Experiment 22

Determination of the Concentration of Carbon Dioxide in the Atmosphere

Objective—The objective of this experiment is to determine the carbon dioxide concentration of the atmosphere by reacting the carbon dioxide with barium hydroxide, precipitating barium carbonate. This experiment also introduces the fundamental ideas of gravimetric analysis.

Introduction—Although there are about a dozen components of the atmosphere, there are only two major components, oxygen and nitrogen. The other chemical species are present in only trace amounts, as shown in Table 22-1. Of the substances listed, only one has a variable concentration that is important, carbon dioxide. Carbon dioxide is a colorless, odorless gas that, although not toxic, does not support respiration and thus causes suffocation at high concentrations.

There has been an increase in the average temperature of the earth of 0.3–0.6°C over the last century. The substances most responsible for maintaining earth's surface temperature are carbon dioxide and water. Carbon dioxide plays a secondary, but crucial role in maintaining the surface temperature of the earth. The worldwide consumption of fossil fuels (coal, petroleum, and natural gas) has sharply increased the CO_2 level in the atmosphere. A gallon of gasoline (density = 0.70 g/mL) with an approximate composition of C_8H_{18} produces about 8 kg of CO_2, which translates to over 20 billion tons produced annually. Large quantities of carbon dioxide are used for refrigeration and the production of carbonated beverages.

Scientists have monitored carbon dioxide levels in the atmosphere since 1958. After the last ice age, the level remained fairly constant until the start of the Industrial Revolution, about 300 years ago. Since that time the CO_2 concentration has increased by 25% and the present level in the atmosphere is about 355 ppm.

Table 22-1 Composition of Dry Air Near Sea Level

Component	Mole Fraction
Nitrogen	0.78084
Oxygen	0.20948
Argon	0.00934
Carbon dioxide	0.000355
Neon	1.818×10^{-5}
Helium	5.24×10^{-6}
Methane	2×10^{-6}
Krypton	1.14×10^{-6}
Hydrogen	5×10^{-7}
Nitrous oxide	5×10^{-7}
Xenon	8.7×10^{-8}

Approximately one-half of anthropogenic carbon dioxide emissions find a sink in seawater. Large amounts are also removed from the atmosphere each spring and summer because of photosynthesis in plants:
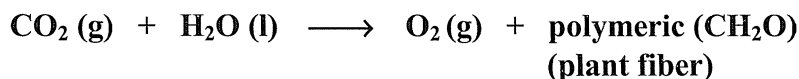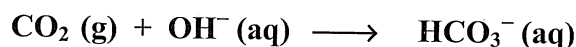
$$CO_2 \text{ (g)} + H_2O \text{ (l)} \longrightarrow O_2 \text{ (g)} + \text{polymeric } (CH_2O)$$
$$\text{(plant fiber)}$$

However, biological decay of plant material occurs in the fall and winter and replaces much of the carbon dioxide.

### Theory—Carbon dioxide readily reacts with base to form bicarbonate or carbonate, according to the equations,

$$CO_2 \text{ (g)} + OH^- \text{ (aq)} \longrightarrow HCO_3^- \text{ (aq)}$$

and

$$CO_2 \text{ (g)} + 2 OH^- \text{ (aq)} \longrightarrow CO_3^{2-} \text{ (aq)} + H_2O \text{ (l)}$$

If sodium or potassium hydroxides are used, the resulting sodium or potassium bicarbonate or carbonate salts are soluble in water. On the other hand, if barium hydroxide is used, a precipitate of carbonate results,

$$Ba^{2+}\text{(aq)} + 2 OH^-\text{(aq)} + CO_2 \text{(g)} \longrightarrow BaCO_3 \text{ (s)} + H_2O \text{ (l)}$$
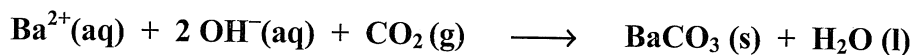
As barium hydroxide is consumed, the pH of the solution and its conductivity decrease considerably. The amount of hydroxide neutralized can be estimated by the conductivity change, but can be more accurately determined by titrating excess OH^- with standard acid after filtering off $BaCO_3$. Filtration is necessary because $BaCO_3$ also reacts with acid.

