

## Determination of Oxygen in Silver-Copper and Gold-Silver-Copper Alloys by Hydrogen Reduction

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A simple apparatus for determination of oxygen in silver and gold is described. The method is based upon the determination of the water formed by reduction of the oxide in the sample with hydrogen gas. In a 1 g sample oxygen contents from 0.0001 to 0.1 % can be determined within 30 min. The apparatus has been used at the Central Institute for Industrial Research, Blindern, Norway, for more than a year with excellent results.

Oxygen in metals is usually determined by the vacuum-fusion method. Since silver is volatile at the temperatures required in this method and because of the cost of such elaborate systems, a more simple method would be desirable. In certain non-ferrous metals, oxygen can be determined by a method based upon reduction with hydrogen. In this method the sample is heated in hydrogen, which reacts with any oxygen present in the sample to form water. The water-vapour formed is either absorbed and weighed<sup>1,2</sup> or condensed in a trap and subsequently vaporized in an otherwise evacuated system<sup>3-7</sup>. The determination of oxide in the sample has also been performed by measuring the hydrogen gas consumed in the above reaction<sup>8</sup>.

In the present work samples containing only a few ppm of oxygen were to be analysed, and an extremely accurate apparatus had to be constructed. The present communication describes an apparatus based upon hydrogen reduction, by which as little as 1 ppm of oxygen can be determined within 30 min. The apparatus is somewhat similar in construction to those by Baker<sup>6</sup> and Nitsche<sup>7</sup>. It is modified in several respects, however, in order to increase the accuracy and speed of the analysis.

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## DESCRIPTION OF APPARATUS

A schematic diagram of the apparatus is shown in Fig. 1. Hydrogen is taken from a cylinder and purified by passing through a Deoxo catalytic purifier (Baker platinum division, London) (A in Fig. 1) in which oxygen is reduced to water. It is then dried in a 800 ml flask (C) containing phosphorus pentoxide. 800 ml of hydrogen is sufficient for one day's analyses and this amount can be dried completely overnight in the flask. A mercury valve (B) between the Deoxo purifier and the reservoir prevents air from entering the apparatus during the filling of the reservoir.

The combustion unit consists of a clear silica tube (D) with a B 19 male joint in one end. The joint fits to a female joint in the apparatus and is held securely in place by a spring clamp. The quartz tube (14 mm bore and an overall length of 40 cm) is heated by means of a small furnace, consisting of a Mullite tube wound with 0.9 mm Kanthal A-1 wire (E).

The temperature was controlled by means of a Variac and measured with a chromel-alumel thermocouple (F) placed in the constricted end of the Mullite tube. By appropriate adjustment of the Variac, any desired temperature between 20 and 1 000°C could be obtained in less than 5 min. The silica

