

CH 424 INSTRUMENTAL ANALYSIS LAB

DETERMINATION OF MERCURY BY FLAMELESS ATOMIC ABSORPTION SPECTROMETRY

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INTRODUCTION

Due to its volatility, mercury atomizes inefficiently in conventional flames, leading to poor sensitivity in flame photometry. In this procedure, mercuric ion in acidic solution is reduced to the elemental state. Finely divided, it has appreciable vapor pressure at room temperature and so can be aerated from solution in a closed system. The mercury vapor is then swept into a quartz-windowed cell where its atomic absorption is measured at 253.6 nm. A direct calibration method designed to minimize mercuric waste is employed.

This method is applicable to any sample that can be prepared in an oxidizing acid solution. Mercury in air, for instance, can be sampled by bubbling a measured volume through an acidified potassium permanganate scrubbing solution. The procedure is free from interferences due to organic matter and other volatile constituents of the sample.

REAGENTS

ADDING THE ACID TO THE WATER, prepare *ca.* 6 M nitric acid and *ca.* 9 M sulfuric acid solutions. Add 1 mL 9 M sulfuric acid to 1 g stannous chloride and then add water to 100 mL (nominally 1% solution). Dissolve 10 g potassium permanganate in 100 mL water (nominally 10% solution). Dissolve 1 g hydroxylamine hydrochloride in 100 mL water (nominally 1% solution). Prepare a stock mercury solution of *ca.* 100 ppm by dissolving mercuric chloride in 100 mL of 0.5 M sulfuric acid and making up to 1.00 L with water. Dilute this 1:100 to obtain a *ca.* 1.00 ppm working standard. **NOTE:** Dispose of all mercuric solutions in the appropriately labeled bottle containing excess permanganate.

PROCEDURE

Turn on the mercury analyzer and after allowing it to warm up, zero the instrument. One third fill the scrubbing bottle with *ca.* 0.25 M nitric acid, 0.1 % in potassium permanganate. Obtain an aqueous solution of unknown mercuric ion concentration from your instructor. Dispense 100.0 mL of this unknown solution into the 250 mL three-necked flask. Connect the fittings to the closed-cycle system, making sure the valves are set to by-pass the scrubber and the aerosol trap is connected just before the IN port on the analyzer. The OUT port should be connected directly to the sample vessel. Drop a magnetic stirring bar into the sample vessel and start the stirrer.

Add 5 mL 6 M nitric acid and 2 mL 10% potassium permanganate. The violet color should persist. If it does not, then add further potassium permanganate. After about 30 seconds, add 5 mL 9 M sulfuric acid and 5 mL 1 % hydroxylamine hydrochloride. If the color persists after 30 second, add further hydroxylamine hydrochloride solution. Now, close the remaining open neck to the sample vessel with a septum ("Subaseal") and inject 1 mL 1% stannous chloride through the septum and into the sample solution using a syringe fitted with a stainless steel needle. Turn on the circulating pump to carry the elemental mercury into the analyzer. Record the maximum reading on the instrument meter. Now switch the scrubbing bottle (containing acidified permanganate) into the line and after a few minutes obtain the blank reading. By-pass the scrubber again, turn off the pump and finally, remove the septum from the sample vessel.

Starting from the addition of a further 5 mL 6 M nitric acid and 2 mL 10% potassium permanganate, the entire procedure should then be repeated four times, "spiking" the sample solution with, respectively, 0.50, 1.00, 2.00 and 5.00 mL aliquots of the working standard mercuric solution. Prepare a calibration curve from the data and calculate the best straight line by a least squares regression analysis. Estimate the concentration of your unknown as supplied to you in ppb and report the result in terms of 95% confidence limits.

QUESTIONS

- i) Write equations for the reactions that occur during the oxidation and reduction processes.
- ii) Why is this procedure not feasible if large amounts of easily reducible components are present in the sample?
- iii) Can you think of any other elements to which this (or a similar) procedure might usefully be applied? Why, or why not?
- iv) What is the minimum analyte concentration (ppb) you can detect?

REFERENCES

D. T. Sawyer, W. R. Heineman and J. M. Beebe, "Chemistry Experiments for Instrumental Methods", John Wiley & Sons (1984) pp. 254-257.

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