Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere

BERNARD E. SALTZMAN

Division of Special Health Service, U. S. Department of Health, Education, and Welfare, Cincinnati, Ohio

The determination of nitrogen dioxide in the atmosphere has heretofore been hampered by difficulties in sample absorption and lack of specificity. A new specific reagent has been developed and demonstrated to absorb efficiently in a midget fritted bubbler at levels below 1 p.p.m. The reagent is a mixture of sulfanilic acid, N-(1-naphthyl)-ethylenediamine dihydrochloride, and acetic acid. A stable direct color is produced with a sensitivity of a few parts per billion for a 10-minute sample at 0.4 liter per minute. Ozone in five-fold excess and other gases in tenfold excess produce only slight interfering effects; these may be reduced further by means which are described.

TOXIC oxides of nitrogen, liberated during the use of explosives, in welding operations, in the exhaust of internal combustion engines, and in chemical processes involving nitration or the use of nitric acid, are well known health hazards. In recent years new interest has been directed toward concentrations of a few tenths of a part per million of nitrogen dioxide, which are believed to play a vital role in the creation of irritating smog (4, 10). Toxicologic studies (8, 9, 15, 22, 24) call attention to the fact that nitrogen dioxide is the most toxic of the various nitrogen oxides by a large factor, and that confusion in the evaluation of the health hazards has resulted from analytical methods which fail to differentiate this oxide from the others in a mixture. In terms of nitrogen dioxide, a figure of 5 p.p.m. is the maximum safe allowable concentration proposed (8, 9). All these considerations require its determination in air at much lower levels than previously thought necessary.

The major problem of past analytical methods has been the difficulty in absorbing the gas from a sufficiently large sample. Results have been uncertain for levels below 5 p.p.m. Samples must be collected in large bottles for the well known phenoldisulfonic acid method (3, 6), and days are required for complete absorption; low results have been reported (16) and confirmed in the present study. Similar difficulties occur with the *m*-xylenol methods (11, 25). Both determine all nitrogen oxides in the form of nitrate, rather than nitrogen dioxide specifically.

Attempts have been made to use reagents for nitrite ion, which would be specific for nitrogen dioxide, but an absorption efficiency of only about 5% was reported (16) when a midget impinger was used. However, these reagents were found to be very convenient for higher levels using a glass syringe for collecting the sample (1, 12, 16); low levels have been determined using a carboy (23). Continuous samples have been collected by using silica gel at liquid air temperatures (7) or alkali bubblers (21), the latter being of unknown efficiency.

The present report deals with the development and demonstration of a reagent which is specific for nitrogen dioxide and can be used for continuous sampling with a high efficiency. The difficult problem of determining absorption efficiency was resolved by the construction of an apparatus capable of generating known concentrations of nitrogen dioxide of a few tenths of a part per million with a variation of less than 1%. The reagent which was finally developed conveniently produces a stable direct color which can be measured visually or spectrophotometrically. When 10 ml. are used in a midget fritted bubbler and air is sampled at a rate of 0.4 liter per minute, a sensitivity of a few parts per billion is attained with a 10-minute sample. The effect of various interfering gases was found to be slight.

APPARATUS

Spectrophotometer, Beckman Model DU. A set of matched test tubes, 22 × 175 mm., giving an optical light path of 2.02 cm. was used in a special holder fitted to the spectrophotometer.

Midget Fritted Bubblers, all-glass, capacity 60 ml., with upward-facing, 8-mm. diameter fritted disks. When used with 10 ml. of the absorbing reagent, drawing air through at the rate of 0.4 liter per minute should produce 20 to 30 ml. of fine froth above the solution.

Grab-Sample Bottles, having standard-taper ground-joint connection to stopcocks for evacuation, with calibrated volumes varying from 30 to 250 ml. Ordinary glass-stoppered borosilicate glass bottles are suitable. Fifty-milliliter glass syringes are convenient for moderately high concentrations.

REAGENTS

All reagents are made from analytical grade chemicals in nitrite-free water prepared by redistilling distilled water in an all-glass still after adding a crystal each of potassium permanganate and of barium hydroxide. They are stable for several months if kept well stoppered in brown bottles in the refrigerator.

N-(1-Naphthyl)-ethylenediamine Dihydrochloride, 0.1%. Dissolve 0.1 gram of the reagent in 100 ml. of water. Stock solution.

Absorbing Reagent. Dissolve 5 grams of sulfanilic acid in almost a liter of water containing 140 ml. of glacial acetic acid, add 20 ml. of the 0.1% stock solution of N-(1-naphthyl)-ethylenediamine dihydrochloride, and dilute to 1 liter.

Standard Sodium Nitrite Solution, 0.0203 gram per liter. One milliliter of this working solution produces a color equivalent to that of 10 μl. of nitrogen dioxide (10 p.p.m. in 1 liter of air at 760 mm. of mercury and 25° C.). Prepare fresh by dilution from a stronger stock solution. The latter may be prepared from Merck reagent grade granular solid, which has been shown (17) to assay 99.4%; in another study (5) it was found to assay 100.4%, drying was said to be unnecessary, and a stock solution of 8 grams per liter was found to be stable for 90 days.

PROCEDURE

Sampling for Levels of 1 P.P.M. and Below. Place 10 ml. of absorbing reagent in a midget fritted bubbler and draw a sample through it at the rate of 0.4 liter per minute until sufficient color has developed (about 10 minutes). Note the total air volume sampled. Pure gum rubber surgical tubing may be used for connections without losses if lengths are kept minimal.

Sampling for Levels above 1 P.P.M. Sample in an evacuated bottle of appropriate size (30 ml. for up to 100 p.p.m., to 250 ml. for down to 1 p.p.m.) containing 10 ml. of absorbing reagent. If a good source of vacuum is available at the place of sampling, it is best to evacuate just before sampling to eliminate any uncertainty about loss of vacuum. A three-way Y stopcock connection to the vacuum pump is convenient. In the first position the bottle is evacuated to the vapor pressure of the absorbing reagent and the actual vacuum is read. In the second position the sampling bottle is closed and the vacuum pump draws air through the sampling line to thoroughly flush it. In the third position the sampling line is connected to the evacuated bottle and the sample is collected. For calculation of the sample volume the pressure is recorded as the difference between the filled and evacuated conditions, and the volume is that of the bottle plus that of the connection up to the stopcock minus the volume of absorbing reagent. Allow 15 minutes with occasional shaking for complete absorption and color development.

