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$$\text{Approximate sampling time} = \frac{\text{Optimum volume}}{\text{Critical orifice flow rate}}$$

16.8 Sample Collection.

16.8.1 Connect the Teflon tubing, Teflon tee, and rotameter to the flow control needle valve as shown in Figure 16A–4. Vent the rotameter to an exhaust hood. Plug the open end of the tee. Five to 10 minutes prior to sampling, open the cylinder valve while keeping the flow control needle valve closed. Adjust the delivery pressure to 20 psi. Open the needle valve slowly until the rotameter shows a flow rate approximately 50 to 100 ml above the flow rate of the critical orifice being used in the system.

16.8.2 Place 50 ml of zinc acetate solution in two of the impingers, connect them and the empty third impinger (dropout bottle) and the rest of the equipment as shown in Figure 16A–4. Make sure the ground-glass fittings are tight. The impingers can be easily stabilized by using a small cardboard box in which three holes have been cut, to act as a holder. Connect the Teflon sample line to the first impinger. Cover the impingers with a dark cloth or piece of plastic to protect the absorbing solution from light during sampling.

16.8.3 Record the temperature and barometric pressure. Note the gas flow rate through the rotameter. Open the closed end of the tee. Connect the sampling tube to the tee, ensuring a tight connection. Start the sampling pump and stopwatch simultaneously. Note the decrease in flow rate through the excess flow rotameter. This decrease should equal the known flow rate of the critical orifice being used. Continue sampling for the period determined in Section 16.7.5.

16.8.4 When sampling is complete, turn off the pump and stopwatch. Disconnect the sampling line from the tee and plug it. Close the needle valve followed by the cylinder valve. Record the sampling time.

16.9 Blank Analysis. While the sample is being collected, run a blank as follows: To a 250-ml Erlenmeyer flask, add 100 ml of zinc acetate solution, 20.0 ml of 0.01 N iodine solution, and 2 ml HCl solution. Titrate, while stirring, with 0.01 N $Na_2S_2O_3$ until the solution is light yellow. Add starch, and continue titrating until the blue color disappears. Analyze a blank with each sample, as the blank titer has been observed to change over the course of a day.

NOTE: Iodine titration of zinc acetate solutions is difficult to perform because the solution turns slightly white in color near the end point, and the disappearance of the blue color is hard to recognize. In addition, a blue color may reappear in the solution about 30 to 45 seconds after the titration endpoint is reached. This should not be taken to mean the original endpoint was in error. It is recommended that persons conducting this test perform several titrations to be able to correctly identify the endpoint. The importance of this should be recognized because the results of this analytical procedure are extremely sensitive to errors in titration.

16.10 Sample Analysis. Sample treatment is similar to the blank treatment. Before detaching the stems from the bottoms of the impingers, add 20.0 ml of 0.01 N iodine solution through the stems of the impingers holding the zinc acetate solution, dividing it between the two (add about 15 ml to the first impinger and the rest to the second). Add 2 ml HCl solution through the stems, dividing it as with the iodine. Disconnect the sampling line, and store the impingers for 30 minutes. At the end of 30 minutes, rinse the impinger stems into the impinger bottoms. Titrate the impinger contents with 0.01 N $Na_2S_2O_3$. Do not transfer the contents of the impinger to a flask because this may result in a loss of iodine and cause a positive bias.

16.11 Post-test Orifice Calibration. Conduct a post-test critical orifice calibration run using the calibration procedures outlined in Section 16.12.4. If the Q_{std} obtained before and after the test differs by more than 5 percent, void the sample; if not, proceed to perform the calculations.

16.12 Calibrations and Standardizations.

16.12.1 Rotameter and Barometer. Same as Method 11, Sections 10.1.3 and 10.1.4.

16.12.2 $Na_2S_2O_3$ Solution, 0.1 N. Standardize the 0.1 N $Na_2S_2O_3$ solution as follows: To 80 ml water, stirring constantly, add 1 ml concentrated H_2SO_4, 10.0 ml of 0.100 N $KH(IO_3)_2$ and 1 g potassium iodide. Titrate immediately with 0.1 N $Na_2S_2O_3$ until the solution is light yellow. Add 3 ml starch solution, and titrate until the blue color just disappears. Repeat the titration until replicate analyses agree within 0.05 ml. Take the average volume of $Na_2S_2O_3$ consumed to calculate the normality to three decimal figures using Equation 16A–5.

