Published in final edited form as:

Talanta. 2006 October 15; 70(3): 668–675.

Conversion of Chromium(III) Propionate to Chromate/dichromate (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 $\text{Fe}^{2+}/\text{Fe}^{3+}$ as catalyst (photo Fenton process) was found to give complete and quantitative $\text{Cr(III)} \rightarrow \text{Cr(VI)}$ conversion and removal of ligands in chromium(III) propionate $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_2\text{CH}_3)_6(\text{H}_2\text{O})_3]\text{NO}_3$, 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 $\text{Fe}^{2+}/\text{Fe}^{3+}$ 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 are 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 low-molecular-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, 6d]. 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].

Wet ashing using strong acids and dry ashing in a high-temperature, O₂-rich environment have been used to remove organic matters prior to the analysis of Cr and other trace metals contained in biological matrices [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 (•OH), generated *in situ* from H₂O₂, 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 (CrO₄²⁻/Cr₂O₇²⁻) by the Advanced Oxidation Process (AOP) using •OH radicals generated from, e.g., H₂O₂ and UV, as oxidants [11]. During AOP, organic ligands are converted to CO₂ 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 H₂O₂ concentration, sample pH, catalyst, UV irradiation length, reactor size, and lamp wattage. Our studies are reported here.

2. Experimental

2.1. Reagents and analytical instrumentation

The chemicals used in this study, including H₂O₂ (Fisher, 30%; Kroger brand, 3%); 1,5-diphenylcarbazine (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-visible spectra were collected using a Hewlett-Packard 8452 photodiode array UV-visible 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 mL, 100 mL, 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).

2.3. Procedures for chromium(III) propionate sample preparation and treatment

2.3.1. A Cr(III) propionate sample used for preliminary AOP testing—An aqueous Cr(III) propionate sample was prepared by dissolving 0.1352 g of Cr(III) propionate crystals (21.5% Cr by mass) in deionized water (300 mL) in the 500-mL photoreactor containing a Teflon-coated magnetic stir bar. H₂O₂ (30%, 5.0 mL) was next added to the solution in the photoreactor. After shielding of the photoreactor with aluminum foil, this sample was irradiated using the 450-W UV lamp for 3.5 hours. At the conclusion of the AOP treatment, 10 mL of the sample was removed for qualitative UV-vis analysis.

2.3.2 A Cr(III) propionate sample used for a control study—An aqueous Cr(III) propionate sample was prepared by adding 0.1144 g of a 1679.8 ppm Cr(III) stock solution [from Cr(III) propionate crystals] to deionized water (10.0 mL) in a 15-mL photoreactor containing a Teflon-coated magnetic stir bar. Fe₂(SO₄)₃ (1.0 mg) was then added to the photoreactor. Next, NaOH (1.05 M, 16 µL) was added to the sample, bringing the pH of the solution to 9.1. There is *no* H₂O₂ in this sample, and the sample was *not* exposed to UV radiation. After 3 hours, this control sample was quantitatively transferred and diluted to 25 mL in a volumetric flask.

2.3.3. Studies of the length of UV irradiation in the AOP treatment.—Aqueous Cr(III) propionate samples were prepared by adding 100 µL of a 147.9 ppm Cr(III) stock solution [from Cr(III) propionate crystals] to 10.0 mL of deionized water in a 15 mL-photoreactor containing a Teflon-coated magnetic stir bar. NaOH (0.110 M, 15 µL) was then added to each sample, bringing its pH to 9.9. One minute before the UV irradiation process started, H₂O₂ (30%, 170 µL) was added to each sample. After shielding the photoreactor with aluminum foil, each sample was UV-irradiated in the 15-mL photoreactor using a 5.5-W UV lamp for varied lengths of time between 0 and 60 min. At the conclusion of the AOP treatment, each sample was quantitatively transferred and diluted to 25 mL in a volumetric flask.

