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A MANOMETRIC METHOD FOR THE
DETERMINATION OF OXYGEN
IN ORGANIC COMPOUNDS

Livermore, California

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A MANOMETRIC METHOD FOR THE DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS

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A vacuum analytical method for the determination of oxygen in organic compounds has been developed. Several milligrams (usually 3 to 5 mg) of the organic to be analyzed are sealed in an evacuated quartz bomb along with 2.5 to 3.5 mg of an organic reducing agent. Next the bomb is fired at 1050-1055°C for 30 minutes or longer. At the end of the heating period the bomb temperature is rapidly lowered from 1055°C to < 650°C. As a last step the gaseous products are removed from the bomb and the volumes of CO and H₂ are determined. From these values the percentage of oxygen can be calculated providing an appropriate blank is obtained. Compounds containing carbon, hydrogen, nitrogen, sulfur, iodine, and chlorine have been successfully analyzed for oxygen. Organic compounds containing fluorine cannot be analyzed for oxygen by this method, because fluorine reacts with quartz to form oxygen and silicon tetrafluoride.

Apparatus and Reagents

The apparatus is a simple Pyrex and quartz vacuum system as shown schematically in Fig. 1. The three-stage mercury diffusion pumps¹ are designed to operate against a back pressure of 1 to 2 cm of Hg. This feature allows them to be used for the circulation of gases at low pressures as well as for transfer pumps.

Palladium tubes² are standard pieces of equipment used to remove hydrogen by diffusion. Commercial tubes* were modified as shown in Fig. 2. This modification is not a necessity. However, it reduces the time required to remove hydrogen from any given sample. For the work reported here the Pd tubes were maintained at 410 to 430°C.

* Jeps, Inc., 680 Main St., Waltham, Mass.

Fig. 1. Vacuum apparatus for the determination of CO and H₂.

- (A) Three-stage Hg diffusion pumps
- (B) Palladium tubes operated at ~420°C for the removal of hydrogen
- (C) Hydrogen reservoirs, 2 and 3 liters capacity
- (D) Transfer line
- (E) Quartz tube containing reduced copper turnings at 900°C
- (F) CO reservoir
- (G) 77°K U-trap containing a glass wool plug
- (H) Trap containing from top to bottom magnesium perchlorate, Hopcalite, Ascarite, magnesium perchlorate
- (I) Bomb holder
- (J) 200-cc reservoir
- (K) Gas buret
- (M) Connections to the main vacuum manifold
- (N) Connections to sources of pressure and vacuum
- (P) Toepler pump
- (Q) Thermocouple gauge

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Fig. 2. Modified palladium leak.

- (A) Quartz tubing to support the heater and also serve as an insulator
- (B) Heater windings
- (C) Palladium tubing
- (D) Quartz adaptor
- (E) Thermocouple

The hydrogen volume is measured by a thermocouple gauge (Q) and any desired combination of the reservoirs (C). The unit is calibrated by admitting hydrogen until a desired reading is obtained on the thermocouple gauge. By means of line (D) the hydrogen can then be removed for measurement in the gas buret. Both of the three-stage diffusion pumps should be operating during the calibration.

The copper-loaded quartz furnace (E) is for the reduction of carbonyl sulfide to carbon monoxide. It is packed with reduced copper turnings and outgassed at 900°C. A final reduction is done in situ at 900°C by admitting CO from a reservoir at (F).

Trap (G) is held at -196°C for the condensation of all gaseous compounds obtained from the bomb reduction except CO, CH₄, H₂, and N₂. A glass wool plug is placed in the trap to reduce the mass transfer of condensible compounds.

Unit (H) is used for the removal of CO. The packing consists of four layers, which are from top to bottom magnesium perchlorate, Hopcalite*, Ascarite,** and magnesium perchlorate. Hopcalite oxidizes carbon monoxide to carbon dioxide which is then absorbed on Ascarite. After the unit is packed and in place, it is activated by heating at 180-200°C for 18 hours with pumping.

A reducing organic compound must be included in the bomb along with the sample. Such a compound is necessary to insure an excess of carbon and thereby obtain a uniform and reproducible attack on the quartz bomb. It also insures the complete reduction of the sample. The reducing compound should contain no oxygen. It also should provide a relatively large percentage of carbon when thermally decomposed in vacuum. For this work phenyl thiourea was used. Although it is an acceptable reducing compound it is not ideal in that a considerable amount of COS is formed due to the presence of sulfur. For routine analyses its presence unnecessarily expends the copper furnace (E). It was used in this work to demonstrate the versatility of the analytical method.

