

Figure 3. Penetration volume vs. pore diameter for iron oxide-A

latter represents the data of interest in calculating pore surface area S_{wm} . This area was determined by considering the volume axis to be divided into a number of small volume increments and obtaining the mean pressure corresponding to each incremental volume. These two values were multiplied together, and the sum of all values was obtained in accordance with Equation 6. Table III represents a typical calculation and the third column of Table II summarizes the results. While the data of Table III indicate a smallest pore radius of 221 Å according to Equation 4, other materials, notably the cupric carbonates, were found to have pore radii down to 18.4 Å or near the minimum attainable at the instrument limit of 50,000 psia.

Total, or gas absorption, surface areas S_{wg} were not determined as a part of this work; this information was obtained from the source of the powder as was the other pertinent information listed in Table IV. It may be noted that carbon black surface areas were calculated from size data taken from electron micrographs rather than obtained by gas adsorption. These particles were essentially spherical and quite uniform in size. Specific surface areas determined from gas absorption and from particle size data under this circumstance have been shown previously to be in essential agreement (12).

CONCLUSION

The particle materials of this study were chosen for no particular reason other than that they were available, that some of the needed information about them was already known, and that they appeared to have widely differing pore and surface properties. The results in Table II, particularly the correspondence evident in the right two columns, reveals that, at least for the 16 powders tested, it is possible to arrive at the total surface area from a summation of external and internal measures. The results support the idea that Knudsen-flow measurements relate to the surface exclusive of micropores. Finally, the results lend confidence to each type of measurement despite the assumptions utilized in arriving at it.

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(12) J. C. Arnell and G. O. Henneberry, *Can. J. Research*, **26A**, 29-38 (1948).

Low Level Calibration Mixtures for Gaseous Pollutants

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IN AIR POLLUTION MEASUREMENTS, there has developed a considerable need for instrument calibration standards in the analysis of gaseous materials at the ppm and ppb level. One response to this need has been the development (1) and certification (2) of SO_2 permeation tubes. These tubes, under constant temperature conditions, effuse SO_2 at a given rate and by controlling the gas flow over the tubes, one can produce low level calibration standards. The tubes have an advantage, through continuous flow, of overpowering any adsorption-desorption effects occurring within the inlet and measurement systems. The permeation rates, however, are sufficiently temperature sensitive so as to require thermostating, and a period of several hours is needed for the establishment of steady state flow conditions. Furthermore, permeation tubes have been limited in practical usage to the easily condensable gases since, for reasonable lifetimes, the tubes must hold an appreciable quantity of liquified gas.

Presented herein is an alternate technique for the production of low level calibration mixtures for gaseous pollutants. The

technique consists of encapsulating, measuring, and storing a very small quantity of pure pollutant gas as a microbubble and then at the time of analysis, of mixing the pollutant gas with a known large quantity of "clean" diluent gas. The mixing operation is done in a separate, passivated dilution cylinder.

Pollution standards are frequently needed in a range from 10 ppb to 100 ppm, and with a usable volume of about 1000 cm^3 . For a volume of 1000 cm^3 , and considering the ppb and ppm levels to be on a volume per volume basis, this means that the volume of pure pollutant will vary from 10^{-5} to 10^{-1} cm^3 . Such volumes are conveniently contained and measured in capillary tubing. If larger volumes of calibrated gas mixtures are needed, the required volumes can be produced by using larger "capillary" tubing and dilution cylinders. Higher pressures in the dilution cylinder may also be used.

Precision bore, glass capillary tubing can be used as a convenient "volumetric flask" for the measurement of the bubble volume and as a readily inspectable storage container for the bubble. Experience has shown that the bubble remains as a stable slug of gas so long as one end of the capillary tube is sealed; it will not float upward when the capillary is held in a vertical position.

- (1) A. E. O'Keefe and G. C. Ortman, *ANAL. CHEM.*, **38**, 760 (1966).
- (2) SO_2 permeation tubes, SRM 1625, may be purchased from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.