2.3.4. Studies of the length of UV irradiation in the photo Fenton process.—Aqueous Cr(III) propionate samples were prepared by adding 100 µL of a 147.9 ppm Cr(III) stock solution [from Cr(III) propionate crystals] to deionized water (10.0 mL) in the 15 mL-photoreactor containing a Teflon-coated magnetic stir bar. Fe₂(SO₄)₃ (1.1 mg) was added to the sample as a catalyst for the photo Fenton process. NaOH (1.05 M, 16 µL) was added to each sample, bringing its pH to 9.6. One minute before the UV irradiation process started, H₂O₂ (3%, 100 µL) was added to each sample. After shielding the photoreactor with aluminum foil, each sample was UV-irradiated in the 15-mL photoreactor using a 5.5-W UV lamp for varied lengths of time (0-60 min). At the conclusion of the photo Fenton process treatment, each sample was quantitatively transferred and diluted to 25 mL in a volumetric flask.

2.3.5. Studies of the optimum H₂O₂ concentration in the photo Fenton process

—Aqueous Cr(III) propionate samples were made by adding 100 μ L of a 147.9 ppm Cr(III) stock solution [from Cr(III) propionate crystals] to deionized water (10.0 mL) in the 15-mL photoreactor containing a Teflon-coated magnetic stir bar. Fe₂(SO₄)₃ (1.1 mg) was added as a catalyst for the photo Fenton process. NaOH (1.05 M, 16 μ L) was then added to each sample, bringing its pH to 9.6. One minute before the UV irradiation process started, a measured volume of 3% H₂O₂ (varied from sample to sample) was added to each sample. After shielding the photoreactor by aluminum foil, each sample was UV-irradiated in the 15-mL photoreactor using a 5.5-W UV lamp for 30 min. At the conclusion of each AOP treatment, each sample was quantitatively transferred and diluted to 25 mL in a volumetric flask.

2.3.6. Studies of the optimum pH in the Advanced Oxidation Process—

Aqueous Cr(III) propionate samples were prepared by adding 1.0 mL of a 2230.6 ppm Cr(III) stock solution [from Cr(III) propionate crystals] to deionized water (100 mL) in the 100-mL photoreactor. Sample pH values were adjusted from 0.23 to 9.97 by addition of H₂SO₄ or NaOH. One minute before the UV irradiation process started, H₂O₂ (30%, 1.680 mL) was added to each sample. A stir bar was not needed in these studies since the design of this photoreactor allows the sample to continuously reside directly in the UV path. After shielding the photoreactor by aluminum foil, each sample was UV-irradiated in the 100-mL photoreactor using a 450-W UV lamp for 30 min. At the conclusion of the AOP treatment, each sample was quantitatively transferred and diluted to 250 mL in a volumetric flask.

2.4. Analysis of total chromium content and Cr(VI) species

Calibration standards were prepared gravimetrically using standard analytical techniques. At the conclusion of the UV-irradiation step, samples were quantitatively transferred and diluted in volumetric flasks. After dilution, samples were analyzed for total chromium content by the comparison of AA results with the total amounts expected gravimetrically. Cr(VI) content was determined by UV-vis.

A UV-vis analysis of Cr(VI) utilizing 1,5-diphenylcarbazide, a ligand selective for chromate/dichromate [20], was then used to measure total oxidized Cr(VI) content in each sample. Upon addition of the ligand to a Cr(VI) solution, a colored complex is formed. Cr(VI) content in the standards and samples was determined by monitoring the absorbance at 544 nm in the UV-vis spectrum.

Total chromium content in each sample was analyzed by atomic absorption (AA) spectrometry using an air-acetylene flame. Standard solutions were prepared by serial dilution of a 1017 ppm Cr(VI) AA standard solution and addition of sample matrix components such as Fe³⁺ or NaOH, depending on the contents of each sample. The sample was then diluted to the proper volume. The standard curves were made by measuring the absorbance at 357.9 nm using a slit width of 0.70 nm with a lamp current of 15 mA [18] during analysis of the standards and samples for total chromium.

