



Project Summary

Determination of Stable Valence States of Chromium in Aqueous and Solid Waste Matrices— Experimental Verification of Chemical Behavior

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The objective of this research effort was to experimentally assess the chemical behavior of the stable species of chromium during the preparation, chemical manipulation, and spectrophotometric analyses of simulated and authentic environmental samples for hexavalent chromium. The effort for this research was divided into four experimental phases, addressing specific objectives: (1) characterization and ruggedness evaluation of the diphenylcarbazide (DPC) spectrophotometric method for hexavalent chromium; (2) evaluation of the stability and reactivity of hexavalent chromium under simulated but controlled aqueous matrix conditions; (3) evaluation of alkaline and acidic digestions for the analysis of insoluble chromate standards and trivalent chromium; and (4) evaluation of alkaline and acidic digestions for chromium analyses of environment samples. Each research phase is individually discussed.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The analyses of solid waste materials for Cr(VI) represent formidable challenges to the analytical scientist. A metal speciation scheme to differentiate between trivalent and hexavalent species, Cr(III) and Cr(VI), must address the solubilization of chromium species from solid matrices, while maintaining the integrity of the individual chromium species during all sample manipulation phases of the analytical method. Whereas much research has focused on the separation and detection of dissolved chromium species in synthetic aqueous mixtures or relatively clean liquid environmental samples, the chemical solubilization and determination of Cr(VI) in solid waste materials have not been adequately addressed.

The present study has focused on evaluations of three digestion methods for the chemical solubilization of Cr(VI) in barium chromate test compounds and in real environmental samples: (1) an alkaline digestion medium, consisting of an aqueous solution of sodium carbonate and sodium hydroxide; (2) a nitric acid digestion method; and (3) a nitric acid/persulfate digestion method. The relative merits of the digestion methods have been based on the analytical results for solubilization of insoluble chromates as

well as stability of Cr(III) and Cr(VI) spikes in various test solutions and environmental samples.

Results and Discussion

The DPC spectrophotometric method, as described in EPA Method 7196, was employed to measure concentration changes in Cr(VI) for each test sample solution resulting from chromium redox phenomena occurring during the digestions. The DPC spectrophotometric method was found to be sensitive and specific for Cr(VI) in aqueous solutions containing up to 1000-fold ratios of Cr(III). Instrument response was linear over two orders of magnitude of Cr(VI) concentration (0.01 to 1.0 mg/L). Problems of chemical reduction were encountered with the method for analyses of simulated samples containing excesses of both Cr(III) and sulfide.

The stability of Cr(VI) in aqueous solutions containing Cr(III) and sulfide as a function of pH was examined. In alkaline solutions, reduction of Cr(VI) to Cr(III) by sulfide was slow. As predicted by standard electrochemical potentials, the reduction of Cr(VI) was increased in acidic solutions. These results have two significant ramifications: (1) environmental samples for Cr(VI) analyses should not be preserved by acidification to pH 2 and (2) DPC reagent should be added to an alkaline sample before pH adjustment to 2 with sulfuric acid to minimize Cr(VI) reduction in the quantification step; this verifies proper order of addition of the two reagents as described in Method 7196.

A digestion medium consisting of 50 percent (v/v) nitric acid and 5 percent (w/v) potassium persulfate was examined predicated on the potential feasibility of the potent oxidizing properties of persulfate keeping the Cr(VI) in an oxidized state even under highly acidic conditions. However, this digestion method failed because the results indicated that persulfate exhibits reducing properties in a 50 percent nitric acid medium. At nitric acid concentrations of 20 percent or less, the nitric acid/persulfate medium exhibited its predicted oxidizing properties.

The 50 percent nitric acid medium (without persulfate) and the alkaline medium (2 percent sodium hydroxide/3 percent sodium carbonate) both successfully solubilized Cr(VI) from the insoluble barium chromate test compound. Furthermore, the valence states of trivalent and hexavalent chromium were maintained in standard solutions carried through either digestion procedure. However, in

the presence of oxidizing or reducing agents, the valence states of chromium species were not maintained in either digestion medium; the extent of valence state conversion was dependent on the concentration of the specific oxidant or reductant added.

Eight environmental solid samples were analyzed for Cr(VI) by DPC spectrophotometry following alkaline digestions. Complete recoveries of Cr(VI) spikes were obtained in alkaline media by the DPC method for most samples (5 out of 8); Cr(VI) spikes were reduced in municipal digested sludge (organic matrix), tannery sludge (organic/sulfide matrix), and NBS-SRM 1646 estuarine sediment. Partial oxidation of Cr(III) spikes was observed for many samples (4 out of 8) in alkaline media; Cr(III) spikes were stable in electroplating sludge, tannery sludge (organic/sulfide matrix), NBS-SRM 1646 estuarine sediment and municipal digested sludge. Partial oxidation of Cr(III) spikes in alkaline media produced measurement errors in Cr(VI) concentration by as much as 100 percent (positive bias). Of the eight solid samples in this study, the electroplating sludge was the only sample analyzed in which both Cr(VI) and Cr(III) spikes were stable in alkaline media.

Conclusions

Of the eight solid samples analyzed in this study, only the electroplating sludge sample was successfully analyzed for Cr(VI) by DPC spectrophotometry following an alkaline digestion. Although unconfirmed by a collaborative method, endogenous Cr(VI) was measured in the electroplating sludge, as determined by spike recovery; Cr(VI) spikes were completely recovered and no measurable oxidation of Cr(III) was observed.

Three solid samples (river sediment, municipal digested sludge and contaminated soil) were digested in the 50 percent nitric acid medium (without persulfate) and analyzed by DPC spectrophotometry. Although no oxidation of Cr(III) spikes was observed in any of the sample, Cr(VI) spikes were completely reduced in all three samples.

DPC spectrophotometry was limited by color interferences encountered in many of the environmental samples. The interferences ranged from turbidity and color formation occurring after DPC addition. Turbidity and color interference was minimized to a certain extent by dilution but this often resulted in high imprecision.

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Ted Martin is the EPA Project Officer (see below).

The complete report, entitled "Determination of Stable Valence States of Chromium in Aqueous and Solid Waste Matrices—Experimental Verification of Chemical Behavior," (Order No. PB 87-140 927/AS; Cost: \$18.95, subject to change) will be available only from:

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54
44

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