)^2}{2R}$$

where R is the absolute diffuse reflectance. $F(R)$ is directly related to the concentration of analyte, C, by

$$F(R) = \frac{\varepsilon C}{s}$$

where ε is the molar absorptivity of the sample and s is the scattering coefficient of the sample surface.

2.3. CSPE procedure

An anion-exchange membrane Empore anion SR extraction disk (3M, St. Paul, MN, USA) was used to extract Cr(VI), and for the cation-exchange membranes either a Bio-Rex AG 50W-X8 cation-exchange membrane (Bio-Rad Labs., Richmond, CA, USA), the Empore chelating, Cation-SR or SDB-XC extraction disks (3M, St. Paul, MN, USA) were used to extract Cr(III). A 13 mm diameter disk was cut from either a 47 or 90 mm extraction disk. These were placed in a plastic Swinnex membrane filter holder (Millipore, Franklin Lake, NJ, USA) in a stack with the anion-exchange disk on top and the cation-exchange disk just below. The disks were used directly without any prior treatment.

A 10 mL portion of a spiked water sample or a standard solution for calibration was drawn into a 10 mL plastic syringe (Becton Dickinson, Franklin Lake, NJ, USA) with a male Luer Lock fitting at the tip of the syringe barrel. The Swinnex holder is attached through a female Luer Lock fitting to the syringe and the water sample is slowly forced through the membrane stack at 10–20 mL/min. Following the sample delivery, the syringe is removed from the Swinnex holder and filled with ~10 mL of air. The syringe is subsequently reattached to the Swinnex holder, and the remaining residual water is forced from the holder and membrane. The membrane holder, now devoid of water, is again removed from the syringe and opened to remove both membranes for diffuse reflectance analysis. The membrane is carefully dabbed dry using a Kimwipe lintless tissue to remove any residual water from the membrane surface. The dry membrane is inserted into the DRS with the top surface mated to the aperture of the integrating sphere. The diffuse reflectance spectrum from the surface of the membrane is collected from three different angles in order to take into account any abnormalities on the membrane surface. The three spectra are averaged and baseline corrected to 100% reflectance and converted to $F(R)$ values, which are in turn used to correlate with concentration of the chromium species in solution. Typically, three separate disks and samples are used to acquire a single calibration point.

3. Results and discussion

3.1. Chromium(III)

Although the common chromium(III) salts have a violet or green color in solution, the color intensity is typically considered to be too weak for a practical spectrophotometric determination. However, passage of an aqueous sample through an extraction disk can offer an approximately 1000-fold concentration factor [16]. Preliminary experiments demonstrated that the chromium(III) is strongly retained on an Empore Cation-SR disk, giving a violet color on the upper surface. However, this disk was brown in color when wetted by water, appeared to have lower capacity and gave a higher background diffuse reflectance