Our work has shown that the direct AA analysis, *using an air-acetylene flame*, of chromium in Cr(III) propionate (Fig. 1), gives a large error (50.6%). After *sufficient* AOP pretreatment, the AA analysis using an air-acetylene flame is consistent with concentration expected gravimetrically, as discussed below [21]. Thus the removal of the ligands present in Cr(III) propionate AOP samples was confirmed when the AA measured amount of total chromium corresponded to the concentration expected gravimetrically. Cr(III) to Cr(VI) conversion was then calculated by dividing the Cr(VI) concentration from the UV-vis analysis by the total Cr concentration from the AA analysis. Detailed procedures and errors in the determination of total Cr and Cr(VI) are given in supplementary data [20].

3. Results and discussion

3.1. The Advanced Oxidation Process

The Advanced Oxidation Process utilizes a combination of hydrogen peroxide (H_2O_2), a common household reagent, and ozone (O_3) or ultraviolet (UV) radiation to generate strongly oxidizing hydroxyl radicals $\cdot\text{OH}$ [10,11]. When H_2O_2 is irradiated with UV light at wavelengths $8 < 300 \text{ nm}$, homolytic splitting of the oxygen-oxygen bonds occurs thus yielding hydroxyl radicals (Eq. 1). The radicals react with organic molecules to yield water and carbon dioxide as the main reaction products. In addition to producing hydroxyl radicals, the UV radiation either decomposes or activates organic complexes as well, since most organic compounds absorb in the UV region. The UV irradiation thus makes the organic compounds more easily oxidized by the hydroxyl radicals.

As shown in Table 1, the standard reduction potential of hydroxyl radicals ($\cdot\text{OH}$) is much higher than that of ozone, hydrogen peroxide, or Cl_2 , three well known oxidants. The reaction times of hydroxyl radicals with organic compounds are short, usually less than a millisecond [10a]. In addition to the formation of hydroxyl radicals from the UV irradiation of H_2O_2 (and addition of O_3 to H_2O_2), these reactions yield several other reactive species such as hydroperoxyl or peroxy radicals. These radicals also decompose organic compounds. In other words, the activation of hydrogen peroxide by UV irradiation or ozone produces several radicals, all of which help decompose organic compounds. The mixture of ozone and H_2O_2 is also called peroxone [22].

The photo Fenton process [10a,23] is an adaptation of the Advanced Oxidation Process. The photo Fenton process utilizes a catalytic amount of Fe^{2+} or Fe^{3+} in addition to H_2O_2 and UV irradiation. Iron species have been shown to act as a catalyst in these oxidation reactions, promoting the formation of active hydroxyl radicals (Eqs. 2 and 3). This process has been shown to improve the effectiveness of the oxidation of certain organic compounds compared to AOP alone [23].

The hydroxyl radicals generated in AOP have been shown to oxidize even relatively stable substances [10a]. AOP has thus been widely used in the decomposition (and removal) of organic compounds that are difficult to degrade, such as contaminants in drinking water and industrial wastewater [10]. Hydrogen peroxide and the UV irradiation process, when properly used, are safe and environmentally benign [24]. The decomposition of hydrogen peroxide leads to the formation of oxygen and/or water.

Several factors contribute to the efficiency of the Advanced Oxidation Process. Those contributing most to the overall efficiency are choice of O_3 or UV to activate H_2O_2 , power of the UV source, length of UV irradiation, use of a catalyst during UV irradiation, H_2O_2 concentration, sample pH, and reactor design. Each of these parameters has been investigated in the conversion of chromium(III) propionate to chromate/dichromate, and the results are discussed below.

3.2. Comparison of AOP and the photo Fenton process

Cr(III) propionate (Fig. 1) was chosen in the current studies for its biomimetic properties. This complex was found to readily dissolve in aqueous solution.

AOP experiments using ozone and H₂O₂ showed *qualitatively* a conversion of Cr(III) propionate to chromate/dichromate (Fig. 3). Ozone was not used in our subsequent AOP studies for the following reasons: (a) Ozone generation *in a research laboratory* usually requires an ozone generator (and a supply of O₂), which gives an O₃/O₂ flow through a solution containing H₂O₂ for a limited amount of time; (b) The excess O₃ in the O₃/O₂ flow was found to be corrosive to laboratory equipment containing plastics, and O₃ itself in air is a health hazard.