Another more convenient but less accurate field method for moderately high levels is to use 50-ml. glass syringes. Ten milliliters of absorbing reagent may be kept in the capped syringes, and 40 ml. of air may be drawn in at the time of sampling. If insufficient color is expected, the absorption may be completed by shaking vigorously for 1 to 2 minutes, after which the air may be expelled and additional air drawn in.

Determination. After collection or absorption of the sample, a direct red-violet color appears. Color development is complete within 15 minutes at ordinary temperatures. Compare

with standards visually or read in a spectrophotometer at 550 mμ, using unexposed reagent as a reference. Colors may be preserved, if well stoppered, with only 3 to 4% loss in absorbance per day; however, if strong oxidizing or reducing gases are present in the sample in concentrations considerably exceeding that of the nitrogen dioxide, the colors should be determined as soon as possible to minimize any loss.

Standardization. Add graduated amounts of standard sodium nitrite solution up to 1 ml. to a series of 25-ml. volumetric flasks, and dilute to marks with absorbing reagent. Mix, allow 15 minutes for complete color development, and read the colors. The 1-ml. standard is equivalent to 4 μl. of nitrogen dioxide per 10 ml. of absorbing reagent.

Calculations. For convenience, standard conditions are taken as 760 mm. of mercury and 25° C.; thus only slight correction is ordinarily required to get V, the standard volume in liters of the air sample. Quantities of nitrogen dioxide may be expressed as microliters, μl., defined as V times the parts per million of nitrogen dioxide. It has been determined empirically that 0.72 mole of sodium nitrite produces the same color as 1 mole of nitrogen dioxide; hence 2.03 γ of sodium nitrite is equivalent to 1 μl. of nitrogen dioxide.

Plot the absorbances of the standard colors, corrected for the blank, against the milliliters of standard solution. Beer's law is followed. Draw the straight line giving the best fit, and determine the value of milliliters of sodium nitrite intercepted at absorbance of exactly 1. This value multiplied by 4 gives the standardization factor, M, defined as the number of microliters of nitrogen dioxide required by 10 ml. of absorbing reagent to give an absorbance of 1. For 2-cm. cells the value was 3.65. Then:

P.p.m. of nitrogen dioxide $=$ corrected absorbance $\times M/V$

If the volume of the air sample, V, is a simple multiple of M, calculations are simplified. Thus, for the M value of 3.65 previously cited, if exactly 3.65 liters of air are sampled through a bubbler, the corrected absorbance is also parts per million directly. If other volumes of absorbing reagent are used, V is taken as the volume of air sample per 10 ml. of reagent.

EXPERIMENTAL

Preparation of Known Low Concentrations of Nitrogen Dioxide. The first step in the study was the development of a suitable reagent which would give a high absorption efficiency with continuous sampling, so that the low levels (below 1 p.p.m.) could be determined. These nitrogen dioxide concentrations were prepared in the apparatus shown in Figure 1.

The source of the nitrogen dioxide was a standardized air mixture contained in a 46-liter carboy and available through an all-glass system of 1-mm. bore tubing and ground joints lightly greased with silicone grease. The mixture was made by introducing a few milliliters of nitric oxide, generated in a nitrometer, into the partially evacuated carboy, and flushing it in with air until normal pressure was attained. A few days were allowed for air oxidation of the nitric oxide to nitrogen dioxide and equilibration with the apparatus. The resulting concentration of nitrogen dioxide was 20 p.p.m., which was well within the range of accurate analysis by existing methods, and could be determined by collecting a sample in a 60-ml. evacuated bottle through stopcocks B and C. The composition of the air in the carboy was found to remain remarkably constant. During a period of 4 months it dropped to 15 p.p.m. Most of this loss could be accounted for by the more than 100 portions which were withdrawn, each amounting to about 1/1000th of the contents of the carboy. The vacuum that developed in the carboy was measured and relieved by admitting outside air periodically, through operation of stopcock D, which was ordinarily kept in the closed position.

Known low concentrations of nitrogen dioxide were prepared by accurate dilution of this standardized carboy air mixture in the following manner: A 50-ml. portion was withdrawn into a glass syringe through stopcock A, and then slowly injected into a 1-liter-per-minute air stream by means of a motor-driven slide. A dilution of 1 to 147 was usually used; the value could be varied by moving the belt on the stepped pulleys of the synchronous motor. (The second syringe driven by the same slide, shown in

Figure 1, was used in later tests to inject an interfering gas into the air stream, by similar manipulation of stopcock E.)

The air stream used for dilution of the nitrogen dioxide was taken in through a universal type gas-mask canister; this reduced the normal nitrogen dioxide concentration in the laboratory air, which at times reached 0.1 p.p.m., to considerably less than 0.01 p.p.m. (A U-tube containing Ascarite was found almost equally efficacious.) A mixing chamber was provided for the stream below each point of gas injection. Flow was controlled by a critical orifice in the suction line to an aspirator in the hood, preceded by a trap with a mercury manometer connection.
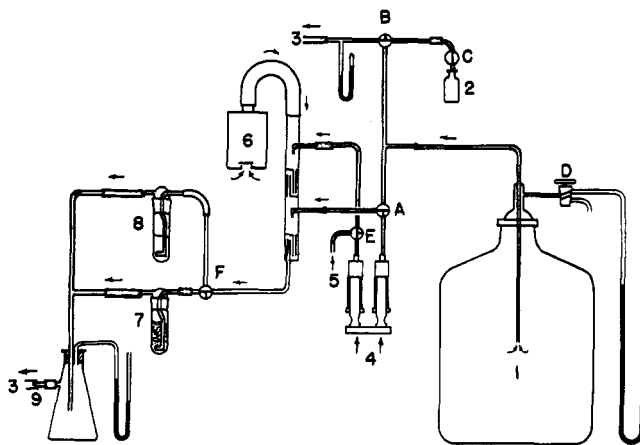

Figure 1. Apparatus for Preparing Known Low Concentrations of Nitrogen Dioxide

1. 46-Liter carboy containing 20 p.p.m. of nitrogen dioxide air mixture
2. 60-Ml. sampling bottle
3. Vacuum connection to aspirator in hood
4. 50-Ml. glass syringes and motor-driven slide
5. Intake for second gas
6. Universal gas mask canister
7. Sampling device
8. Bypass device
9. Critical orifice

Precise measurement of the amount of nitrogen dioxide injected was made by reading a counter on the motor drive. The apparatus was started and flushed with stopcock F in position to divert the air stream through a bypass of the same resistance as the sampling device. At the moment when a predetermined reading was obtained, F was turned to direct the air through the sampler. When the syringe was fully discharged, a limit switch stopped the motor, and F was again turned at that instant to the bypass position again. The volume of carboy air mixture which had passed through the sampling device could be calculated from the difference in counter readings and from micrometer measurements of the syringe plunger diameter.

