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Direct Determination of Oxygen in Organic Compounds

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The method for direct oxygen analysis as described by Schütze, Zimmerman and Unterzaucher has been modified. The Körbl catalyst was employed to remove some interfering gases and to oxidize carbon monoxide to carbon dioxide. The described method has been successful for the determination of oxygen in compounds which, in addition to carbon, hydrogen and oxygen contain nitrogen, halogens or sulphur.

With various types of organic samples the determinations showed a standard deviation of 0.13%. The time required for the analysis is thirty minutes if a series of analyses is being made in succession. The oxidation tube needs repacking after 150—200 analyses.

INTRODUCTION

Several comprehensive reviews on the determination of oxygen in organic compounds have been published. The most noteworthy method is that described by Schütze[1], Zimmerman[2], and Unterzaucher[3] based on thermal decomposition of the sample in a stream of nitrogen and on conversion of all oxygen containing products to carbon monoxide by reaction with specially prepared heated carbon.

Hitherto there have been numerous modifications of the original method, relating to apparatus, carrier gas, the prepurification system for carrier gas, combustion tube filling, retention of interfering products and determination of the final reaction product.

Belcher, Davies, and West[4] examined some of these modifications. They recommended pyrolysis in a stream of nitrogen over platinized carbon heated at 900°, reduced copper and soda asbestos for retention of interfering gases, the conversion of carbon monoxide to carbon dioxide with Schütze reagent at room temperature and gravimetric measurements of carbon dioxide.

Besides the conventional oxidation catalyst employed by Schütze, anhydroiodic acid, copper oxide[5-7] and red mercury(II) oxide[8] have also been used for the oxidation of carbon monoxide. Pella[9] tried to apply Körbl catalyst. According to the author the catalyst, with argon as carrier gas, led to exaggerated blank values, because of the high oxidising power.

More or less all known methods suffer from some deficiency and therefore a more accurate method for direct oxygen determination is still needed.

A modification of the direct method for the oxygen determination is described in this paper. The decomposition product of silver permanganate is used to remove some interfering gases and to oxidize carbon monoxide to carbon dioxide. The results obtained were satisfactory and no difficulties were encountered in the preparation. The Körbl catalyst slowly releases oxygen and survives 150—200 determinations. In the compounds analysed, with exception of those containing sulphur this oxidant does not lead to any difficulties in determining the blank value. It was shown that the blank value varied with different pyrolysis tubes and increased as the tube ages. No attempt was made to analyse samples of low oxygen content, since we were not able to obtain a zero blank value.

EXPERIMENTAL

Reagents

Nitrogen. Purified nitrogen obtained from »Dalmacija« Dugi Rat.

Reduced copper in wire form 4—5 mm long for elementary analysis. The product was reduced by a stream of hydrogen in a column heated to 290°.

BTS catalyst, obtained from Badische Anilin und Soda Fabrik A. G., Ludwigshafen. It was ground in a mortar and granules of 3—5 mm size were reduced with hydrogen in a column heated to 120°.

Carbon, »Gasruss CK 3« was treated with hot hydrochloric acid (1 : 1) for two hours, washed thoroughly with redistilled water, dried, filled into a quartz tube and then heated for 12 hours at approximately 1000° in a stream of hydrogen.

Decomposition product of silver permanganate according to Körbl[10].

Silver wool, *p. a.*

Ascarite, *p. a.*

Anhydrone, *p. a.*

Platinized quartz wool, *p. a.*

Quartz wool, *p. a.*

Quartz chips, *p. a.* (washed with hydrofluoric acid)

Sulphuric acid, *p. a.*

If not otherwise stated, all reagents were obtained from W. C. Heraeus GMBH.

Apparatus

The apparatus consisted (Fig. 1) of a nitrogen supply *1*, a nitrogen purification system *3—17*, a »Standard« W. C. Heraeus automatic micro-apparatus for the C, H, N, and O determination *19, 20* with pyrolysis tube *18*, an oxidation tube *22* with a small electric heater *23*, and the absorption tubes for interfering gases *21*, water *23* and carbon dioxide *25*. For the analysis of sulphur containing samples a small electric furnace with a copper scrubbing tube is placed between the pyrolysis tube and the absorber for the removal of acid products.

Purification of Nitrogen. — Nitrogen should be free from oxygen and oxygen containing compounds. Traces of oxygen are removed by passing a stream of nitrogen over reduced copper in wire form (heated to 500°) and over the BTS catalyst (at room temperature). Traces of water are removed by anhydrone, phosporus pentoxide and sulphuric acid.