We have found that Cr(III) propionate undergoes oxidation by H₂O₂ under UV irradiation (Eq. 4). UV-vis spectra of a Cr(III) propionate solution were collected before and after AOP treatment using the 450-W UV lamp and 500-mL photoreactor [20]. A comparison of the UV-vis spectra of the Cr(III) propionate solution after AOP to that of a potassium dichromate solution shows qualitatively that the Cr(III) complex has been oxidized to Cr(VI). In comparison, control experiments using solutions of Cr(III) propionate, H₂O₂ and Fe₂(SO₄)₃ as a catalyst *without* UV irradiation showed *no* conversion of Cr(III) propionate to chromate/dichromate. The control studies indicate that the Fenton process *alone* does not decompose the Cr(III) complex to chromate/dichromate. In other words, UV irradiation is critical to the current Cr(III) Cr(VI) conversion. In comparison, H₂O₂ in the presence of Fe(II) as a catalyst was adequate to digest environmental water samples and urine for total mercury analysis, as Ping and Dasgupta have shown [13a].

A set of experiments were also conducted to see if direct analysis of Cr(III) propionate by AA using an *air-acetylene flame*, *without prior AOP treatment*, would give accurate Cr analysis. These tests show such a direct AA analysis of chromium in these Cr(III) propionate samples using an air-acetylene flame gives an error of 50.6% [21]. In comparison, an AOP treatment and subsequent AA analysis of total chromium gives an error of <5% in comparison with the amounts expected by gravimetric calculations, indicating that AOP had sufficiently removed the ligands and had converted Cr(II) ions in the samples to Cr(VI) species for an accurate assessment of the total chromium in the samples by AA. In other words, the differences between the AA analysis using an *air-acetylene flame* and the Cr concentrations expected gravimetrically for the samples indicate how complete the AOP pretreatment is.

The length of UV irradiation of AOP samples has been found to play a major role in the degree of oxidation of the samples in earlier studies [10,23]. In the current studies, identical solutions of Cr(III) propionate were prepared, and their pH was adjusted to 9.9 by NaOH. After addition of H₂O₂, the 15-mL samples were UV-irradiated for varied lengths of time using the 5.5-W UV lamp [20]. Increasing the length of UV irradiation from 0 to 60 min was found to increase the conversion of Cr(III) in the sample to Cr(VI) ions (Fig. 4). After 60 min of UV irradiation, approximately 50% of the total Cr in the sample was in the Cr(VI) oxidation state. We then decided to study the use of Fe²⁺/Fe³⁺ as catalyst in the hope that it would enhance the Cr(III) to Cr(VI) conversion.

Studies similar to those discussed earlier were conducted, this time with the addition of an Fe³⁺ catalyst. These studies also showed that the length of UV irradiation in the photo Fenton process samples play a major role in the amount of Cr(III) oxidized to Cr(VI). With longer exposure to UV radiation, more active •OH radicals are generated thus increasing the overall efficiency of the oxidation process. To determine the optimum length of UV irradiation for the current photo Fenton process samples, experiments were conducted in which the length of UV

irradiation (with a 5.5-W UV lamp) of multiple identical Fe^{3+} -containing, Cr(III) propionate samples (pH 9.9) was varied. Experimental results (Fig. 4) show that, with increasing lengths of UV irradiation from 0 to 60 min, the amount of Cr(III) oxidized to Cr(VI) also increased. After 60 min of UV irradiation, $(99 \pm 3)\%$ of the total chromium has been converted to Cr(VI) chromate/dichromate.