16.12.3 Iodine Solution, 0.01 N. Standardize the 0.01 N iodine solution as follows: Pipet 20.0 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Titrate with standard 0.01 N $Na_2S_2O_3$ solution until the solution is light yellow. Add 3 ml starch solution, and continue titrating until the blue color just disappears. If the normality of the iodine tested is not 0.010, add a few ml of 0.1 N iodine solution if it is low, or a few ml of water if it is high, and standardize again. Repeat

the titration until replicate values agree within 0.05 ml. Take the average volume to calculate the normality to three decimal figures using Equation 16A–6.

16.12.4 Critical Orifice. Calibrate the critical orifice using the sampling train shown in Figure 16A–4 but without the H_2S cylinder and vent rotameter. Connect the soap bubble meter to the Teflon line that is connected to the first impinger. Turn on the pump, and adjust the needle valve until the vacuum is higher than the critical vacuum determined in Section 16.7.4. Record the time required for gas flow to equal the soap bubble meter volume (use the 100-ml soap bubble meter for gas flow rates below 100 ml/min, otherwise use the 500-ml soap bubble meter). Make three runs, and record the data listed in Table 16A–1. Use these data to calculate the volumetric flow rate of the orifice.

16.13 Calculations.

16.13.1 Nomenclature.

B_{wa} = Fraction of water vapor in ambient air during orifice calibration.

C_{H_2S} = H_2S concentration in cylinder gas, ppmv.

$$K_2 = 32.03 \frac{mg}{meq} \frac{24.05L}{mole} \frac{1\,mole}{64.06g} \frac{1g}{10^3 mg} \frac{10^3 mL}{L} \frac{10^3 \mu L}{l\,mL}$$

$$= \frac{12025 \mu L}{meq}$$

M_a = Molecular weight of ambient air saturated at impinger temperature, g/g-mole.

M_s = Molecular weight of sample gas (nitrogen) saturated at impinger temperature, g/g-mole.

NOTE: (For tests carried out in a laboratory where the impinger temperature is 25 °C, M_a = 28.5 g/g-mole and M_s = 27.7 g/g-mole.)

N_I = Normality of standard iodine solution (0.01 N), g-eq/liter.

N_T = Normality of standard $Na_2S_2O_3$ solution (0.01 N), g-eq/liter.

P_{bar} = Barometric pressure, mm Hg.

P_{std} = Standard absolute pressure, 760 mm Hg.

Q_{std} = Average volumetric flow rate through critical orifice, liters/min.

T_{amb} = Absolute ambient temperature, °K.

T_{std} = Standard absolute temperature, 293 °K.

θ_s = Sampling time, min.

θ_{sb} = Time for soap bubble meter flow rate measurement, min.

$V_{m(std)}$ = Sample gas volume measured by the critical orifice, corrected to standard conditions, liters.

V_{sb} = Volume of gas as measured by the soap bubble meter, ml.

$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, liters.

V_I = Volume of standard iodine solution (0.01 N) used, ml.

V_T = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used, ml.

V_{TB} = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used for the blank, ml.

16.13.2 Normality of Standard $Na_2S_2O_3$ Solution (0.1 N).

$$N_T = \frac{1}{mL\,Na_2S_2O_3\,consumed} \qquad \text{Eq. 16A-5}$$

16.13.3 Normality of Standard Iodine Solution (0.01 N).

$$N_I = \frac{N_T V_T}{V_I} \qquad \text{Eq. 16A-6}$$

16.13.4 Sample Gas Volume.

$$V_{m(std)} = \overline{Q}_{std} \Theta_s \left(1 - B_{wa}\right) \frac{M_a}{M_b} \qquad \text{Eq. 16A-7}$$

16.13.5 Concentration of H_2S in the Gas Cylinder.

$$C_{H_2S} = \frac{K N_T (V_{TB} - V_T)}{V_{m(std)}} \qquad \text{Eq. 16A-8}$$

17.0 References

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