Filling of the Pyrolysis Tube. — A new pure quartz tube, treated with 40% hydrofluoric acid (Fig. 2) is filled starting at the capillary end, with a 30-mm silver wool layer, 20-mm quartz chips, 15-mm silver wool, 20-mm quartz chips, quartz wool plug, 150-mm specially prepared carbon, and 30-mm platinized quartz wool. Curve I (Fig. 2) shows the distribution of temperature in the main heater. It is evident that only about 70 mm of the carbon packing is maintained at 1120°.

Filling of the Oxidation Tube. — The oxidation tube (⌀ 10 mm), is filled, starting at the capillary end, with a 10-mm silver wool layer, 70-mm Körbl catalyst and a 15-mm silver wool layer. The catalyst layer is heated to 450—500° by a small electric heater. The oxidation tube needs repacking after 150—200 analyses.

Copper Scrubbing Tube[6]. — A quartz tube, approximately the same size as the oxidation tube, is packed with a 100-mm layer of copper wire. Small plugs of quartz wool are added to hold the copper in place. The reduced copper layer is heated to 900° by a small furnace.

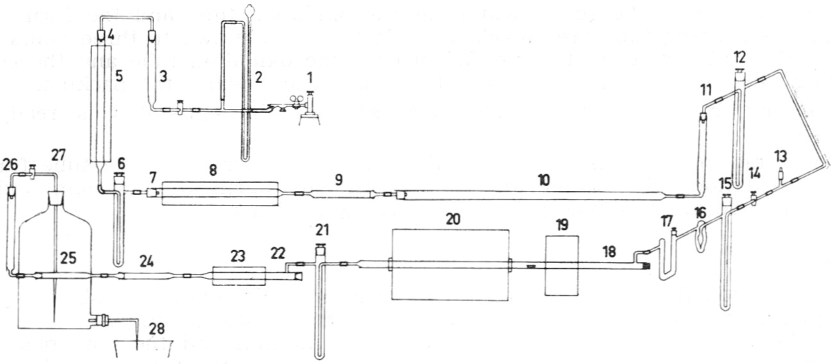

Fig. 1. Apparatus for the determination of oxygen.
1 Nitrogen supply; *2* Manometer; *3, 6, 9, 11, 24, 26* Absorbers filled with anhydrone; *4, 7*, Columns filled with reduced copper (∅ 10 mm layer 200 mm); *5, 8* Heaters; *10* Column filled with BTS catalyst (∅ 10 mm, layer 300); *12, 21, 25* Absorbers filled with ascarite and anhydrone; *13, 14* stopcocks; *15* Absorber filled with phosphorus pentoxide; *16* Bubbler-counter filled with concentrated suphuric acid and connected to a *17* U tube containing ascarite and anhydrone*; *18* Pyrolysis tube; *19* Movable electric burner; *20* Main electric furnace; *22* Oxidation tube with *23a* small furnace; *27* Mariotte flask.

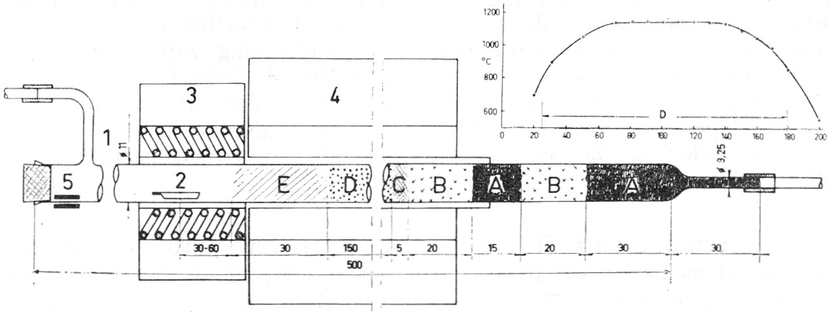

Fig. 2. Assembled pyrolysis tube.
1 Pyrolysis tube; *2* Platinum boat; *3* Movable electric burner; *4* Main electric furnace; *A* Silver wool; *B* Quartz chips; *C* Quartz wool; *D* Carbon; *E* Platinized quartz wool; *I* Distribution of temperature in the main electric furnace.

Absorbers. — The interfering compounds in effluent gases are absorbed in a small gas washing bottle filled with ascarite and anhydrone which is placed between the pyrolysis tube and the oxidation tube.

Water and carbon dioxide absorption tubes (Heraeus design) are filled with anhydrone and ascarite, respectively. The carbon dioxide absorption tube is filled also with an anhydrone layer at the exit end.