These two studies provide a direct comparison of the Advanced Oxidation Process and the photo Fenton process for the oxidation of Cr(III) propionate samples (Fig. 4). The photo Fenton process was found to be more efficient than AOP alone (H_2O_2 + UV irradiation) for the oxidation of Cr(III) propionate solutions. In other words, Fe^{3+} ions play the catalytic role in the AOP treatment of Cr(III) propionate. After 60 min of UV irradiation by the 5.5-W quartz mercury lamp in the 15-mL photoreactor, samples from the photo Fenton process showed $(99 \pm 3)\%$ conversion of Cr(III) propionate to Cr(VI), whereas the control samples treated by AOP alone only showed approximately 50% conversion of Cr(III) propionate to Cr(VI). The $\text{Fe}^{2+}/\text{Fe}^{3+}$ catalyst likely helps yield larger quantities of active $\bullet\text{OH}$ radicals in the photo Fenton process. The majority of the current studies were thus conducted with the Fenton catalyst.

3.3. Optimum H_2O_2 concentration in the photo Fenton process

One critical factor regarding Advanced Oxidation Processes and the photo Fenton process is the concentration of H_2O_2 during the UV irradiation of the sample. Studies have been conducted to determine the optimum concentration of H_2O_2 for the oxidation of various organic compounds, and different optimum concentrations of H_2O_2 have been reported for the treatment of different chemicals [10,11]. At high concentrations of H_2O_2 , the AOP and photo Fenton process efficiency is reported to decrease in some instances [10a,23b]. The decrease in efficiency is suspected to arise from the recombination of two $\bullet\text{OH}$ radicals, thus effectively lowering the number of $\bullet\text{OH}$ radicals in solution as well as the efficiency of the overall oxidation process. At low concentrations of H_2O_2 there is not enough H_2O_2 to generate the adequate concentration of $\bullet\text{OH}$ radicals for the oxidation.

Several experiments in the current studies were conducted to determine the optimum concentration of H_2O_2 during the photo Fenton process. Cr(III) propionate samples at approximately pH 9.0 (by NaOH) were prepared containing a catalytic amount of $\text{Fe}_2(\text{SO}_4)_3$. The H_2O_2 concentration was varied from 0.09 g/L to 0.44 g/L. Each sample was UV-irradiated in the 15-mL photoreactor for 30 min using the 5.5-W UV lamp. Our results show that the influence of H_2O_2 concentrations (between 0.09 g/L and 0.44 g/L) is relatively small (Figure 5). Samples at the H_2O_2 concentration of 0.26 g/L were found to show the highest Cr(III) to Cr(VI) conversion and were thus considered to be the optimum concentration for use in the current system.

3.4. Optimum pH in the Advanced Oxidation Process

In order to establish the optimum pH during AOP treatment of these samples, AOP experiments were carried out using a 100-mL photoreactor with a 450-W UV lamp. Samples containing a constant concentration of Cr(III) propionate and H_2O_2 were prepared and UV-irradiated for 30 min. Sample pH was varied from 0.23 to 9.97 during AOP. At $\text{pH} > 4$, the conversion of Cr(III) propionate to chromate/dichromate was found to be $>90\%$ (Figure 6). At $\text{pH} < 4$, no Cr(VI) was detected in the AOP-treated samples. As shown in Eq. 5, the Cr(III) to Cr(VI) conversion yields acid, and OH ions in solutions of higher pH remove the H^+ ions generated from the Cr oxidation. The pH in these solutions after AOP was measured to be between pH 7.0 and 8.0.

3.5. Reactor sizes and UV lamps

Various reactor designs and sizes have been used in the current AOP and photo Fenton process reactions. One of the most important factors in the design of a reactor is the ability to adequately stir/mix the sample in the reactor. Thorough mixing of the sample is required to ensure that the contents are in the path of the UV radiation for the activation of H_2O_2 . Another important factor regarding reactor design is the pathlength of UV radiation through the sample [10d]. With a longer pathlength, the UV intensity is decreased towards the outer portion of the sample. This is due to the fact that a large portion of the UV radiation is often absorbed by the inner portion of the sample. Our reactor for the 5.5-W UV lamp was thus designed with a minimal length between the outer wall of the immersion well and the inner wall of the reactor.