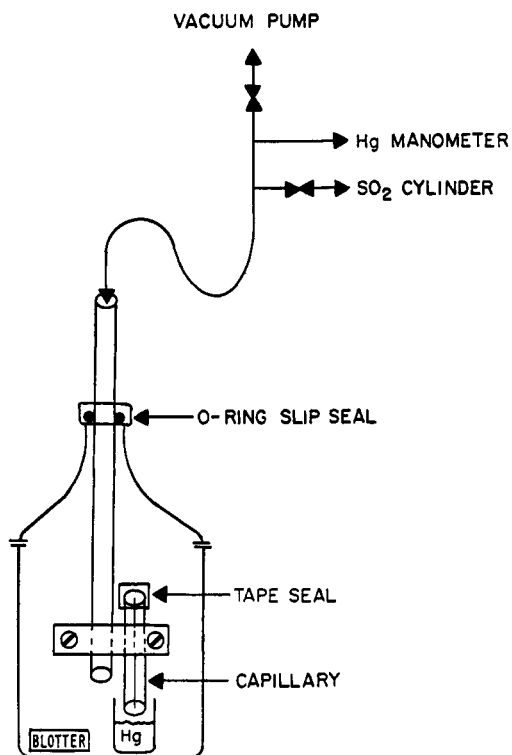


Figure 1. Encapsulation apparatus

The separate storage of the pure pollutant gas in the form of a microbubble and the use of a freshly prepared gas calibration mixture minimizes several problems which are frequently encountered in the use of pressurized cylinders of premixed and calibrated low level gas pollutant standards. Reactions are minimized since the long term storage of the microbubble of pure pollutant gas is under conditions of atmospheric pressure and minimum surface area. Use is made of relatively inert and inexpensive container materials. After storage, a visual indication of the stability of the pollutant gas is easily made. Finally, the passivation of the large surfaces of the dilution cylinder is not extremely critical since the length of exposure of the pollutant gas to the cylinder is small.

SO₂, NO, and mixtures of SO₂ + NO gases have been encapsulated and stored for periods of six months or more without apparent deterioration, as indicated by lack of volumetric changes. Quantitative chemical measurements for the SO₂ bubbles show that full recovery is obtained.

EXPERIMENTAL

Equipment shown in Figure 1 was used to encapsulate the pollutant gas (bubble) in a capillary tube. An O-ring slip seal was used to introduce the capillary support and SO₂ inlet tube through the lid of a small glass envelope. This envelope is about 4 inches in diameter. In the encapsulation procedure, a capillary tube whose upper end has been sealed by plastic tape and the glass envelope are evacuated, and through a downward motion of the support rod, the capillary is inserted into the encapsulating liquid (Hg, in this case). The vacuum pump valve is then closed and a small pressure of SO₂ is introduced to drive the encapsulating fluid half way up the capillary. The capillary is next withdrawn from the fluid, the bottom of the tube blotted dry (if necessary), and the SO₂ pressure further increased causing the liquid column to move to the top of the capillary and the open volume in the capillary to be filled with SO₂ at a pressure of somewhat less than one atmosphere, as measured on the manometer.

The capillary is then reinserted into the liquid and the pressure is increased to one atmosphere causing the trapped bubble to contract and the bottom end of the capillary to fill with liquid. The capillary and encapsulated bubble are then removed from the apparatus and stored for future use. The amount of encapsulated gas can be controlled by adjusting the SO₂ pressure just prior to making the final liquid seal, or by using different diameters and lengths of capillary tubing.

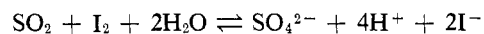
At the time of analysis, the temporary plastic tape seal is removed from the one end of the horizontally positioned capillary; the end of the tube is connected to a valved-off, evacuated, dilution cylinder and the other end connected to a cylinder of pressurized dry nitrogen and to a Hg manometer. The use of commercially available O-ring couplings allows the open end capillary tube to be connected without disturbing the SO₂ bubble. The dilution cylinder and the N₂ cylinder valves are next opened and the bubble and encapsulating liquid are blown into the dilution cylinder. By pressuring a 1-liter dilution cylinder to two atmospheres (absolute), one obtains a calibration mixture from which a spontaneous flow of 1-liter-atmosphere excess gas can be obtained. For calculating the SO₂ concentration, one only needs to know the volume of SO₂ in the bubble, and the volume and final pressure in the dilution cylinder. The ideal gas law is adequate for this calculation.

The calibrated gas mixture can be used in any of the usual flow-type SO₂ detection and measurement systems. It should be noted that for a new measurement system, some initial excess flow of the gas mixture may be needed in order to "saturate" the gas inlet train.

A 316 stainless steel dilution cylinder and valve were used in this investigation. Passivation of the cylinder walls and valve are required in order to eliminate problems associated with adsorption of SO₂. The passivation was accomplished by successive 30-minute treatments of the surfaces with concentrated HNO₃, distilled H₂O, O₂, and SO₂. This was followed by a cold-trapped, mechanical pump evacuation of the cylinder and valve for a period of several days.

RESULTS

SO₂ bubbles were mixed with N₂ in a 2-liter passivated dilution cylinder and quantitative measurements at the 0.5–1.5 ppm (v/v) level were made using a commercial microcoulometer. The microcoulometer operated on the basis of the reaction of I₂ with SO₂. The number of coulombs needed to electroregenerate the I₂ to match a constant reference signal was measured. The overall reaction was:



Absolute (coulometric) SO₂ yields were measured in a series of analyses made over a period of several hours on a given SO₂ calibration mixture. A series of relative SO₂ yields were also measured over a period of several hours on another SO₂ calibration mixture. Here the coulometric yields were normalized to 100%, using an NBS permeation tube (2) for the calibration. The two sets of analyses (absolute and relative) are tabulated below.