A modified Shaw scrubber (14) was used as the sampling device for the screening tests of various reagents, although a midget fritted bubbler was later found more efficient. In the Shaw scrubber the air stream entered a lift pump raising absorbing reagent to the top of a column, which had a 40-mm. diameter and was 90 mm. high, packed with glass helices. The sample was absorbed on the wetted surfaces of these helices as the gas and liquid both flowed downward; the air then flowed to the vacuum source while the absorbing liquid drained back to the pump. Twenty milliliters of absorbing reagent were required.

The absorption efficiency that could be obtained in the scrubber at low concentrations of nitrogen dioxide was the critical factor in the tests. This efficiency was calculated as follows:

$$\text{Absorption efficiency} = \frac{A_s R_s V_b}{A_b R_b V_s}$$

where A_s is the absorbance of the color obtained from the scrubber

reagent (corrected for the value obtained in a blank run with no nitrogen dioxide addition), A_b is the absorbance of the color obtained using the same reagent in the evacuated bottle and sampling directly from the carboy (corrected for the blank value of unexposed reagent), R_s and R_b are the volumes of the reagent used in the scrubber and evacuated bottle, and V_s and V_b are the corresponding volumes of carboy air mixture which these colors represent. The colors obtained from the evacuated bottle were known or expected to be true values with the types of reagent tested.

Tests of Various Absorbing Reagents. Only reagents for nitrite were tested because it was expected that they would not only be specific for nitrogen dioxide but also possess the required sensitivity. Studies were made of various combinations of chemicals and their resultant absorption efficiencies, color stabilities and sensitivities, of the optimal methods of color development, of the optimum concentrations and acidities for these chemicals, and of the effect of various metals added as catalysts. Table I presents the data which were obtained. The reagent finally adopted, listed as No. 23, showed the highest efficiency (77%) and excellent color stability and sensitivity, the maximal absorption of the red-violet color being at 550 mμ.

Four combinations of chemicals were tried:

The combination of sulfanilic acid and 1-naphthylamine (Reagents 1 to 6) was finally rejected because of poor color stability and occasional false color production after aeration. Reagent 4 is similar to but somewhat stronger than one previously found by Patty (16) to give 5% efficiency in a midget impinger but successfully used in a 50-ml. glass syringe.

More stable and intense colors were obtained with sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride (Reagents 7 to 17), with an efficiency as high as 64% (Reagent 12). These chemicals were used in powder form with tartaric acid by Jacobs (12) and found to be stored conveniently and satisfactorily used in a 50-ml. glass syringe after dissolving in water.

A higher efficiency was obtained by substituting anthranilic acid for the sulfanilamide (Reagent 18), since this was known to have a very rapid diazotization rate, but poor color intensity and very slow color development were found.

Best results were obtained with the previously unreported combination of sulfanilic acid and N-(1-naphthyl)-ethylenediamine dihydrochloride (Reagents 19 to 32), which was the one finally adopted.

Two methods of color development were investigated.

STEPWISE METHOD, in which sample absorption in the diazotizing reagent is carried out under the optimal strongly acid conditions, after which the pH is increased with a buffer and the coupling reagent is added for optimal color development. The method, which is in accordance with studies of procedures for nitrite (2, 18, 19), was used for Reagents 1 to 3 and 7 to 10 (Table I), as well as in other tests not shown with sulfanilic acid and sulfuric or hydrochloric acid, followed by various buffers and 1-naphthylamine. This method is subject to losses due to decomposition of the unstable diazo intermediate during the intense aeration of sampling.

DIRECT COLOR METHOD, in which the reagent contains all ingredients and after absorption produces the color with no further operations. This method is subject to losses because of side reactions between nitrite and the coupling reagent, and because of not having optimal pH for diazotization and coupling. This method, which was used for the remainder of the reagents listed in Table I, was found to produce more color in the scrubber, even though it produced less with a standard bottle sample or nitrite portion. The direct color type of reagent, containing all ingredients, was therefore adopted because of greater convenience and a higher absorption efficiency.

Optimum concentrations and acidities for each combination of chemicals were determined in order to obtain a true evaluation of their worth. The results in Table I showed that the highest

Table I. Screening Tests for Reagents to Obtain High Absorption Efficiency

No.	Absorbing Reagent[a]	Procedure for Color Development and Remarks[a]	Absorption Efficiency, %[b]	Absorbance Std. air sample[c]	Absorbance Std. nitrite portion[d]
		D = Sulfanilic acid, C = 1-Naphthylamine, 520 mμ			
1	0.01 N NaOH	Add 10% AcOH, 0.05% D, after 20 min. add 0.03% C	30		
2	0.05% D	After 10 min. add 0.03% C	27	0.188	0.142
3	0.05% D, 15% AcOH	After 10 min. add 0.03% C	46		
4	0.05% D, 0.03% C, 14% AcOH	Direct color	52–60	0.183	0.134
5	0.12% D, 0.075% C, 14% AcOH	Direct color	66		
6	0.5% D, 0.03% C, 14% AcOH	Direct color	55		
		D = Sulfanilamide, C = N-(1-naphthyl)-ethylenediamine dihydrochloride, 544 mμ			
7	0.02% D, 1% HCl	After 6 min. add 0.002% C	56	0.199	
8	0.02% D, 10% AcOH	After 15 min. add 0.002% C	40		
9	0.02% D, 10% AcOH, 2.5% H₂SO₄	After 15 min. add 0.002% C. Very slow color development	40		
10	0.5% D, 1% HCl	After 15 min. add 0.002% C	52		
11	0.02% D, 0.002% C, 1% HCl	Direct color	48	0.184	
12	0.5% D, 0.002% C, 1% HCl	Direct color	64	0.329	
13	4.0% D, 0.003% C, 1% HCl, 40% Ethylene glycol	Direct color. Ethylene glycol added to increase solubility of D	...	0.080	
14	4.0% D, 0.004% C, 1% HCl, 10% AcOH, 8% Ethylene glycol	Direct color. Ethylene glycol and AcOH added to increase solubility of D	...	0.195	
15	Same as 12 + 0.0025% Cu(II)	Direct color. Test of catalytic effect	48		
16	Same as 12 + 0.05% Fe(II)	Direct color. Test of catalytic effect	57		
17	0.5% D, 0.002% C, 2.5% H₃PO₄, + 0.05% Fe(II)	Direct color. Test of catalytic effect	62		
		D = Anthranilic acid, C = N-(1-naphthyl)-ethylenediamine dihydrochloride, 560 mμ			
18	0.05% D, 0.002% C, 0.1% HCl	Direct color. Very slow color development	82	0.140	
		D = Sulfanilic acid, C = N-(1-naphthyl)-ethylenediamine dihydrochloride, 550 mμ			
19	0.05% D, 0.002% C, 14% AcOH	Direct color	53		
20	0.5% D, 0.002% C, 5% HCl	Direct color. Slow coupling	...	0.239	
21	0.5% D, 0.002% C, 2% tartaric acid	Direct color	68		
22	0.4% D, 0.025% C, 14% AcOH	Direct color.	65		
23	0.5% D, 0.002% C, 14% AcOH	Direct color. Final reagent	77	0.270	0.191
24	Same as 23 + 0.005% Zn(II)	Direct color. Test of catalytic effect	75		
25	Same as 23 + 0.125% Zn(II)	Direct color. Test of catalytic effect	75		
26	Same as 23 + 0.005% Fe(II)	Direct color. Test of catalytic effect	78		
27	Same as 23 + 0.05% Fe(II)	Direct color. Test of catalytic effect. Unstable colors obtained	71–82	0.294	
28	Same as 23 + 2.5% Fe(II)	Direct color. Test of catalytic effect. Unstable colors obtained	78		
29	Same as 23 + 0.01% Fe(III)	Turbid brown color developed	...		
30	Same as 23 + 0.005% V(V)	No color developed; C destroyed	...		
31	Same as 23 + 0.005% Co(II)	Direct color. Test of catalytic effect	72		
32	Same as 23 + 0.09% As(III)	Direct color. Test of catalytic effect	65		

