

Proposed Alternate Sample Preservation Buffer for Hexavalent Chromium

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In the January 2001 UCMR Guidance document for Hexavalent Chromium Sample Collection and Preservation (<http://www.cdph.ca.gov/certlic/drinkingwater/Documents/UCMR/ucmrguidance.pdf>), the Department proposed the use of an ammonium sulfate/hydroxide buffer for sample pH adjustment different from that specified in EPA Method 218.6. That modified buffer, which contains ten times less ammonium sulfate (33 g/L) but the same concentration of ammonium hydroxide as the buffer prescribed in EPA 218.6, was intended to overcome problems with adjusting the pH of water samples to the prescribed range of 9.0-9.5.

In the meantime it has become apparent that the original pH-adjustment buffer prescribed in EPA 218.6 has a fundamental problem in that its pH is below 9.0. Based on the formal concentrations of ammonium ions and ammonia (5 mol/L and 1 mol/L respectively) and a pK_a of the ammonium ion of 9.25, the calculated pH for this buffer is 8.55. This means that any water sample with an original pH below 9.0 cannot be brought to pH 9.0-9.5 by adding any amount of the prescribed buffer. It should also be noted that the use of a large volume of the original buffer specified in Method 218.6 in conjunction with a strong base, such as sodium or potassium hydroxide, can interfere with the ion chromatographic determination of hexavalent chromium by raising the sulfate concentration of the sample to a level similar to that of the eluent.

The calculated pH for the CDPH-modified ammonium sulfate/hydroxide buffer is 9.55. Although this buffer should be suitable to adequately pH-adjust any drinking water sample, it has several drawbacks. Since the buffer contains a volatile component (NH_3), it has a strong odor and its composition is not stable with time. Therefore, the stock solution of the buffer has to be replaced frequently and it is not practical to add a fixed amount of the buffer to sample containers before sampling (which would be desirable in order to facilitate sampling and to determine reagent blanks).

To overcome these problems the Department is now proposing an alternate buffer based on sodium tetraborate (borax). Boric acid has a pK_a of 9.18, which is very similar to that of the ammonium ion (the pK_a values cited in this text are for 25 °C and were taken from the 60th edition of the CRC Handbook). Since borate is a very weak ion chromatographic eluent, even high concentrations are not likely to interfere with the hexavalent chromium analysis.

When borax, $Na_2B_4O_7 \cdot 10 H_2O$, is dissolved in water it forms an ideal buffer with equal concentrations of the acid and base forms of borate:



The pH of the resulting solution is 9.18. In order to gain more capacity to bring samples with low pH and high acidity into the desired pH range of 9.0-9.5 with a small fixed

volume of the buffer, the pH of the buffer stock solution can be raised through the addition of strong base (NaOH or KOH). It should be noted that EPA has recently specified a target pH range of 9.3-9.7 for the preservation of hexavalent chromium in water although the reasons for this change are unclear (http://www.azdhs.gov/lab/license/tech/murfaqs_hexchrome.pdf).

The following protocol is proposed for the preparation and use of the borate buffer:

Add 1.907 g of analytical reagent grade $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ to 53.6 mL of 0.1 mol/L NaOH or KOH and make up to a final volume of 100 mL. The pH of this solution should be 9.7. Use 1 mL of this buffer for each 100 mL of water sample to be preserved. Prepare a reagent blank by diluting 1 mL of the buffer to 100 mL with reagent water. For samples which are known to be of low pH and high acidity, a larger, known volume of the buffer may be used.

Caution: The Department's Sanitation and Radiation Laboratory has observed that commercially available sodium and potassium hydroxide often contains traces of hexavalent chromium. Therefore, reagent blanks need to be carefully evaluated. One convenient way to obtain very clean sodium or potassium hydroxide is to use an ion chromatography eluent generator.

For questions regarding this text please contact Raimund.Roehl@cdph.ca.gov.