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Conversion of chromium(III) propionate to chromium(VI) by the Advanced Oxidation Process Pretreatment of a biomimetic complex for metal analysis

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Abstract

The use of H_2O_2 and UV irradiation to remove organic ligands in a chromium(III) complex for the subsequent chromium analysis is reported. The Advanced Oxidation Process (AOP) using a 5.5-W UV lamp, H_2O_2 and Fe^{2+}/Fe^{3+} as catalyst (photo Fenton process) was found to give complete and quantitative Cr(III) → Cr(VI) conversion and removal of ligands in chromium(III) propionate $[Cr_3O(O_2CCH_2CH_3)_6(H_2O)_3]NO_3$, a biomimetic chromium species, as subsequent chromium analyses by the 1,5-diphenylcarbazide method and atomic absorption revealed. The current process eliminates the need for mineralization and/or dissolution of the matrix in order to remove the organic ligand, the traditional pretreatments of a sample for metal analysis. Studies to optimize the conditions for the oxidation processes, including the use of Fe^{2+}/Fe^{3+} catalyst, length of UV irradiation, H_2O_2 concentration, pH, power of UV lamp, and reactor size, are reported.

Keywords: Chromium; Advanced Oxidation Process; Pretreatment; Metal analysis; Hydrogen peroxide

1. Introduction

Chromium is an essential trace element for mammals [1,2], and chromium in biological fluids is known to be present in two biologically occurring chromium-containing biomolecules [3]: (1) iron transport protein transferrin which doubles as a Cr(III) transport agent; and (2) oligopeptide chromodulin (also known as the weight chromium-binding substance, LMWCr). Chromium(III) complexes have been used as a low-cost dietary supplement for the treatment of diabetes and its complications [4]. These chromium supplements as an adjuvant therapy hold the prospect of helping achieve euglycemia, or a normal level of glucose in the blood. Chromium deficiency has also been linked to increased risk of nonfatal myocardial infarction and cardiovascular disease [5].

Chromium levels in biological systems therefore need to be monitored. Biological sample matrices containing the chromium(III) species are usually complex, containing proteins, amino acids and various other organic species [6], and the levels of chromium present in biological tissues and fluids are extremely low (e.g., ca. 3–10 ppb in blood of mammals). The detection of chromium in biological fluids has thus been conducted by neutron activation, mass spectrometry, and graphite furnace atomic absorption spectroscopy (GFAAS) [6,7]. In GFAAS analysis, samples are usually heated to, e.g., 2500 °C for pretreatment and atomization [6c,d]. These methods are usually costly and not readily available [6a]. There is currently a need to develop new, reliable methods for the analysis of chromium in biological fluids to assess chromium deficiency and the effect of chromium as adjuvant therapy for Type 2 diabetes [6a]. The organic ligands in chromium species as well as other organic species contained in biological samples often interfere with the chromium detection and quantification. Pretreatment to remove ligands is thus needed prior to the Cr analysis. Such pretreatments are often used to remove and/or decompose organic ligands in inorganic and organometallic complexes as well as in catalysts prior to the qualitative and quantitative analysis of other metals by standard metal analyses such as ion selective electrodes (ISEs) and other electrochemical techniques [8].

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Wet ashing using strong acids and dry ashing in a high-temperature, O_2-rich environment have been used to remove organic matters prior to the analysis of Cr and other trace metals contained in biological matrices [7,9]. The use of strong acids in these procedures is a possible source of contamination and hazards. In addition, the time requirement for complete oxidation of organic materials by these procedures is often time consuming, thus making them less desirable for routine analysis of samples. Although these methods have been proven effective for oxidation of metals as well as organic matrix components, safer, environmentally benign, and cost-effective methods are desirable. Pretreatment using hydroxyl radicals ($^{\bullet}OH$), generated in situ from H_2O_2, has been reported [10–14]. They have been used to destroy the organic matters in biological samples and water prior to metal analyses [12,14].