[a] % refers to final concentration in mixture: w./v. for solids and v./v. for liquids. D = diazotizing reagent. C = coupling reagent for color development. AcOH = glacial acetic acid.
[b] Modified Shaw scrubber used at 1 liter per minute, 0.14 p.p.m. of nitrogen dioxide.
[c] Calculated for a standard sample of 1μl. of nitrogen dioxide (or 50 ml. at 20 p.p.m.) absorbed in 10 ml. of reagent in an evacuated bottle.
[d] Calculated for 1.74 γ of potassium nitrite (would be equivalent to 1 microliter of nitrogen dioxide if 0.5 mole of potassium nitrite were equivalent to 1 mole of nitrogen dioxide) in 10 ml. of reagent.

possible concentration of diazotizing reagent was desirable; not only was the absorption efficiency increased, but even the color obtained in a bottle with a standard air sample (Reagents 11 and 12). Too high a concentration of the coupling reagent, on the other hand, reduced the color produced (Reagents 22 and 23), probably because of increased side reaction directly between this reagent and the nitrite. A high acidity (Reagent 20) greatly slowed the coupling step for the finally adopted combination of chemicals. Acetic acid was best because it provided the best compromise pH and also had surface tension properties which provided a fine froth in the sampling device. Reagent 23, based on these principles, was found to give the highest absorption efficiency.

The effect of various metals added as catalysts was slight (Reagents 15 to 17, 24 to 32). The most effective metal was 0.05% iron(II) (Reagent 27), which improved absorption and color intensity, but was considered undesirable because of color instability which would result if oxidation to the iron(III) form occurred (Reagent 29).

Nitrite Equivalent of Nitrogen Dioxide. Practically, standardization of the reagent is best achieved with standard nitrite solution, rather than with difficultly prepared standard gas samples. The initial presumption was that 0.5 mole of nitrite would be equivalent to 1 mole of nitrogen dioxide, by dissolution in water of the latter to give equal quantities of nitric and nitrous acids (Equation 1 below). The last two columns of Table I, giving the absorbances obtained with 1 μl. of nitrogen dioxide in an air sample, and with the equivalent amount of nitrite on the above basis, showed that this presumption was not correct; dividing the first figure by twice the second gives the actual molar equivalent obtained. The previously mentioned study by Patty (16) found a relationship of 0.57, although a satisfactory explanation of the difference from 0.5 was not presented. In an effort to find the cause of disagreement, a more complete investigation was undertaken of the relationship between the color obtained in an evacuated bottle with a standardized air sample, and the color obtained in solution with standard nitrite reagent.

The effect on the color intensity, which could be produced by varying the concentrations and combinations of the ingredients of the final reagent, is shown in Table II. All solutions gave about the same color intensity with a standard nitrite portion, but the color intensity with a standard air sample varied more widely. Values close to 0.5M equivalence were obtained when the air sample was absorbed in acetic acid alone (Reagent 33) or in a dilute sulfanilic-acetic acid reagent (Reagent 34). A value of 0.51M equivalence was obtained with Reagent 23 (the finally adopted reagent) in another test not shown in which the air sample was increased to 500 μl. (of nitrogen dioxide). In this case the range of the reagent was exceeded and only a weak orange-red color was obtained, but upon dilution 100 times with additional reagent the characteristic color was obtained. However, higher values were obtained with stronger sulfanilic acid (Reagent 35), and

Table II. Influence of Reagent Composition on the Nitrite Equivalent of Nitrogen Dioxide

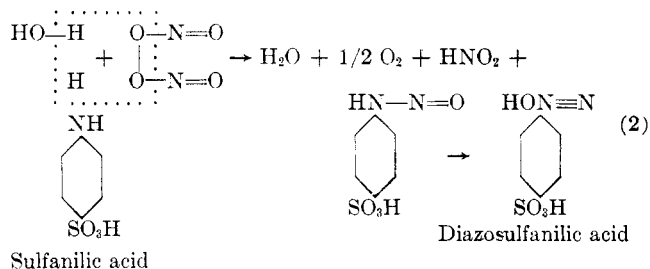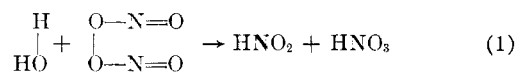| No.	Absorbing Reagent[a]	Procedure for Color Development and Remarks[a]	Absorbance Std. air sample[b]	Absorbance Std. nitrite portion[c]	Moles of Nitrite Equivalent to 1 Mole of NO2[d]
	D = Sulfanilic acid, C = N-(1-naphthyl)-ethylenediamine dihydrochloride, 550 mμ				
33	14% AcOH	Absorb 20 min., add 0.02% D, after 15 min., add 0.002% C	0.183	0.189	0.48
34	0.02% D, 14% AcOH	Absorb 20 min., add 0.002% C	0.196	0.186	0.53
35	0.5% D, 14% AcOH	Absorb 20 min., add 0.002% C	0.250	0.191	0.65
36	0.5% D, 0.002% C	Absorb 20 min. Direct color	0.245	0.170	0.72
23	0.5% D, 0.002% C, 14% AcOH	Absorb 20 min. Direct color. Final reagent	0.276	0.191	0.72
37	0.5% D, 0.002% C, 50% AcOH	Absorb 20 min. Direct color	0.231	0.182	0.64

