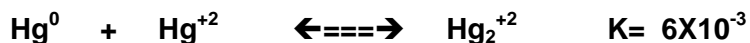


US EPA ARCHIVE DOCUMENT

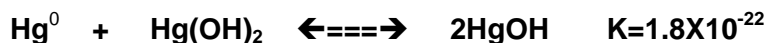
## APPENDIX 7.2

### Analytical Considerations

Mercury exists in three forms that are an equilibrium mixture according to the following equation:



Other anions in solution have a dramatic effect on the position of this equilibrium due to the large variety of strong complexes formed between mercury and the ions.



Due to the very large formation constant between hydroxide and  $\text{Hg}^{+2}$  ( $1.8 \times 10^{-22}$ ),  $\text{Hg}_2^{+2}$  will not exist in the presence of high concentrations of hydroxide ions. Product caustic soda and caustic potash will only contain  $\text{Hg}^0$  and  $\text{Hg}(\text{OH})_2$ .

Mercury is typically analyzed by cold vapor atomic absorption. In this method, a weighed portion of caustic is diluted with water, acidified with a suitable acid and digested at elevated temperatures for time periods of at least one hour in the presence of excess potassium permanganate. This digestion process oxidizes all of the mercury forms present in the sample to  $\text{Hg}^{+2}$ . The excess potassium permanganate is destroyed by the addition of a solution of hydroxyl amine hydrochloride until a clear solution is obtained. This solution is placed into a gas scrubbing bottle along with acidic tin chloride solution to reduce the  $\text{Hg}^{+2}$  to  $\text{Hg}^0$  and scrubbed with an inert gas to transport the elemental mercury from the solution into the gas phase and through the detection cell. The amount of light absorbed in the detection cell is proportional to the amount of mercury removed from solution.

Although the actual detection limit of this method is subject to a number of factors like sample size, detection cell length, volume of scrubbing gas and the volume of the gas scrubbing bottle, this method will generally detect mercury down to about 1-10 parts per billion range. There are practical limits to the sample size used by this method because of the need to dilute and acidify the sample.

ASTM has recently published a new method of mercury analysis in caustic products using cold vapor atomic absorption and an alkaline reducing agent that does not dilute, acidify, or digest the sample. The alkaline tin reducing agent is a much more aggressive and stronger reducing agent than the acidic tin. Since the sample and the reducing agent are both alkaline, the sample size limitation seen in the acidic reducing agent method is removed. Since the alkaline reducing agent is a stronger and more aggressive reducing agent, the need to digest the sample is removed greatly reducing the analysis time of the method. The new method detection limit is easily extended by a factor of ten over the old method to the 0.1-1 parts per billion range. This method is given in test method A of ASTM E 538-98 which first appeared in the 1999 edition of volume E15.05.

The EPA has recently published two methods of mercury analysis in water samples using atomic fluorescence spectrometry: method 1631 and method 245.7. These methods call for the acidification of the sample and oxidation of the mercury species

present in the sample to  $\text{Hg}^{+2}$  with bromine chloride for up to an hour. Excess bromine chloride in the sample is destroyed with a solution of hydroxyl amine hydrochloride. The  $\text{Hg}^{+2}$  is reduced to  $\text{Hg}^0$  with an acidic tin solution and purged from solution into the gas flow followed by detection with atomic fluorescence. In this case the amount of light emitted by the mercury atoms in the gas phase is proportional to the mercury concentration in the sample.

Although each of these methods was written for environmental and wastewater samples, the basic methods and instruments can be adapted to the analysis of caustic samples with great success. The extreme measures taken in the sample handling in each of the methods go far beyond what is required for a normal product analysis.

Atomic fluorescence instruments are about a factor of 1000 times more sensitive than the atomic absorption instruments and detection limits in the 1-10 parts per trillion range can be easily achieved with just moderate controls of the laboratory environment. Be forewarned that with this type of instrument you will find detectable levels of mercury in every thing that is analyzed. This makes control of the instrument blank and having clean reagents and water very important.

As with the earlier methods, these new fluorescence methods use an acidification and oxidation step followed by an acidic tin reducing agent. Each of these reagent additions adds to the amount of mercury background in the blank of the method. By adapting the atomic fluorescence methods to the alkaline tin reducing agent the need for the acidification and oxidation are removed from the method. The sample preparation consists of a 1 to 1 dilution of the 50% caustic in high purity water to simply reduce its viscosity in being pumped into the instrument. This ultimately reduces the instrument blank and lowers the detection limit because of fewer mercury containing reagents being added to the sample and the reduced sample handling out in the room air.