In the current work, we have focused on the detection and quantification of chromium in chromium(III) propionate (Fig. 1), a biomimetic complex that mimics the ability of chromodulin [15] to act as an insulin production trigger in vivo. We have studied the removal of organic ligands and oxidation of Cr(III) in chromium(III) propionate to chromate/dichromate ($CrO_4^{2-}/Cr_2O_7^{2-}$) by the Advanced Oxidation Process (AOP) using $^{\bullet}OH$ radicals generated from, e.g., H_2O_2 and UV, as oxidants [11]. During AOP, organic ligands are converted to CO_2 and removed, thus eliminating the potential interference from organic ligands. In addition to the removal of ligands in the current case, AOP converts Cr(III) in chromium propionate to Cr(VI). Established procedures for chromate/dichromate analysis may then be used to determine the total amount of Cr present. Previous studies have used AOP for the pretreatment of natural water samples and subsequent voltammetric techniques for Cr determination [16]. The processes developed here using the biomimetic complex as a model for Cr in oligopeptide chromodulin may help lead to the pretreatment of biological fluids for Cr analysis. In the current work, experimental parameters in the oxidation processes have been investigated including H_2O_2 concentration, sample pH, catalyst, UV irradiation length, reactor size, and lamp wattage. Our studies are reported here.

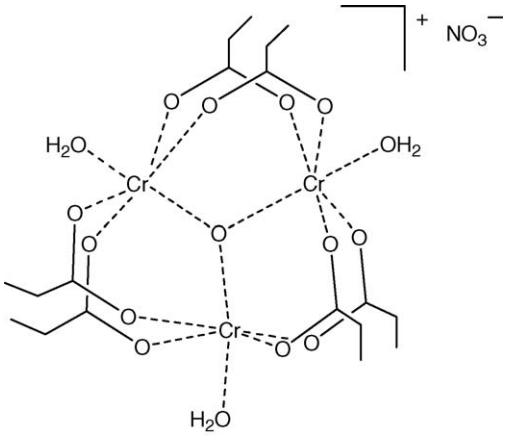

Fig. 1. Chromium(III) propionate, a biomimetic compound used in the current studies.

2. Experimental

2.1. Reagents and analytical instrumentation

The chemicals used in this study, including H_2O_2 (Fisher, 30%; Kroger brand, 3%); 1,5-diphenylcarbazide (Aldrich, ACS reagent); ferric sulfate (Mallinckrodt, analytical reagent); and chromium(VI) atomic absorption (AA) standard (Aldrich, 1017 ppm Cr), were used as received. The biomimetic chromium complex, chromium(III) propionate, was prepared by a literature procedure [17]. Deionized water (18 MΩ cm) was used in the preparation of all solutions and standards.

All UV–vis spectra were collected using a Hewlett-Packard 8452 photodiode array UV–vis spectrophotometer or an Ocean Optics S-2000 spectrometer and a standard 1.0 cm quartz cuvette. Blank spectra of solutions containing all matrix components other than the analyte were recorded and subtracted from all subsequent spectra.

AA analyses were performed using a Perkin-Elmer 5100 atomic absorption spectrophotometer using an air-acetylene flame under standard conditions [18] unless otherwise noted. Each sample after AOP pretreatment was analyzed for the total Cr content by AA and for Cr(VI) by the 1,5-diphenylcarbazide method [19].

2.2. Photochemical reactors and UV lamps

Three different photochemical reactor designs were used in the current studies. These photoreactors consist of an outer vessel containing the sample, into which a quartz immersion well/water jacket housing the UV lamp is immersed (Fig. 2) [20]. Three different reactors with volumes of 500, 100, or 15 mL, respectively, were used in the current studies [20]. These reactors were designed and built in house, except for quartz immersion wells, which were purchased from Ace Glass. UV lamps used in the current studies were either a 450-W quartz medium-pressure mercury-vapor immersion lamp (Ace Glass 7825-34) or a 5.5-W quartz low-pressure cold cathode mercury gaseous discharge lamp (Ace Glass 12132-08).

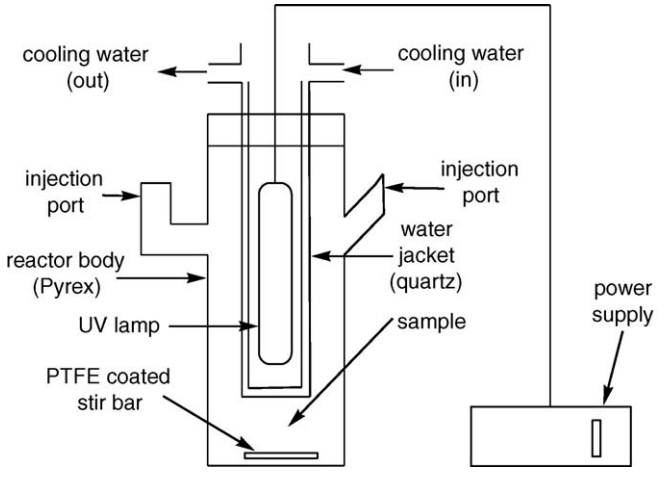

Fig. 2. Schematic of the photochemical reactor used in the current studies.