[a] % refers to final concentration in mixture: w./v. for solids and v./v. for liquids. D = diazotizing reagent. C = coupling reagent for color development. AcOH = glacial acetic acid.
[b] Calculated for a standard sample of 1 μl of nitrogen dioxide (or 50 ml. at 20 p.p.m.) absorbed in 10 ml. of reagent in an evacuated bottle.
[c] Calculated for 1.74 γ of potassium nitrite (would be equivalent to 1 microliter of nitrogen dioxide if 0.5 mole of potassium nitrite were equivalent to 1 mole of nitrogen dioxide) in 10 ml. of reagent.
[d] Obtained by dividing absorbance of standard air sample by twice the absorbance of standard nitrite portion.

Table III. Absorption Efficiency with Various Sampling Devices

Device	Vol. of Reagent, Ml.	Sampling Rate, Liter/Min.	Head Loss, Mm. of Hg	Test P.P.M. of NO2	Absorption Efficiency, %
Standard midget impinger	10	1	1	0.14	32
Standard midget impinger	10	0.5	1	0.3	31
Modified Shaw scrubber used for screening tests; 110 ml. of glass helices	20	1	0.7	0.14	77
Midget impinger with fritted tube end	10	0.5	2	0.28	75-92
Midget bubbler with 8-mm. fritted disk	10	0.4	54	0.3	99
Midget bubbler with 8-mm. fritted disk	10	0.4	36	0.3	94
Midget bubbler with 8-mm. fritted disk	10	0.4	34	0.4	95

these were even higher when the coupling reagent was also present (Reagents 36, 23, and 37).

These results may be explained by hypothesizing that the nitrogen dioxide may react either as in Equation 1, with water alone to produce equimolar quantities of nitrite and nitrate (50% equivalence), or as in Equation 2, directly with sulfanilic acid and water as a peroxide to yield 100% equivalence, and that the presence of high concentrations of sulfanilic acid, as well as of a small amount of coupling reagent, permits the latter reaction to occur with equal frequency. In the formulas presented below, nitrogen dioxide is written as the peroxide form of the dimer, nitrogen tetroxide, to simplify structural relationships:

$$\begin{matrix} H & O\!-\!N\!=\!O \\ | & | \\ HO & O\!-\!N\!=\!O \end{matrix} \rightarrow HNO_2 + HNO_3 \qquad (1)$$

$$\begin{matrix} HO\!-\!H & O\!-\!N\!=\!O \\ + & | \\ H & O\!-\!N\!=\!O \end{matrix} \rightarrow H_2O + 1/2\,O_2 + HNO_2 +$$

$$(2)$$

Sulfanilic acid   Diazosulfanilic acid

In either reaction the nitrous acid formed produces another molecule of diazosulfanilic acid. In Equation 2 either oxygen or hydrogen peroxide may be produced. It was found experimentally that small amounts of hydrogen peroxide did not prevent color development or bleach the color. Equation 2 may also be written to show two molecules of sulfanilic acid combining with the nitrogen tetroxide, with the same end result.

Absorption Efficiency with Various Sampling Devices. After the most suitable reagent had been developed in conjunction with the modified Shaw scrubber, it was found that much better efficiency could be obtained using midget fritted bubblers. The acetic acid content of the reagent made possible a fine and stable foam of 20- to 30-ml. volume above 10 ml. of reagent and

provided a large surface area for good absorption. An upward-facing fritted disk was better than vertical or downward-facing disks because there was less coalescing of bubbles with consequent loss of surface area. In Table III are shown the absorption efficiencies obtained for various sampling devices. The three midget fritted bubblers tested showed 94 to 99% efficiency at 0.3 to 0.4 p.p.m. of nitrogen dioxide. By using two in series if necessary, practically 100% efficiency may be obtained; a test with such arrangement showed the second bubbler recovered 64% of the few hundredths of a part per million which passed the first bubbler. The fritted bubbler with the highest pressure drop also showed the highest efficiency.

Standardization against Known Concentrations of Nitrogen Dioxide. In the work described above, the assumption was made that the final reagent gave true values when used in the evacuated bottle to sample undiluted carboy air mixture, and absorption efficiencies were calculated on the basis of the relative color obtained in this manner as compared to that obtained when sampling diluted carboy air mixture. It remained to demonstrate the accuracy of this presumption by sampling higher concentrations of nitrogen dioxide of known value. Three systems were used to prepare such concentrations in an absolute manner by direct measurement of pure nitrogen dioxide from a tank, and simultaneous samples were collected in evacuated bottles using both the present reagent and the phenoldisulfonic acid method (3).

In the first system a small evacuated pipet was used to measure nitrogen dioxide gas, and the contents were introduced into bottles or carboys. In a typical run in this group, 0.3 ml. of gas was pipetted into a 4.6-liter bottle to give a theoretical concentration of 106 p.p.m. after allowing for the deviation from ideal gas volume. Analysis by the present procedure gave 60.2 and 61.5 p.p.m.; by phenoldisulfonic acid 59.0, 57.9, and 59.0 p.p.m. Thus while good analytical agreement was obtained, half of the nitrogen dioxide appeared to be lost on the glass or stopcocks and the system was unsuccessful in preparing known concentrations. Similar losses previously had been noted when the observed value of 20 p.p.m. in the carboy of Figure 1 was compared with the value expected from the amount of nitric oxide introduced from the nitrometer. The following two systems, however, yielded good agreement between calculated and obtained values.

In the second system, 0.4 gram of liquid nitrogen dioxide was accurately weighed in a sealed glass ampoule, which was then broken in a closed, stainless-steel, cubical chamber which measured 5 feet on edge. An electric fan was used to mix the contents. The theoretical concentration was computed at 66.4 p.p.m. The following results were obtained:

Minutes after breaking	10	20	30	35	90	125	155
P.P.M., present method	66.7	66.6	...	...	62.8	63.1	61.7
P.P.M., phenoldisulfonic acid method	...	...	64.2	65.9	...	...	...