* Purchased from Mine Safety Appliances Co., Pittsburgh, Pa.

** Purchased from Arthur H. Thomas Co., Philadelphia, Pa.

The quartz bombs used for sample reduction are identical to those used for the simultaneous determination of carbon, hydrogen, and nitrogen.³⁻⁵ They are about 12 mm in diameter by 20 cm long and of standard wall thickness. The body of the bomb minus the drawn tip is 12 to 13.5 cm long after sealing. The only preliminary treatment given the quartz bombs is air firing at about 1000°C for 1 hour.

Procedure

The compound to be analyzed is weighed directly into the quartz bomb along with the reducing agent. Sample sizes of 3 to 5 mg are adequate for compounds containing 14% or more oxygen by weight. Blank variations are of such a magnitude that slightly larger samples are required when very accurate results are desired for compounds which contain < 14% by weight oxygen. The alternative is to make at least duplicate determinations. For this work 2.5 to 3.5 mg of phenyl thiourea was used with each sample and blank.

After the sample and reducing agent are weighed into the bomb, the bomb is connected via heavy-walled gum rubber tubing to a standard vacuum joint such as an 18/9 ball. Next the bomb is constricted by heating and pulling until a long thin (~ 1 × 80 mm) capillary is formed. After this assembly is attached to a vacuum line and evacuated to $< 10^{-4}$ torr the bomb is sealed.

Reduction is obtained by heating the bomb at 1050-1055°C for approximately 1/2 hour or longer as desired. At the completion of the heating period the furnace is adjusted to 1055°C and the bombs are removed one at a time and rapidly cooled to < 650°C. The furnace must be allowed to recover to 1055°C before each successive bomb is removed.

Upon completion of the reduction step the quartz bomb is loaded into the breaker unit (I) and the system is evacuated. Next the bomb tip is broken and the reduction products (CO, COS, H₂O, CO₂, H₂, N₂, HCN, CS₂, CH₄, etc.) are pumped from the bomb through the 900°C copper turnings (E) and the -196°C trap (G). The noncondensable fraction (CO, H₂, N₂, and CH₄) is collected by pump (A₁) in the Pd tubes (B) and the 200-cc reservoir (J).

Hydrogen is then removed and collected for measurement by circulating the noncondensable fraction through the 410-430°C Pd tubes (B). After the hydrogen is removed, the residual gases (CO, N₂, and CH₄) are transferred

to the gas buret (K) and measured. Next these gases are circulated through (H) where the CO is oxidized and quantitatively absorbed. As a last step the residual N_2 and CH_4 are collected and measured in the gas buret. The difference of these last two measurements is the CO formed during reduction.

In order to obtain the best oxygen determination, it is necessary to run one or two blanks with each set of samples. These blanks consist of quartz bombs containing 2.5 to 3.5 mg of the reducing agent. The CO found from such a blank is due mainly to reduction of the quartz bomb and adsorbed water on the inside quartz surface. Therefore, the results obtained are normalized to the geometric surface area of the inside of the bomb. This procedure was used for obtaining all the data in Table I. Duplicate blanks were run for every set except the 30-min reduced p-chlorobenzoic acid samples, for which only one blank was available due to an accident.

Discussion

The total oxygen of the sample is determined from the amount of CO found minus the normalized blank plus the oxygen present in H_2O and CO_2 as calculated from thermodynamic data. It is necessary to calculate the amounts of CO_2 and H_2O present because these are removed in trap (G) along with all other compounds condensable at $-196^\circ C$.

When work was first begun on developing this method, it was thought that a hydrogen determination and subsequent calculation of the water concentration could be circumvented by the diffusion of hydrogen out of the quartz bomb during reduction. To facilitate the diffusion all reductions were carried out for 24 hours at $1050-1055^\circ C$. Such a procedure requires no additional analyst's time and only a small expenditure of electricity. Determinations obtained from such a procedure were generally good. However, there was a definite bias toward low results. Although most of the hydrogen (60-75%) was diffused from the bomb, that remaining could not be ignored. Therefore, to obtain a hydrogen determination with a minimum of work, the apparatus described above was designed and constructed.

In order to be able to calculate the amount of H_2O and CO_2 present in the bomb at the end of the heating period, equilibriums (1) and (2) below must

be frozen at a known temperature. For this reason the furnace is adjusted to 1055°C and the bombs are removed one at a time. A satisfactory method

Table I. Oxygen determination data for a reduction temperature of 1050-1055°C.