Large-scale photoreactors such as 500 mL photoreactor in the current work [20] have the advantage of use with relatively large, higher wattage UV lamps and the ability to treat large samples. However, they also require large samples and intense UV irradiation from, e.g., a 450-W lamp. The drawback with larger reactors is the large pathlength through which the UV radiation must travel to treat the sample. As discussed earlier this leads to decreased efficiency towards the outer portions of the sample due to decreased UV intensity. A medium-size photoreactor [20] was used for treating smaller volumes (up to 100 mL) using a 450-W UV lamp and it was found to have much better efficiency, since the pathlength is shortened and the entire sample is contained directly in the path of continuous UV radiation.

Small-scale photoreactors have the advantage of a shorter UV pathlength through the sample, and better mixing of the sample, which both lead to increased efficiency of the oxidation process. These smaller reactors also require smaller sample volumes. The primary disadvantage of using a smaller reactor is that often, only small, low wattage UV lamps may be used.

A small-scale photoreactor was designed in house to treat samples up to 15 mL in volume using a 5.5-W UV lamp [20]. This photoreactor was designed so that the sample could be stirred to maximize the sample residence time in the UV radiation path. Studies using this photoreactor in combination with the 5.5-W UV lamp gave very good yields for the oxidation of the Cr(III) complex, and it was found to be highly efficient.

The photo Fenton process using H_2O_2 , $\text{Fe}^{2+}/\text{Fe}^{3+}$ catalyst and UV irradiation has been proven as a viable method to oxidize a Cr(III) complex to Cr(VI) chromate/dichromate. This has been accomplished using a low power UV lamp (5.5 W) and a small-scale reactor. Neither AOP (H_2O_2 + UV irradiation) nor Fenton process (H_2O_2 + $\text{Fe}^{2+}/\text{Fe}^{3+}$) alone is adequate in our studies for the effective conversion of the biomimetic Cr(III) complex to chromate/dichromate for subsequent Cr analysis. The success of the photo Fenton process as demonstrated in the current studies has thus eliminated the need for harsh mineralization and/or dissolution procedures for the pretreatment of the Cr(III) complex.

4. Conclusions

The current work is, to our knowledge, one of few studies to compare the analyses of samples after AOP treatments with theoretical Cr concentrations (using pure crystals of the molecular complex gravimetrically) [11]. Our oxidation process using H_2O_2 and a 5.5-W UV lamp gives quantitative conversion of the complex to chromate. The straightforward approach reported here may potentially be used as pretreatment in the analysis of other metal complexes. In addition, the optimized parameters presented here can be used as a basis for the Cr analysis in actual biological samples. Further investigation regarding this matter is currently underway.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgement

We thank the US National Institutes of Health (5R21DK068107-02) for financial support.

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

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

Fig. 3. UV-vis spectra of a chromium(III) propionate solution before (◆) and after AOP treatment (▲) with O₃ and H₂O₂. A spectrum of a standard K₂Cr₂O₇ solution (•) is given for comparison.

Fig. 4.

A comparison of the Advanced Oxidation Process (•) and the photo Fenton process (▲) for the oxidation of Cr(III) to Cr(VI) as a function of time. Samples were treated in the 15-mL photoreactor using the 5.5-W UV lamp and H_2O_2 .

Fig. 5. Conversion of chromium(III) propionate to chromate/dichromate as a function of H₂O₂ concentration during UV irradiation. Samples were treated in the 15-mL photoreactor using the 5.5-W UV lamp.

Fig. 6. Conversion of Cr(III) in chromium(III) propionate to Cr(VI) present as chromate/dichromate as a function of sample pH during UV irradiation. Samples were treated in the 100-mL photoreactor using the 450-W UV lamp.

Table 1Comparison of standard (reduction) potentials of $\bullet\text{OH}$, O_3 , H_2O_2 , and Cl_2 .

Oxidizing agent	Chemical formula	Standard potential (V)
hydroxyl radical	$\bullet\text{OH}$	2.8
ozone	O_3	2.07
hydrogen peroxide	H_2O_2	1.78
chlorine	Cl_2	1.35