The concentration dropped slowly, but the data indicate that the early samples were substantially identical. This run was used as the absolute standard of the entire investigation. The analyses showed good agreement, although samples of different size were taken.

In the third system known concentrations of nitrogen dioxide were prepared by means of four flowmeters. A special flowmeter was constructed to measure very small tank nitrogen dioxide flows below 10 ml. per minute. The principle of this flowmeter was that the gas was made to flow through a fine fritted-glass filter and a fine capillary tube, and the pressure drop was measured by a manometer containing fluorocarbon liquid; it was calibrated by passing the gas directly into weighing bottles containing Ascarite and noting the gain in weight, manometer readings, the flow time. This flow was injected into a metered air stream, and a portion of the mixture was taken off through an all-glass rotometer into a second metered air stream. The final mixture flowed into a glass jar from which samples could be collected. It was necessary to scrub all the air with dilute dichromate-sulfuric acid to remove impurities such as ammonia which precipitated or consumed nitrogen dioxide.

The results of the analyses of simultaneous samples were as follows:

	P.P.M.			
Flow meter value	8.8	15.1	27.2	40.6
Analysis by present method	8.2	15.5	27.8	42.0
Analysis by phenoldisulfonic acid method	5.3	10.9	20.5	33.4

Good agreement was obtained with the present method even with sample sizes varying from 45 to 250 ml.

The phenoldisulfonic acid procedure was systematically low, as has been reported for similar gas concentrations (16). Previous tests with this procedure had shown that absorption of lower concentrations in large bottles was very slow; although 3 days had been allowed, slightly higher results could be obtained with 1-week absorption. These samples were collected in 2.5-liter acid bottles with 15 ml. of absorbing reagent; in the figures previously quoted for the stainless-steel chamber, 500-ml. bottles were used because of the higher concentrations and 1 day of absorption in the refrigerator was adequate.

The result of these studies was the absolute standardization of the method and the establishment of the validity of the absorption efficiencies which were obtained with the apparatus shown in Figure 1.

EFFECT OF INTERFERING GASES

The effect of various interfering gases was found to be unimportant unless the concentration was much higher than that of the nitrogen dioxide. Because of the possibility of widely varying sample sizes and concentrations, all the results below are expressed in terms of microliters (corrected volume in liters times parts per million) per 10 ml. of absorbing reagent. For comparison, 2 or 3 μl. of nitrogen dioxide are ordinarily required to develop a color of suitable intensity; the normal color was found to fade at the rate of 3 to 4% of absorbance per day.

Ozone. The effect of ozone is complicated by the fact that this gas reacts very rapidly with nitrogen dioxide producing nitrogen pentoxide and oxygen. Calculations made on the basis of published kinetic data (13) indicated that, assuming the nitrogen dioxide concentration was much smaller than that of the ozone, and that the concentration of the latter therefore remained substantially constant as the reaction proceeded, the half life of the nitrogen dioxide was 4.5 minutes divided by the parts per million of ozone. For 1 p.p.m. of ozone the half life would be 4.5 minutes; for 10 p.p.m. it would be 0.45 minute. Thus, for appreciable amounts of ozone the system is actively changing, and evaluation of the interference is difficult.

For test purposes the apparatus shown in Figure 1 was modified so that a stream of ozonized air, from a Westinghouse 794H ultraviolet lamp, could be mixed with the stream containing nitrogen dioxide just in front of the sampling device. The age of the mixture could be varied by adding U-tubes to the train. Ozone was determined by absorption in alkaline iodide and spectrophotometric estimation of iodine liberated on acidification with sulfamic-phosphoric acid. The sulfamic acid destroyed any interfering nitrite which might be present.

Two microliters of ozone caused a slightly orange tint to an otherwise normal color. Eleven microliters caused an increase in the absorbance equivalent to $^1/_{30}$th of that amount of nitrogen dioxide, the maximal effect occurring in 3 hours. Thirty microliters completely destroyed the coupling reagent and also the diazosulfanilic acid. The reagent assumed a yellow-brown tint with an absorbance equivalent to about 2 μl. of nitrogen dioxide.

The most convenient method found for removing ozone was to pass the sample over a specially prepared manganese dioxide catalyst at room temperature. The manganese dioxide completely destroyed the ozone, and no visible interference from 30 μl. occurred. The catalyst, however, was found to accelerate the

oxidation of nitrogen dioxide by the ozone. The correction to the analysis for this effect was roughly computed as +10% for 1 p.p.m. of ozone, +21% for 2 p.p.m., and +60% for 5 p.p.m.; the log of the correction factor was proportional to the concentration of ozone. This method was very convenient and satisfactory for less than 2 or 3 p.p.m. of ozone; at higher values the correction became high and uncertain.

Ordinary, reagent-grade manganese dioxide was found unsatisfactory for this use because of its appreciable absorption of nitrogen dioxide. After attempting to purify various batches, success was attained in the following manner: A plug of glass wool, cleaned with dichromate cleaning solution and washed, was moistened with manganese(II) nitrate solution and dried in an oven at 200° C. for 1 hour. The final plug used was 1 cm. in diameter and 1.5 cm. long and required about 0.5 ml. of 75% manganese(II) nitrate hexahydrate. Manganese dioxide was produced as the salt decomposed with loss of nitrogen dioxide. The plug was placed in a U-tube and air was drawn through for an hour to sweep out the nitrogen dioxide and reduce the blank to about 0.01 p.p.m.; an even lower value may be obtained by electrically heating the tube at temperatures up to 200° C. during this aeration. Better than 99% of 0.3 p.p.m. of nitrogen dioxide passed through unabsorbed. After long use the catalyst becomes exhausted and requires replacement.

Sulfur Dioxide. Tests with this gas were made using the twin syringe of the apparatus shown in Figure 1. Sulfur dioxide alone produced no color with the reagent. Extremely large amounts slowly bleached the color formed with nitrogen dioxide. Thus, 20 μl. of sulfur dioxide produced no effect; 90 μl. reduced the recovery 4% and required the color to be read within 45 minutes, the fading after 18 hours being 16%; 900 μl. reduced the recovery by 11%, and all color was lost after 17 hours. Numerous materials were tried as color stabilizers. It was found that the addition of 1% acetone to the reagent before use greatly retarded the fading by forming a temporary addition product with sulfur dioxide. With 90 μl. of sulfur dioxide, good results could be obtained by reading the color within 4 to 5 hours, instead of the 45 minutes required without the acetone. Tests were also made with water solutions of sodium bisulfite equivalent to 125 μl. of sulfur dioxide. Color loss in 2 hours was 64% without acetone, and 15% with 1% acetone.