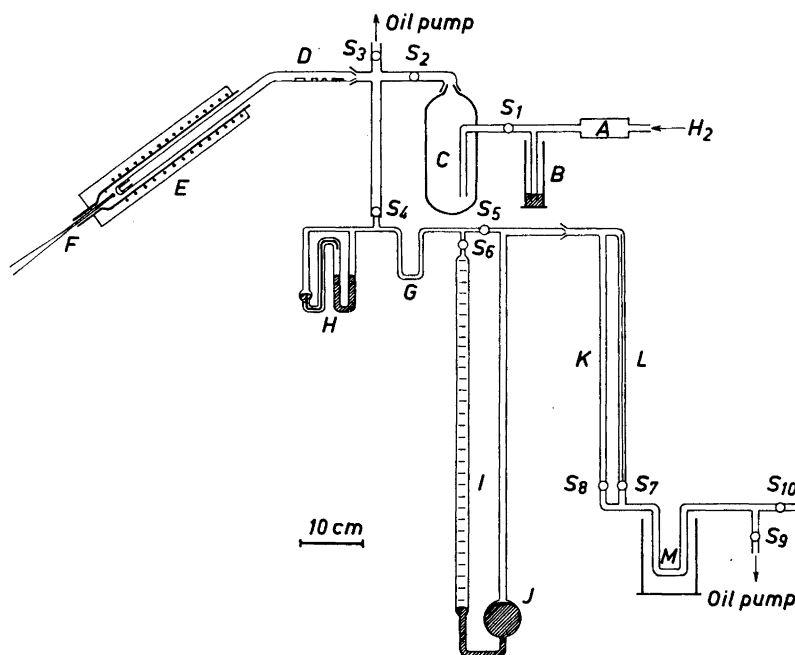


Fig. 1. Schematic diagram of apparatus for determination of oxygen in metals by hydrogen reduction. A Deoxo catalytic purifier, B mercury valve, C 800 ml flask containing phosphorus pentoxide, D combustion tube, E furnace, F thermocouple, G water trap, H mercury manometer, I 100 ml buret, J mercury reservoir, K 8 mm bore tube, L 0.5 mm bore tube, M water trap,  $S_1$ – $S_{10}$  stopcocks.

tube was bent at an angle in order to reduce heat radiation to the joint. The specimens to be analysed were placed in the horizontal part of the combustion tube, in front of a small magnet. The lower end of the tube contained a crucible of sintered alumina.

A U-formed tube (G) with 4 mm bore served as a water trap. It was cooled by a mixture of solid carbon dioxide and acetone. The trap was sealed to a small mercury manometer (H) and a buret (I). The manometer consisted of a 1 mm capillary sealed to 8 mm bore tubes. The capillary and the attached U-tube of the manometer was filled with redistilled mercury. When evacuated, the mercury stem in the upper part of the capillary is broken, and the pressure is recorded as the difference in height of the mercury columns in the U-tube. The buret had a capacity of 100 ml and was graduated into 0.2 ml. The lower end of the buret communicated with a mercury reservoir (J) with a capacity of approximately 120 ml.

The pump train consisted of two 40 cm long tubes (K and L) with 8 mm and 0.5 mm bore, respectively. Between the tubes and the oil pump was placed a U-formed trap immersed in solid carbon dioxide/acetone mixture. The purpose of this trap was to prevent moisture from the air to enter the apparatus, and also to prevent mercury vapour from diffusing to the oil pump, which is connected at  $S_9$ .

The entire apparatus, with exception of the combustion tube, was made of Pyrex glass. The stopcocks  $S_2$ ,  $S_3$ , and  $S_4$  were of the hollow plug type with 4 to 5 mm hole through the plug. The rest of the stopcocks had an oblique bore of 4–5 mm through a compact plug. Stopcocks and glass joints were lubricated with a silicone base lubricant. The apparatus could be maintained at a vacuum of 0.01 mm Hg for several days.]

#### PROCEDURE

The specimens to be analysed were cleaned by filing with a clean file, or scraping with a sharp knife in order to remove surface oxide, and then degreased by means of benzene. The samples were then placed in the horizontal part of the combustion tube. Powdered samples were wrapped in a tin foil of known oxygen content.

The apparatus is evacuated through  $S_9$  by a Hyvac oil pump, capable of exhausting the system to 0.01 mm Hg.  $S_9$  is then closed and pure hydrogen admitted to the system through  $S_2$ . The apparatus is evacuated once more, and pure hydrogen again admitted until the pressure is 40–60 mm Hg, as indicated by the mercury manometer. A thermos bottle containing the cooling mixture is added to the water trap (G) and the furnace pushed over the inclined part of the combustion tube. After heating the sample at 900°C for 20 min tap  $S_7$  is opened, and excess hydrogen is slowly removed through the capillary by pumping. After 5 min,  $S_8$  is opened, and the system is evacuated for a few more minutes. Stopcocks  $S_4$ ,  $S_5$ , and  $S_6$  are then closed, the cooling mixture removed from the trap and the water vapour allowed to vaporize. The pressure of the water vapour is recorded on the manometer, using a low power microscope or a cathetometer.

Normally a blank run shows less than 0.2 mm Hg. If the blank exceeds this value, the whole procedure is repeated until successive blanks agree to within 0.1 mm Hg. The water vapour is removed through the pump train.