In this experiment, $BaCO_3$ will be measured gravimetrically since it is the most direct method, is very accurate, and introduces the principles of this important area.

Although usually extremely accurate, a gravimetric method is time-consuming and requires good technique, as well as strict attention to details. The following general principles are necessary to ensure good results:

1. There must be a quantitative precipitation of the precipitate, at least 99.9% complete. This can be ensured if the K_{sp} of the precipitate is small enough, and if not, using excess precipitating agent to shift the equilibrium to the right.

2. It is often necessary to prevent the precipitate from forming a colloid (sol) that will pass through a filter. Heating and stirring the precipitate aids coagulation and the subsequent growth of large crystals. Rinsing the precipitate with electrolyte solutions prevents the precipitate from spontaneously becoming colloidal again.

3. Prevent the coprecipitation of excess reactant ions.

4. Use a final rinse of the precipitate that will replace nonvolatile adsorbed ions with ions that will decompose or volatize at the temperature of the drying oven, preferably between 110 and 200°C.

To see if $BaCO_3$ is precipitated quantitatively, consider the K_{sp}, which at 25°C is 4.9 x 10^{-9}. In a saturated solution its solubility is 7.0 x 10^{-5} mol/L, or 9.6 mg/L. Thus, if 1 g of barium were precipitated out in 100 mL of solution, there would be an error of about 0.1%. When an excess of barium ion is used in the analysis, the reaction will be quantitative.

To prevent the precipitate from reverting to the colloidal state, it is rinsed with an electrolyte solution, in this case, barium nitrate. The barium salt is used to prevent solubility losses of the precipitate. A final rinse with ammonium nitrate replaces excess barium on the surface of the precipitate with the ammonium ion, which is lost on drying. On drying the following reaction occurs,

$$2\ NH_4NO_3\ (s)\ \longrightarrow\ 2\ N_2O\ (g)\ +\ 4\ H_2O(g)$$
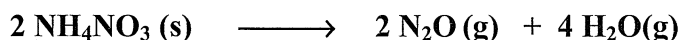
Air Sampling

Most air samplers contain the components shown in the air-sampling train of Figure 22-1.

Figure 22-1   General Diagram of an Air-Sampling System
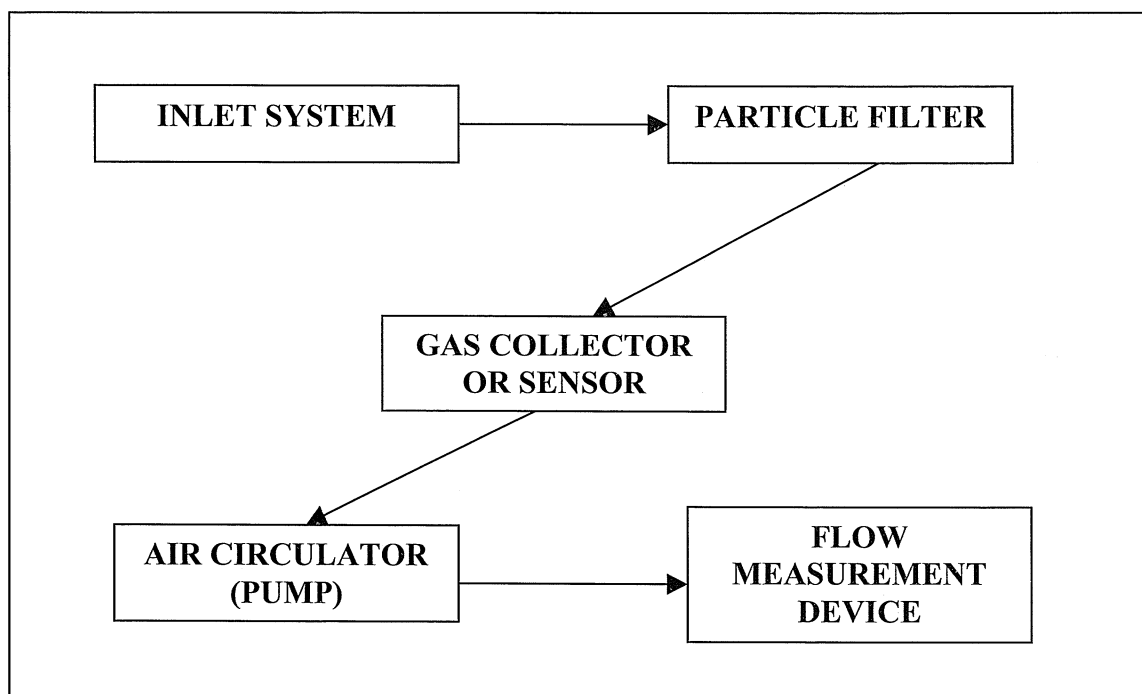
The inlet system must be inert to the analyte being studied and is commonly made of Teflon, glass, or stainless steel. The inlet must be located away from any solid surfaces or physical obstructions. It must also be located away from possible point sources (factories, electric plants, highways, etc.) if the sample is to be representative.