Numerous experiments were made using a U-tube containing chromium trioxide on glass wool, as previously recommended (23), to destroy the sulfur dioxide. It was found that 30 p.p.m. of this gas was completely removed so that perfectly stable colors were obtained. The moisture content was found to be rather critical. When the chromium trioxide was visibly wet (after sampling air of high humidity) only 70% of 0.3 p.p.m. nitrogen dioxide was passed; when it was dried again 96% was passed. However, a completely dry tube did not remove the sulfur dioxide. The losses of nitrogen dioxide appeared to be related more to the moisture content than to the amount of reduced chromium, since good performance was obtained from a tube which contained 20% of the chromium in reduced form. A number of experiments were made using desiccants to control the humidity. It was found that the best desiccants also removed the nitrogen dioxide; for 0.3 p.p.m. at 0.3 liter per minute the losses were: magnesium perchlorate, 93%, Drierite, 80%; calcium chloride dihydrate, 24%; granular anhydrous calcium chloride, 20%, and phosphorus pentoxide, 10%.

In summary, no interference from sulfur dioxide occurred from amounts up to 10 times that of nitrogen dioxide; interference from larger amounts may be reduced by using acetone if the color can be read without great delay, or a chromium trioxide U-tube. The moisture content of the latter must be kept between visibly wet and bone dry. The use of desiccants in the train is not permissible.

Other Nitrogen Oxides. The interference from other nitrogen oxides is negligible.

The evaluation of the interference of nitric oxide, NO, is complicated by the fact that this compound is slowly converted by air to nitrogen dioxide. However it has been studied in the absence of air in the gas industry (20), using sulfanilic acid and 1-naphthylamine, and found not to produce any color unless converted to nitrogen dioxide by a special oxidizing scrubber. Since the present reagent produces a color by a similar reaction, it may safely be said that this gas does not interfere.

Equilibrium calculations show that nitrous acid anhydride, N_2O_3, and nitrogen tetroxide, N_2O_4, do not exist at concentrations of 100 p.p.m. and below. Kinetic data show that their dissociation is practically instantaneous. Hence these nitrogen oxides may be disregarded.

Nitrogen pentoxide is rarely found, because it is readily hydrated to nitric acid vapor, and is also an unstable compound which is very sensitive to heat; the half life is 6 hours at 25° C., 86 minutes at 35° C., and only 5 seconds at 100° C. The decomposition products are nitrogen dioxide and oxygen. This compound was prepared by mixing a stream of nitrogen dioxide with ozone in 0.5 p.p.m. excess using the flowmeter apparatus previously referred to. The stream contained 25 p.p.m. of nitrogen pentoxide (equivalent to 50 p.p.m. as nitrogen dioxide), and gave a test for about 5 p.p.m. of nitrogen dioxide. It is likely that this was due to impurity or decomposition of the nitrogen pentoxide.

Nitric acid does not interfere with the determination. When added in solution to the reagent it produced no color, nor did it affect the development of color with nitrite solution or nitrogen dioxide gas. In the form of vapor, a 5000-p.p.m. sample collected in an evacuated bottle gave a test for only 23 p.p.m. of nitrogen dioxide. The sample was prepared by allowing a small amount of concentrated nitric acid to stand in a closed bottle, with the addition of a crystal of sulfamic acid to destroy nitrous acid impurities. The small interference found may actually be nitrogen dioxide produced by decomposition in spite of this precaution.

Other Interfering Gases. A number of other gases were investigated by adding them in the form of water solution to a reagent solution which contained a color equivalent to about 2 μl. of nitrogen dioxide. The amount added was equivalent to 125 μl. of interfering material. Hydrogen sulfide produced no effect. Chlorine partially bleached the color instantly, causing a 45% loss and changing the tint to orange; the final color remained perfectly stable. Hydrogen peroxide increased the color slightly (+4% in 2 hours); after 3 days the color had increased 16% and had a slightly different tint with less violet than the normal color. Formaldehyde produced no appreciable effect in 2 hours; in 3 days a 15% greater than normal color loss occurred with production of an orange-yellow tint. In the presence of 1% acetone (used for sulfur dioxide) the interferences of all these materials was the same, except for that of formaldehyde, which still did not interfere within 2 hours, but caused almost complete loss of color in 3 days.

LITERATURE CITED

(1) Averell, P. R., Hart, W. F., Woodbury, N. T., and Bradley, W. R., ANAL. CHEM., **19**, 1040 (1947).
(2) Barnes, H., and Folkard, A. R., *Analyst*, **76**, 599 (1951).
(3) Beatty, R. L., Berger, L. B., and Schrenk, H. H., U. S. Bur. Mines, *Rept. Invest.* **3687** (1943).
(4) Blacet, F. E., *Ind. Eng. Chem.*, **44**, 1339 (1952).
(5) Brasted, R. C., ANAL. CHEM., **23**, 980 (1951).
(6) Cholak, J., and McNary, R., *J. Ind. Hyg. Toxicol.*, **25**, 354 (1943).
(7) Edgar, J. L., and Paneth, F. A., *J. Chem. Soc.*, **1941**, 511, 519.
(8) Elkins, H. B., *J. Ind. Hyg. Toxicol.*, **28**, 37 (1946).

(9) Gray, E. LeB., MacNamee, J. K., and Goldberg, S. B., *Arch. Ind. Hyg. and Occupational Med.*, **6**, 20 (1952).

(10) Haagen-Smit, A. J., *Ind. Eng. Chem.*, **44**, 1342 (1952).

(11) Holler, A. C., and Huch, R. V., ANAL. CHEM., **21**, 1385 (1949).

(12) Jacobs, M. B., "The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents," 2nd ed., p. 358, New York, Interscience Publishers, 1949.

(13) Johnston, H. S., and Yost, D. M., *J. Chem. Phys.*, **17**, 386 (1949).

(14) Kieselbach, R., IND. ENG. CHEM., ANAL. ED., **16**, 766 (1944).

(15) LaTowsky, L. W., et al., *J. Ind. Hyg. Toxicol.*, **23**, 129–47 (1941).

(16) Patty, F. A., and Petty, G. M., *Ibid.*, **25**, 361 (1943).

(17) Reindollar, W. F., IND. ENG. CHEM., ANAL. ED., **12**, 325 (1940).

(18) Rider, B. F., with Mellon, M. G., *Ibid.*, **18**, 96 (1946).