Hydrogen is again admitted to a pressure of 40–70 mm Hg, the cooling mixture added to the trap, and one of the specimens is pushed into the hot zone of the combustion tube by means of the magnet. After heating for 20 minutes, excess hydrogen is slowly pumped out through the capillary. 5 minutes afterwards tap  $S_8$  is opened and the apparatus exhausted for a few more minutes. Stopcocks  $S_5$ ,  $S_7$ ,  $S_8$ , and  $S_9$  are then closed, and  $S_{10}$  opened. Stopcock  $S_7$  is then opened slowly, letting air through the capillary, and forcing the mercury in the reservoir to fill the buret. The last trances of hydrogen are then pumped out through  $S_3$ . Stopcocks  $S_3$ ,  $S_4$ , and  $S_7$  are closed, the cooling mixture removed and the water allowed to vaporize. The pressure and temperature of the vapour are recorded.

Since water vapour at room temperature deviates appreciably from ideal gas behaviour for pressures exceeding 10 mm Hg, useful vapour pressures are confined to lower values. Whenever a vapour pressure above or near 10 mm Hg is recorded, the air pressure in the mercury reservoir is reduced by opening  $S_9$  and  $S_7$  of the pump train. The mercury in the buret falls correspondingly, thus increasing the volume of the water vapour. By appropriate adjustment of the pressure in the pump train, any desired volume of the water vapour at its corresponding pressure can be obtained.

Before proceeding with the next sample, the apparatus is exhausted and a new blank determined. If the blank is unchanged compared to the previous check, this indicates that the last specimen has been completely reduced and that no leaks in the apparatus have occurred.

#### CALIBRATIONS AND CALCULATIONS

The total volume enclosed by stopcocks  $S_4$ ,  $S_5$ ,  $S_6$  (*i.e.* water trap, manometer and associated tubings) was calibrated by introducing small volumes of air and recording their pressures at a number of different readings of the buret. The apparatus was also calibrated by reducing known amounts of lead oxide following the above procedure. Both methods gave concordant results, *i.e.* 14.2 ml. The buret had a capacity of 100 ml and, consequently, the volume in which the water vaporizes could be adjusted to any desired value between 14.2 and 114 ml.

If the total volume of the water vapour is  $V$  ml, the pressure recorded on the manometer  $P$  mm Hg and the room temperature  $t^\circ\text{C}$ , the weight  $W_0$  of the water formed by the reduction can be calculated from the equation:

$$W_0 = \frac{P}{760} \cdot \frac{V}{1 + \gamma t} \cdot \frac{18.016}{22414} \text{ g H}_2\text{O}$$

The corresponding weight of oxygen ( $W$ ) in the sample is:

$$W = 9.39 \times 10^{-7} \times \frac{P \cdot V}{1 + \gamma t} \text{ g O}_2$$

By means of a cathetometer the water vapour pressure can be measured to  $\pm 0.1$  mm Hg. From the above equation it is evident that a pressure of 0.1 mm Hg in a volume of 14.2 ml corresponds to 0.00128 mg oxygen, which is the smallest amount of oxygen that can be detected with the apparatus described. The volume in which the water vaporizes can be increased to a maximum value of 114 ml. A water vapour pressure of 10 mm Hg in this volume corresponds to 0.996 mg oxygen. By using a sample weighing 1 g and adjusting the volume appropriately, the apparatus will cover the entire range from 0.00013 to 0.1 % of oxygen. The determination of oxygen contents lower than 0.00013 % might be performed by increasing the sample weight, or by decreasing the volume of the water trap and associated tubings.

The blank was found to be independent of the initial hydrogen pressure, indicating that the hydrogen gas was completely dry and oxygen-free. At furnace temperatures below 850°C, the blank usually showed  $1 \times 10^{-6}$  g oxygen. At temperatures above 850°C, however, the blank increased with increasing temperature and time of heating. This is probably due to diffusion of oxygen from the atmosphere through the hot zone of the quartz tube. Consequently, the diameter of the tube was chosen as small as possible and the same temperature and time of reaction were employed in both the blank and analysis.

In order to speed up the reduction of the oxides, the specimens were heated to a temperature slightly above the melting point. Metals with high melting

Table 1. Determination of oxygen in lead and copper.