A small guard tube containing anhydrone followed by the bubble counter or a Mariotte flask is always attached at the end of the apparatus.

Starting the Apparatus

When the apparatus is set up as shown in Fig. 1 the nitrogen supply is opened and the heaters for the columns packed with copper wire are switched on. Nitrogen is passed at a rate of 10 ml/min through the purification system with stopcock 14 closed and stopcock 13 open. After about one hour the main electric furnace is switched on and the nitrogen is allowed to pass through the whole apparatus (the carbon dioxide absorption tube was not attached at that time). The main furnace is maintained at 1120° and the apparatus is left to stand at least twenty four hours.

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* Nitrogen purification system can be simplified by using nitrogen of better purity.

In the next step the small heater for the oxidation tube and the furnace for the copper scrubbing tube are switched on. It takes about two to three hours until the oxidation tube is ready for use. When once the oxidation tube and the copper scrubbing tube are used it takes only fifteen minutes to warm the packing.

After pyrolysis of several unweighed samples the apparatus is ready for analysis.

When the apparatus is out of use the reduced copper scrubbing tube furnace and the oxidation tube heater are turned off. The purification system and the combustion tube are continually kept at working conditions.

Procedure

The nitrogen flow rate is increased to 20 ml/min, the pyrolysis tube is opened and a platinum boat with 3—5 mg sample is inserted into the tube. The pyrolysis tube is closed, the nitrogen flow decreased to 10 ml/min and the boat pushed to approximately 3—5 cm from the packing. An iron rod in the tube is used to push the boat with a magnet to the desired position. The pyrolysis tube was sweeped out for next five minutes. The same effect, as with reverse flushing, was obtained by increasing the flow rate of nitrogen and by pushing the boat with a magnet rod. The weighed carbon dioxide absorption tube is then attached and the sample is pyrolysed slowly with a movable electric burner. Thermal decomposition and conversion of all oxygen containing compounds to carbon monoxide requires twenty minutes. At this stage the movable electric heater is switched off and nitrogen is allowed to sweep out the effluent gases for another ten minutes. The carbon dioxide absorption tube is then removed, wiped and weighed immediately.

Combustion and final sweeping require careful timing with a stopwatch, or 200 ml + 100 ml water should be removed from the Mariotte flask.

Daily, a blank test is run and the blank value is taken into account.

When the apparatus is left to stand for more than one hour an unweighed sample is run prior to the analysis to reestablish operation conditions in the apprаratus.

RESULTS

Numerous samples with different constituents were pyrolysed and oxygen was determined as described in the preceeding chapter. A series of analyses of test samples is shown in Table I. Standard deviation for oxygen is 0.13%. The results are given in Table II.

As seen from the results obtained, the described method, using the decomposition product of silver permanganate as the oxidation catalyst, has proved to be successful in the determination of oxygen in compounds which in addition to carbon, hydrogen and oxygen contain nitrogen, halogens or sulphur.

DISCUSSION

When organic compounds containing carbon, hydrogen, nitrogen, and oxygen are pyrolysed in a stream of nitrogen over heated carbon it is generally assumed that carbon monoxyde, hydrogen, nitrogen and hydrogen cyanide are present in the effluent gases. Oxygen or oxygen containing products with the exception of carbon monoxide are present only when the carbon packing is inactive or when the sample is pyrolysed too fast and the reduction is not completed.

The effluent gases are allowed to pass through the gaswashing bottle filled with ascarite and anhydrone in order to remove completely acidic products. Hydrogen and carbon monoxide are then oxidized by Körbl catalyst and water and carbon dioxide are absorbed by anhydrone and ascarite, respectively.

TABLE I

The Determination of Oxygen

Sample	Sample weight, mg	O %		
		Theory	Found	Error
Sucrose	4.825	51.42	51.44	+ 0.02
$C_{12}H_{22}O_{11}$	3.339		51.60	+ 0.18
	2.267		51.38	— 0.04
Benzoic acid	4.506	26.20	25.90	— 0.30
C_6H_5COOH	3.801		26.39	— 0.19
	3.751		26.26	+ 0.06
	2.408		26.30	+ 0.10
8-Hydroxyquinoline	7.083	11.05	11.17	+ 0.12
C_9H_7NO	4.928		11.01	— 0.04
	5.522		11.18	+ 0.13
Isatin	3.429	21.75	21.91	+ 0.16
$C_6H_4NHCOCO$	4.376		21.80	+ 0.05
	3.690		21.78	+ 0.08
2,4-Dinitrophenylhydrazine	3.909	32.30	32.29	— 0.01
$(NO_2)_2C_6H_3NHNH_2$	4.376		32.26	— 0.04
	2.546		32.32	+ 0.02
p-Chlorobenzoic acid	6.226	20.43	20.21	— 0.22
ClC_6H_4COOH	3.204		20.33	— 0.10
	2.988		20.44	+ 0.01
p-Bromobenzoic acid	3.417	15.92	15.81	— 0.11
BrC_6H_4COOH	2.896		15.98	+ 0.06
	4.675		15.96	+ 0.04
Sulphanilic acid	4.810	27.71	27.90	+ 0.21
$NH_2C_6H_4SO_3H$	3.245		27.69	— 0.02
	4.450		27.87	+ 0.16
Sulphamic acid	6.482	49.43	49.37	— 0.06
NH_2SO_3H	3.580		49.64	+ 0.21
	4.396		49.51	+ 0.08

