Analyte:	Ozone	Method No.: S8
Matrix:	Air	Range: 0.1-0.4 mg/cu m
OSHA Standard:	0.1 ppm (0.2 mg/cu m)	$CV_T = 0.0806$
Procedure:	Colorimetric-Alkaline KI Method	Validation Date: 10/11/74

1. Principle of the Method

1.1 Air containing ozone is drawn through a midget impinger containing 10 ml of 1 percent potassium iodide in 1 N sodium hydroxide. A stable product is formed that can be stored with little loss for several days.

1.2 The analysis is completed in the laboratory by the addition of phosphoric-sulfamic acid reagent, which liberates the iodine.

1.3 The yellow iodine color is read in a spectrophotometer at 352 nm.

2. Range and Sensitivity

2.1 This method has been validated over the range 0.1 to 0.4 mg/cu m. This is the limit of the useful range for the 45 liter sample size. The method is capable of measuring smaller or larger concentrations if the sampling size is adjusted, but it has not been validated for other sample sizes.

3. Interferences

3.1 Chlorine, hydrogen peroxide, organic peroxides, and various other oxidants will liberate iodine by this method.

3.2 The response to nitrogen dioxide is limited to 10 percent by the use of sulfamic acid in the procedure to destroy nitrite, thus minimizing any error due to the collection of NO_2.

3.3 The negative interferences from reducing gases such as sulfur dioxide and hydrogen sulfide are very serious (probably on a mole-to-mole equivalency).

3.4 The procedure is very sensitive to reducing dusts that may be present in the air or on the glassware. Losses of iodine also occur even on clean glass surfaces and thus the manipulations should minimize this exposure.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 0.1 to 0.4 mg/cu m is 0.0806. The standard deviation at the OSHA standard level is 0.0077 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average, the values obtained using the overall sampling and analytical method were the same as the true value at the OSHA standard level.

4.3 These data are based on validation experiments in which neutral buffered KI was used to determine the actual ozone concentration.

5. Advantages and Disadvantages

5.1 The method is simple, accurate and precise.

5.2 Those compounds listed in 3.1 will liberate iodine by this method.

5.3 A delay of several days is permissable between sampling and completion of analysis. However, the relationship between delay and analytical results has not been established.

6. Apparatus

6.1 Midget impinger with 1 mm ID nozzle, graduation marks and Teflon-coated ground glass stopper.

6.2 Personal sampling pump capable of drawing the required sample flow for intervals of up to 45 minutes.

6.3 Air metering device capable of measuring a flow of 1 to 2 liters per minute, including a prefilter to prevent liquid droplets from reaching the measuring device.

6.4 Spectrophotometer capable of measuring the yellow color at 352 nm with stoppered tubes or cuvettes.

6.5 Associated laboratory glassware.

7. Reagents

The reagents described must be made up using ACS reagent grade or better grade of chemical.

7.1 Double distilled water.

7.2 Absorbing reagent. Dissolve 40.0 g of sodium hydroxide in almost a liter of water, then dissolve 10.0 g of potassium iodide and

make the mixture to 1 liter. Store in a clean glass bottle with a screw cap (with inert liner) or rubber stopper (previously boiled for 30 minutes in alkali and washed). Age for at least 1 day before using. The reagent should be used within two weeks.

7.3 <u>Acidifying reagent</u>. Dissolve 5.0 g of sulfamic acid in 100 ml of water, then add 84 ml of 85 percent phosphoric acid and dilute to 200 ml.

7.4 <u>Standard potassium iodate solution</u>. Dissolve 0.758 g of potassium iodate in water and dilute to 1 liter. One ml of this stock solution is equivalent to 400 µl of ozone. Prepare a dilute standard solution just before it is required by pipetting exactly 5 ml of stock solution into a 50-ml volumetric flask and making to mark with distilled water.

8. <u>Procedure</u>

8.1 Cleaning of equipment. All glassware should be cleaned with dichromate cleaning solution followed by 3 tap and 3 distilled water rinses.

8.2 <u>Collection of samples</u>

  8.2.1 Assemble a train composed of a midget impinger, a rota-meter, and pump. Use ground glass connections upstream from the impinger. Insure that all fittings are vacuum tight.