If the sampling objective is to collect airborne particles (an aerosol), the nature of the filter material is important. Commonly used filter materials are glass fibers, cellulose ester, and Teflon membranes. Typical pore sizes for membrane filters are about 0.5 µm.

If the analyte of interest is a gas, a gas collector or sensor follows the particle filter. The collector may be a wash bottle containing a liquid reagent, or it may be an absorbent porous polymer, depending on what is to be collected. For example, SO_2 may be collected in dilute hydrogen peroxide solution where it forms sulfuric acid, which may be analyzed by titration of acidity, measurement of SO_4^{2-}, or solution conductivity:

$$SO_2\,(g) \;+\; H_2O_2\,(aq) \;\longrightarrow\; H_2SO_4\,(aq)$$
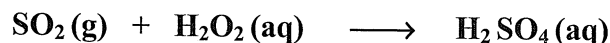
Air is drawn through the system by a pump, which is always used to draw, rather than blow air. This prevents sample contamination from the pump that might occur if the air was drawn through the pump. Flow rates vary for different pumps but typically lie in the range of 0.5–20 L/min for "low-volume" samples, and are about 1–2 m^3/min for "high-volume" samples. The flow rate can be measured with a gas meter, which measures an integrated air volume. Alternatively, a flow-rate meter, such as a rotameter, can be used to measure flow rate, which may be converted to a volume of air by multiplying by the sampling time. Some commercially available gas analyzers have all the components built into a compact arrangement and may have a continuous sensor to measure the concentration of analyte(s).
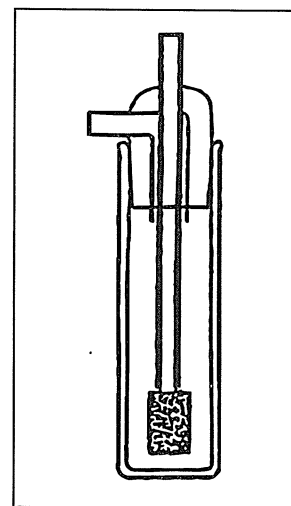
Safety Issues

1. Safety glasses must be worn at all times in the chemistry laboratory.

2. Use gloves when handling barium hydroxide and its solutions. If any hydroxide gets on your skin, rinse for several minutes with cool water.

Procedure

Figure 22-2 Bubbler Sampler for Collection of Carbon Dioxide

1. Assemble the sampling apparatus in the order shown in Figure 22-1. In this experiment, the gas collector is a bubbler sampler like the one shown in Figure 22-2. If more than one set-up is available, it would be informative and interesting to locate them at different sites to see if there are differences in the CO_2 levels. Outdoor samples near traffic, for example, may yield different results than those found in the laboratory. If few setups are available, the experiment can be carried out over several lab periods to obtain results over a time span. The pump is a compressor with an adjustable air flow. However, the system is operated by connecting the air input of the pump to the side arm of the bubbler. This draws air into the bubbler and the solution. The air drawn through the system is measured with a flow meter.

2. Accurately weigh (to 0.1 mg) about 5 g of barium hydroxide into a small beaker or a weighing boat. Quantitatively transfer to the collection tube and add about 150 mL DI water.