Oxide taken mg	Oxygen equivalent mg	Reaction temperature °C	Reaction time min	Oxygen found mg	Error %
<i>Lead oxide</i>					
9.95	0.713	650	5	0.642	- 10.0
9.90	0.710	700	10	0.660	- 7.0
9.75	0.698	700	10	0.654	- 6.3
12.30	0.882	700	15	0.845	- 4.2
9.40	0.674	650	20	0.674	0
9.65	0.692	650	25	0.698	+ 0.9
12.75	0.914	650	30	0.901	- 1.4
9.22	0.661	650	20	0.646	- 2.3
4.45	0.319	650	20	0.320	0
8.36	0.599	650	20	0.606	+ 1.1
<i>Cupric oxide</i>					
3.15	0.634	900	10	0.600	- 5.4
3.56	0.716	980	10	0.681	- 4.9
2.45	0.493	980	20	0.494	+ 0.2
3.69	0.742	950	25	0.742	0
3.31	0.666	950	30	0.654	- 1.8
2.25	0.453	900	20	0.452	- 0.2
3.79	0.762	950	20	0.747	- 2.0
3.12	0.628	950	20	0.638	+ 1.6

The samples were wrapped in tinfoil of known oxygen content. All values are corrected for the blank.

Table 2. Oxygen contents of silver-copper and gold-silver-copper alloys

Sample	Weight, g	Oxygen found mg	Oxygen found %
83 % Ag, 17 % Cu	2.0320	0.105	0.0051
	2.3930	0.129	0.0054
	1.4582	0.072	0.0049
	1.0212	0.053	0.0052
	3.0520	0.156	0.0051
			Mean 0.00514 ± 0.00024 %
92.5 % Ag 7.5 % Cu	3.8205	0.078	0.0020
	4.0502	0.087	0.0021
	2.4350	0.049	0.0020
	4.5900	0.105	0.0023
			Mean 0.0021 ± 0.0002 %
83 % Ag, 17 % Cu (Vacuum melted)	3.0880	0.0012	0.00004
	2.8605	0.0012	0.00004
58.4 % Au 20.8 % Ag 20.8 % Cu	1.0219	0.015	0.0015
	2.3500	0.033	0.0014
	1.4350	0.023	0.0016
			Mean 0.0015 ± 0.0001 %
58.5 % Au 16.6 % Cu 24.9 % Ag	1.7650	0.015	0.0009
	1.3700	0.012	0.0009
	3.8450	0.031	0.0008
			Mean 0.0009 ± 0.0001 %

points (copper for instance) were added to a previously deoxidized melt of tin. In this way the reduction temperature could be kept below 900°C, thus taking advantage of a low blank value. Surface oxides in copper and copper-silver alloys are fairly rapidly reduced even at a temperature of about 400°C. This is important when analysing samples having a very rough surface, as the surface oxide could be removed by heating in a hydrogen atmosphere at 400°C prior to the determination of oxygen in the bulk of the sample. According to Baker <sup>6</sup>, cleaning with oxidising acids should be avoided as they are liable to leave an oxygen film on the surface.

## RESULTS

To test the accuracy and precision of the method, samples of lead oxide (Analar C.P. product of yellow PbO) and cupric oxide (Merck C.P. product of CuO) were analysed by the procedure outlined above. The reduction temperatures were 650 and 950°C for the lead and copper samples, respectively. From the results in Table 1 it appears that only 90 % of the oxygen content is extracted during the first 5 min. A heating time of 20 min, however, was found sufficient for a quantitative reduction of oxygen in the samples. This is in contrast with the results by Nitsche <sup>7</sup> who claims that heating for 5 min at 900°C is sufficient for quantitative reduction of oxygen in copper.

A series of determinations oxygen in silver-copper and gold-copper-silver alloys were then performed. As shown in Table 2, the oxygen content found in different samples of the same alloy, showed a deviation of  $\pm 2$  ppm from the mean value. Considering the small samples and a non-uniform distribution of oxygen in the metal, the results must be considered satisfactory.

The apparatus described is obviously applicable to all metals in which the oxide is reduced by hydrogen below 1 000°C. Volatile constituents in the samples will vaporize and condense in the cool part of the combustion tube. Metallic mirrors of silver and lead were observed, but apparently they did not influence the results of analysis. This was verified by adding samples of known oxygen content to the melt. As stated by Baker<sup>6</sup> errors due to volatile constituents, as zinc for instance, may be minimised by using a large bath of tin in the combustion tube. Metallic mirrors may sometimes be of analytical interest. Thus, even minute amounts of cadmium in gold was detected as a black deposit well separated from those of less volatile constituents as for instance silver.

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