  8.2.2 Pipette exactly 10 ml of the absorbing solution into the midget impinger and sample at a flow rate of 1 liter per minute. Note the volume of air sampled. Record atmospheric temperature and pressure.

  8.2.3 Cap the impinger with the stopper supplied for shipment to the laboratory.

8.3 <u>Analysis</u>

  8.3.1 If the liquid level is below the 10-ml mark in the impinger, add distilled water to bring the level up to the mark.

  8.3.2 Add 2 ml of the acidifying reagent with a volumetric pipette. Swirl gently to expel the carbon dioxide released immediately. Then cap and shake vigorously until bubbling ceases. It is imperative that <u>all</u> of the carbon dioxide is expelled, otherwise more may be released while the u.v. measurement is being made.

  8.3.3 Place the stoppered impinger in a water bath at room temperature for 5 to 10 minutes to dissipate the heat of neutralization.

8.3.4 Transfer a portion of the sample to a cuvette and deter-
mine the absorbance at 352 nm. A cuvette containing dis-
tilled water is used as the reference. Do not delay the
reading since reducing impurities sometimes causes rapid
fading of the color.

8.3.5 Prepare a reagent blank by adding 2 ml of the acidifying
reagent to ml of unexposed absorbing reagent. Cool and
determine the blank absorbance. The blank absorbance
should be determined each day and should be subtracted
from the absorbance of the samples.

8.3.6 Samples may be aliquoted before or after acidification if
very large concentrations of oxidant are expected. In the
former case dilute the aliquot to 10 ml with unexposed
absorbing reagent and proceed in the usual manner. In the
- latter case dilute the aliquot to 10 ml with reagent blank
mixture. Aliquoting after acidifcation is not as reliable
as before acidification and should be used only to save a
sample when unexpectedly large concentrations of oxidant
are encountered. The calculations should include the
aliquoting factor.

9. Calibration and Standards

9.1 Add the freshly prepared, dilute standard iodate solution in
graduated amounts of 0.10 to 0.5 ml (measured accurately in a
graduated pipette or small burette) to a series of 25-ml glass
stoppered volumetric flasks. Make at least 4 standards.

9.2 Add alkaline potassium iodide solution (measured accurately in a
graduated pipette) to make the total volume of each exactly
10 ml.

9.3 Acidify and determine the absorbance of each standard as with the
samples.

10. Calculations

10.1 Plot the absorbance of the standards (corrected for the blank)
against the concentration of dilute standard iodate solution.
One (1) ml of the diluted standard iodate solution (in a total
of 10-ml absorbing solution per Section 9) is equivalent to 51 mg
of ozone. To readily determine ambient ozone concentrations in
units of mg/m^3, it is convenient to plot absorbance versus mg
equivalents of ozone per 10 ml of absorbing solution.

10.2 Upon determining the absorbance of the sample solutions, use the
standard absorbance curve to find the ozone equivalence. The
concentration of ozone in the air sample equals the ozone equiva-
lence divided by the air volume in liters.

$$O_3 \ (mg/m^3) = \frac{\text{ozone equivalence}}{\text{air volume (liters)}}$$

The reaction of ozone with alkaline KI is not quantitative and the yield of iodine is concentration dependent. The following correction equation was developed during validation of the method.

$$O_3 \ (mg/cu \ m) = 0.038 + 1.038A - 0.010505A^2$$

where A is the concentration of ozone (also in mg/cu m) read from the absorbance curve.

10.3 Another method of expressing concentration is ppm, defined as µl of ozone per liter of air

$$ppm \ O_3 = O_3 \ (mg/cu \ m) \ X \ \frac{24.45}{48} \ X \ \frac{760}{P} \ X \ \frac{T + 273}{298}$$

where:

     P = pressure (mm Hg) of air sampled
     T = temperature (C) of air sampled
 24.45 = molar volume (1/mole) at 25 C and 760 mm Hg
    48 = molecular weight (g/mole) of ozone
   760 = standard pressure (mm Hg)
   298 = standard temperature (K)

11. References

11.1 "Selected Methods for the Measurement of Air Pollutants" USDHEW Public Health Service Publication Number 999-AP-11, 1965.

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.