3. Attach the tubing from the flowmeter and measure the initial flow rate. It should be about 2 L/min. Collect a sample for 90–120 minutes; measure the flow rate at the end of this time.

4. While the carbon dioxide is being collected, obtain a clean filter crucible of either medium or fine

porosity. Put into a drying oven at 110°C for 0.5 hour, and then transfer to a desiccator to cool. Then weigh (to 0.1 mg).

5. Before and after sample collection, measure ambient temperature and barometric pressure.

6. Disassemble the apparatus, add 75 mL DI water to the tube, mix and then allow the precipitate to settle for 10 minutes. Decant the supernatant liquid quickly through the filter crucible using suction. Then transfer the precipitate to the filter crucible, using 0.1 M barium nitrate wash solution to rinse the collection tube and the precipitate.

7. Finally, rinse the precipitate with several small portions of 0.1 M NH_4NO_3.

8. Suction for an additional minute after all liquid has passed through the funnel. Put the crucible in a drying oven at 110–120°C for 1 hour.

9. Transfer the crucible to a desiccator to cool, then weigh and obtain the mass of $BaCO_3$ by difference.

10. Return the crucible to the oven for 0.5 hour and repeat step 9 until the crucible with sample reaches constant weight.

Waste Minimization and Disposal

1. Excess barium hydroxide solution and barium nitrate solution can be treated with dilute sulfuric acid. This neutralizes the base and also forms a very insoluble precipitate of barium sulfate. The barium sulfate precipitate and the precipitate of barium carbonate can be combined in a waste bottle. These precipitates take little space and can be stored until a sufficient amount is accumulated, at which time it can be given to a commercial waste disposal facility.

2. Ammonium nitrate solutions in small amount and concentration can be disposed of by rinsing down the laboratory drain (after approval by the lab instructor).

Data Analysis

1. Report the mass of $Ba(OH)_2$ used, the collection time, and the mass of $BaCO_3$ produced. From the latter, calculate the mass and number of moles of carbon dioxide collected.

2. Calculate the moles of air collected, using the ideal gas law, $n = PV/RT$. Use the average atmospheric pressure and temperature during the collection period. The volume is the flow rate times the time. Be careful to use the correct units.

3. Calculate the ppm CO_2, which is equal to its mole fraction, and is equal to $n(CO_2) / n(air)$, and compare with:

   a. the value presently known for the atmosphere

b. values obtained by other groups in your class

4. Discuss factors that would give low results and factors that would give high results in this experiment.

Supplemental Activity—The remaining hydroxide can be analyzed by direct titration with standard acid to check the results obtained gravimetrically.

Questions and Further Thoughts

1. When carbon dioxide is produced by the combustion of a fossil fuel, water, another greenhouse gas, is produced. Compare the amount of water produced when 1 gallon of C_8H_{18} is burned (see the Introduction) to the amount of carbon dioxide produced. Is the water produced as much of a problem as the carbon dioxide? Why?

2. Are there other pollutants that can interfere with the analysis for carbon dioxide? If so, write the equations for the reactions.

3. Can the carbon dioxide level in the atmosphere be determined by a precipitation titration of the excess barium present in the reaction mixture? If so, how could it be done?

4. Gas chromatography can also be used to determine the CO_2 level in the atmosphere. What are some of the advantages and some of the disadvantages of this method for such an analysis?

Notes

1. A sampling train consisting of a tube containing $Mg(ClO_4)_2$ to absorb water connected to a tube containing NaOH can be used to determine ppm CO_2 in the atmosphere. A difficulty with this method is that when humidity is high, excess water may break through the $Mg(ClO_4)_2$ tube into the NaOH tube.

2. After collecting the carbon dioxide, water is added to the reaction mixture to dilute the hydroxide since sintered glass is very soluble in strong base. Also, the time the base is in the funnel should be kept as short as possible. Without diluting the base the loss is still small, typically being 0.01 g.

3. An aquarium pump can put out more than 3 L/min and could be used in this experiment.

4. Too much frothing occurs if the air flow is greater than 3 L/min.

Literature Cited

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