A recent study by the Environmental Working Group reported the detection of hexavalent chromium (Cr(VI)) in tap water at 31 out of 35 states investigated in the United States. Even though Cr(III) is an essential element for human diet, Cr(VI) is a potential carcinogen. Previous work has clearly identified a linear trend of increasing risk of lung cancer mortality with increasing cumulative exposure to water soluble Cr(VI). Regardless, Cr(VI) is still not regulated or monitored in drinking water in the US. There is an existing method (EPA 218.6) for the analysis of Cr(VI), however, this analytical method does not addresses detailed sample preservation techniques and optimization process to achieve lowest detection limit possible. In this study, five buffer solutions with pH of 9 and above were compared to determine the most suitable buffer to preserve Cr(VI) in drinking water samples for an extended period of time. Results showed that the five buffers responded very differently to Cr(VI)-fortified drinking water. The best preserving reagent was found to be Ammonium Hydroxide + Ammonium Sulfate (pH 9.2) and Sodium Carbonate + Sodium Bicarbonate+ Ammonium Sulfate (pH 9.7), whereas a buffer solution with Sodium Hydroxide + Sodium Carbonate (pH 11.5+) resulted in a poor chromatographic resolution. A controlled study with a fortified Cr(III) at 1 ppb was also conducted to ensure no false positive detection of Cr(VI) due to the potential oxidation of Cr(III) during sample storage. The optimal preserving reagent identified from this study was compatible with the existing EPA method 218.6 using ion chromatography followed by post column reaction, with a method quantitation limit of 0.020 ppb and matrix spike recovery of ± 10%.