Sample	Heating period, hours	Weight, mg	Oxygen found, wt %	Deviation, %
Anisic acid, 31.55 wt % O ₂	24	3.109	31.82	+0.27
		2.781	31.58	+0.03
		3.235	31.51	-0.04
			31.64 av	
O-iodobenzoic acid, 12.90 wt % O ₂	24	5.839	12.63	-0.17
		6.406	12.87	-0.03
		6.217	12.82	-0.08
			12.77 av	
Cystine, 26.63 wt % O ₂	24	3.031	26.66	+0.03
		3.448	26.87	+0.24
		3.018	26.82	+0.19
			26.78 av	
P-chlorobenzoic acid, 20.44 wt % O ₂	24	4.188	20.13	-0.31
		3.892	20.53	+0.09
		5.066	20.46	+0.02
			20.37 av	
Cystine, 26.63 wt % O ₂	1/2	3.266	26.68	+0.05
		3.050	26.81	+0.18
		2.878	26.67	+0.04
			26.72 av	
P-chlorobenzoic acid, 20.44 wt % O ₂	1/2	3.828	20.46	+0.02
		4.052	20.31	-0.13
		3.453	20.12	-0.32
		4.056	20.80	+0.36
			20.42 av	

of quenching these reactions is to roll the hot bombs on a piece of asbestos board maintained at ambient temperature. By this method about 8 sec is required to remove a bomb from the furnace and reduce the temperature to $< 650^{\circ}\text{C}$. The data in Table I were obtained from bombs cooled by this method.

If the bombs are allowed to cool slowly, the equilibrium is shifted to some unknown point depending upon the diffusion-controlled nature of the system being examined. That is, the final H_2O and CO_2 concentrations will depend upon the rate of cooling, gas pressure, gas composition, and surface-to-volume ratio of the bomb.

The equilibrium constants K_1 and K_2 ,

$$K_1 = \frac{[\text{CO}]^2}{\text{CO}_2}, \quad (3)$$

$$K_2 = \frac{[\text{CO}][\text{H}_2]}{\text{H}_2\text{O}}, \quad (4)$$

are easily determined from free energy values by means of the equation

$$RT \ln K = -\Delta F. \quad (5)$$

Free energy values⁶ give K_1 and K_2 values of 262 and 141, respectively, at 1055°C . A shift in temperature of 25°C to 1030°C results in a change of these values to 196 and 112, respectively. It can thus be readily seen that a rapid decrease in temperature is necessary in order to quench reactions (1) and (2).

Results

Oxygen results are presented in Table I for a series of four compounds and two reduction periods.

Upon completion of the new apparatus 24-hour reductions were continued as a standard procedure. Although such long reductions result in increased blank corrections, the correction due to the presence of H_2O is lower. The first section of Table I lists the results obtained for a series of determinations using this procedure (i. e., 24 hours at 1050°C). The results of 30-minute reductions are also included in Table I to illustrate the versatility of the determination.

All determinations were made using sets of three samples and two blanks, with the exception of p-chlorobenzoic acid for the 30-minute heating period. For this set four samples and two blanks were analyzed. Although the duplicate blanks were generally in good agreement for any one set, there was considerable variation from set to set. This variation in blanks from one firing to the next was prevalent throughout the development of this procedure. For this reason blanks must be run with every firing. Since only 20 to 25 minutes are required for a carbon monoxide and hydrogen determination, the necessity of frequent blanks is a minor inconvenience.

A specific example will best illustrate the difference in the blank, H_2O , and CO_2 corrections involved for the two different heating periods described above. The system investigated was 3 mg of cystine and about 3 mg of phenyl thiourea confined in 8-cc quartz bombs at $1055^\circ C$. Typical blanks for the 1/2-hour and 24-hour reductions were 0.0225 cc and 0.0450 cc carbon monoxide, respectively. The difference between these carbon monoxide values corresponds to 16 μg of oxygen or about 0.53 wt % of the sample.

For a 1/2-hour reduction about 2.5 cc of hydrogen remains in the bomb as compared to only about 0.65 cc if a 24-hour reduction is used. This difference in hydrogen concentration results in the formation of water corresponding to about 0.21 wt % oxygen.

A shift in the equilibrium temperature from the $1055^\circ C$ used for determining the CO_2 and H_2O concentrations is also serious. If the bomb cools slowly and the apparent "quench" temperature is $1030^\circ C$ instead of $1055^\circ C$, the CO_2 and H_2O concentrations as calculated will result in an oxygen value that is about 0.12 wt % high.

The magnitudes of the correction differences as described only point out that good techniques are as essential in vacuum analytical chemistry as in solution and gravimetric analytical chemistry. The simplicity of an oxygen determination by this method, coupled with its accuracy, makes it a reasonable method for routine determinations.

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