SO ₂ yield, %	
Absolute	Relative
94	105
101	104
102	105
98	101
	105
	99
	99

The scatter of the yields is typical of the variability of measurement obtained from the commercial microcoulometer. The above results indicate that essentially complete SO₂ recovery was obtained and that, over a period of several hours, there is no significant reaction of SO₂ with the dilution cylinder walls.

A single passivation of the dilution cylinder was satisfactory for a period of at least several weeks experimentation. No subsequent SO₂ adsorption-desorption problems were observed. Desorption of SO₂ from the cylinder walls, over a period of several hours resulted in backgrounds of less than 5 ppb SO₂.

DISCUSSION OF RESULTS

The above results show that the general technique works and that full SO₂ recovery is obtained. The technique should also be useful with other gases. Further application of the technique, however, requires an understanding of factors that can adversely affect the results. Calibrations at the ppm and ppb level are subject to many errors that are insignificant at higher levels.

The gas can dissolve in or react with the encapsulating liquid. This was not a problem with Hg and SO₂ or NO. The following encapsulating liquids, however, were unsuitable due to solution of SO₂: Dow Corning 550 and 704 oils, Apiezon B and W oil, Kel-F-10, Halocarbon oil, Octoil-S, cyclooctane, mineral oil, and perfluorokerosene. The dissolved SO₂ is easily detected since a slight warming of the capillary tube causes some of the SO₂ to come out of solution and the expansion of the bubble far exceeds that predicted by simple thermal expansion of the gas.

Raoult's law predicts a significant SO₂ solubility since pure liquid SO₂ at room temperature has a vapor pressure, $P_{\text{SO}_2}^\circ$, of about 3.5 atm. For the case of a SO₂ bubble at a pressure of 1 atm ($P_{\text{SO}_2} = 1$ atm), an ideal solution would contain N mole fraction SO₂:

$$P_{\text{SO}_2} = N_{\text{SO}_2} \times P_{\text{SO}_2}^\circ$$

$$N_{\text{SO}_2} = 1/3.5$$

Hg is sufficiently non-ideal so that practically no SO₂ (or NO) dissolves.

NO₂ was found to react with Hg. The apparent reaction is (3):



Gases such as NO₂ may require the use of glass or other inert capillary plugs.

In this work, the microcoulometer was sensitive to Hg vapor and gave high background readings. Hg at room temperature has a vapor pressure of about 10⁻⁶ atm so that the gas mixture which is normally in contact with Hg droplets

would contain about a ppm Hg. Dry ice-acetone cold trapping of the outlet to the N₂ diluted SO₂ mixtures eliminated this source of error.

The passivation procedure for the dilution cylinder should be useful for other gases. Substitution of SO₂ by the gas to be used should be made in the last step of the passivation procedure.

In the current passivation procedure, care was taken to clean all lubricant from the stainless steel valve. It is recommended that the dilution cylinder and valve be made completely of stainless steel. The valve used in this work contained a polytetrafluoroethylene packing around the upper valve stem and on one occasion the polymer fuzz got into the lower valve chamber which resulted in an abnormally low SO₂ recovery (55%). Similar low results were initially obtained when the dilution cylinder had not been passivated.

Relatively inexpensive precision bore glass capillary tubing is readily available with diameters as small as 0.020 cm and with standard tolerances of ± 0.001 cm; special tolerances of ± 0.0001 cm are also available (Ace Glass, Inc., Vineland, N.J. 08360). The variation in the diameter of the capillary is normally not a major source of error, and becomes negligible in larger diameter tubing. For a diameter of 0.040 cm, a variation of ± 0.001 cm amounts to a $\pm 5\%$ volume error. This error may be eliminated by calibration with a traveling microscope or by measuring the weight of Hg contained in a given length of tubing.

An increase in the accuracy of measurement of the bubble volume may be made by measuring the bubble length under a known reduced pressure. Measurement of the longer bubble will also minimize the effect of minor errors in estimating the length attributable to the rounded ends of the bubble.

The microbubble technique has advantages in that the stability and the purity of the microbubble can be easily checked by a variety of techniques. Several of these techniques are: observing the bubble length as a function of time; chilling the bubble just above and just below the normal boiling point of the gas to visually observe the extent of condensation; and visually and/or spectroscopically examining the gas. With the exception of the spectroscopic examination of the gas, all three techniques have been used in this study.

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(3) J. W. Mellor, "Inorganic and Theoretical Chemistry," Vol. VIII, Supplement II, Nitrogen (Part II), John Wiley and Sons, New York, N.Y., 1967, p 263.