(19) Shinn, M. B., *Ibid.*, **13**, 33 (1941).

(20) Shnidman, L., and Yeaw, J. S., *Am. Gas Assoc. Proc.*, **24** (1942), 277.

(21) Stanford Research Institute, "Third Interim Report on the Smog Problem in Los Angeles County," 1950.

(22) U. S. Public Health Service, *Public Health Bull.*, No. **272**, 1941.

(23) Usher, F. L., and Rao, B. S., *J. Chem. Soc.*, **111**, 799 (1917).

(24) Wade, H. A., Elkins, H. B., and Ruotolo, B. P. W., *Arch. Ind. Hyg. and Occupational Med.*, **1**, 81 (1950).

(25) Yagoda, H., and Goldman, F. H., *J. Ind. Hyg. Toxicol.*, **25**, 440 (1943).

Extension of Isotopic Method for Determining Oxygen in Metals To Copper Containing 0.01 to 0.1 Weight % of Oxygen

A. D. KIRSHENBAUM and A. V. GROSSE

Research Institute of Temple University, Philadelphia, Pa.

The isotopic method, originally developed for the determination of oxygen in organic compounds and fluorocarbons and recently applied to metals and metal-oxygen alloys in the oxygen range of 0.2 to 30 weight %, has now been extended to the oxygen range of 0.01 to 0.1 weight % in copper samples. Although the method, making use of oxygen-18, does not require quantitative separation or recovery of the oxygen, it gives accurate results rapidly. The only requirement of this method is that all of the oxygen atoms in the system be exchanged at the temperatures and under the conditions used.

IN THE past the oxygen content of metals has been determined directly by several different methods—the vacuum-fusion (*1*, *14–17*, *19*, *20*, *22*), carbon reduction (*12*, *18*), hydrogen reduction (*2*, *21*), and chemical methods (*3–5*, *13*), and indirectly by difference (*13*). The vacuum-fusion and hydrogen reduction are at present the most popular methods for the analysis of copper samples. Both methods, however, require quantitative removal and recovery of all the oxygen in the metal. The "isotopic method" (*6–8*, *11*), applied recently to metals and metal oxides (*9*, *10*), does not incorporate this difficulty because quantitative removal and recovery of the oxygen are not necessary.

APPARATUS

The apparatus consists essentially of a 6-kw. converter and high-frequency induction furnace, and a vacuum system for separating and sampling gases.

High-Frequency Induction Furnace. The furnace used is an Ajax-Northrup 6-kw. converter-type high-frequency induction furnace manufactured by the Ajax Electrothermic Corp., Trenton, N. J.

Glass Vacuum System. The apparatus as shown in Figure 1 consisted essentially of a vertical platinum or molybdenum reaction vessel and a borosilicate glass vacuum system. The reaction vessel consisted of a platinum test tube, *H*, 32 mm. in outside diameter, 30 cm. long, with a wall thickness of 0.4 mm., centered in an evacuated quartz tube, *E*, 64 mm. in outside diameter, and 32 cm. long, and sealed with de Khotinsky cement to a brass water-cooled head, *B*, 5 cm. long. The platinum tube was cooled by means of a 7.5-cm. long water jacket, *C*, 2.5 cm. below the de Khotinsky seal outside the induction furnace, *F*. The brass head was sealed with de Khotinsky cement to a borosilicate glass three-way vacuum stopcock which in turn was connected to a Toepler pump, *J*, 3 mm. in outside diameter sampling tubes, *K*, and the vacuum system. An optically clear sight-glass window, *A*, was sealed to the top of the brass water-cooled head for temperature readings. A metal hook on which a crucible, *I*, and a platinum reflector, *D*, were hung, was centered in the head. The crucible was hung by means of molybdenum

wire 0.23 mm. in diameter, *G*, into the platinum tube centered in the induction furnace, *F*, 10 cm. long, 64 mm. in internal diameter, with the platinum reflector 0.07 mm. thick centered 1.3 cm. outside the furnace. The crucibles can be made out of graphite, hydrogen-reduced molybdenum or platinum, the latter two being preferred. The graphite crucibles 1.6 cm. in outside diameter, 3 cm. long with a wall thickness of 0.4 to 0.5 cm., weighing 1.5 to 1.8 grams, were made from Dixon E-821 grade graphite rods. They had an oxygen content of 0.0853% by weight. The hydrogen-reduced molybdenum and platinum crucibles had a wall thickness of 0.1 mm., weighed 1.5 to 2 grams, and had an oxygen content of 0.0001%.

EXPERIMENTAL PROCEDURE

In determining the oxygen content of the copper samples, a known weight of the copper to be analyzed (8 to 10 grams) was mixed with a known weight (about 100 mg.), of oxygen-18 labeled
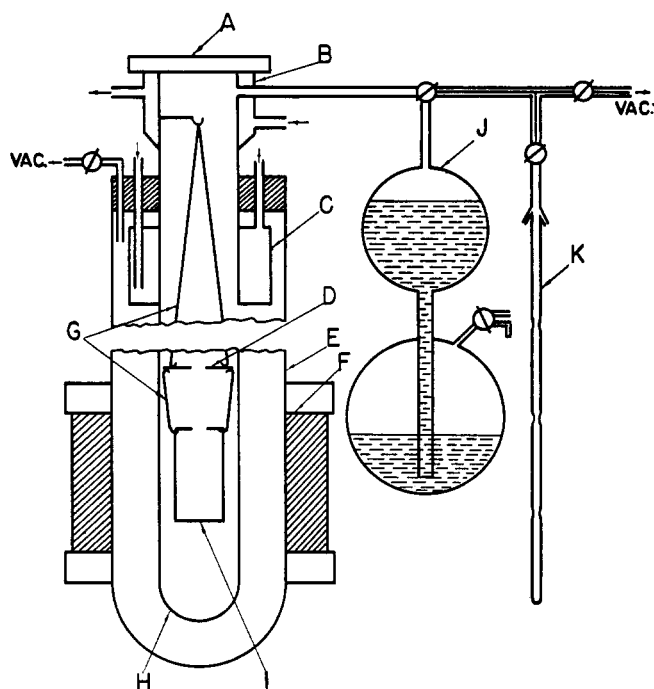

Figure 1. Glass Vacuum System

A. Sight glass	**E.** Quartz tube	**I.** Graphite crucible
B. Water-cooled head	**F.** Induction furnace	**J.** Toepler pump
C. Water jacket	**G.** Molybdenum wire	**K.** 3-mm. sampling
D. Platinum reflector	**H.** Platinum tube	tubes