The analyses were run without the copper scrubbing tube in the order as they appear in the Table.

TABLE II

The Standard Deviation

Sample	Number of Results	Standard Deviation O %
Sucrose	< 10	0.12
Benzoic acid	15	0.16
Isatin	9	0.11
Sulphanilic acid	15	0.13
Sulphonal	6	0.15
Sulphamic acid	10	0.12
Overall standard deviation		0.13

The analyses were run with the copper scrubbing tube.

The absorbed carbon dioxide is weighed and the percent of oxygen is calculated as follows:

$$\% \text{ oxygen} = \frac{[(CO_2)_s - (CO_2)_b] \times 36.36}{\text{weight of sample}}$$

where $(CO_2)_s$ = weight increase of the carbon dioxide absorption tube for sample, $(CO_2)_b$ = weight increase of carbon dioxide absorption tube for blank. The blank determination was carried out using the described procedure but omitting the sample. The correction values fall within 0.100 — 0.250 mg CO_2 but were consistent within several days. By the calibration method, which involves analyses of standard test samples, the same blank values were obtained.

The blank could have been caused by oxygen in the carrier gas, by reaction between carbon and the quartz tube, or by oxygen retained by carbon packing.

In order to eliminate the blank value as much as possible we modified the nitrogen purification system. In addition hydrogen was applied to flush oxygen from the carbon mass and to condition rapidly the carbon packing. To minimize the reaction between the quartz tube and the carbon packing the combustion tube was washed, prior to filling, with hydrofluoric acid. However, with all this precautions we did not succeed in substantially reducing the blank value.

When sulphur containing organic compounds are pyrolysed, sulphur appears mainly as hydrogen sulphide but if there is not enough hydrogen, carbonyl sulphide and carbon disulphide are formed. The ascarite filling absorbs hydrogen sulphide whereas carbonyl sulphide and carbon disulphide appear in the effluent gases and are oxidized by Körbl catalyst to carbon dioxide. Sulphur is retained on silver. Therefore, the presence of carbon disulphide is the source of a positive error.

After several analyses of sulphur containing compounds an increase in the blank values was observed. Therefore, a blank was run after each fifth analysis. The mean error for oxygen in sulphonal was ± 0.26% after about 40 pyrolyses of various sulphur containing compounds. The blank was 0.365 mg CO_2. After several further analyses the blank values started to become inconsistent and excessively high. To lower the blank value the pyrolysis tube was continuously heated and swept with nitrogen during seven days. However, the high value was only slightly reduced.

In order to ensure better results for S-containing samples the copper scrubbing tube maintained at 900^0 was placed between the pyrolysis tube and the absorber for the acid products.

The results obtained for oxygen in sulphur containing test samples, where interfering carbon disulphide is retained on copper are given in Table II.

Besides the difficulties in the case of S-containing compounds the modification of the method has proved to be satisfactory for the determination of oxygen in many different types of material. Using the decomposition product of silver permanganate no interferences encountered with other methods of oxidation of carbon monoxide have been found.

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IZVOD

Direktno određivanje oksigena u organskim spojevima

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Modificirana je metoda za direktno određivanje oksigena koju su opisali Schütze, Zimmerman i Unterzaucher. Za uklanjanje nekih plinova, koji smetaju kod određivanja oksigena i za oksidaciju karbon-monoksida, primijenjeni su raspadni produkti argentum-permanganata. Opisana metoda može se uspješno primjeniti za određivanje oksigena u spojevima koji uz karbon, hidrogen i oksigen sadrže nitrogen, halogenide i sulfur.

Za različite organske spojeve standardna devijacija određivanja jest 0,13%.

Određivanje oksigena u seriji analiza traje pola sata. Punjenje cijevi za oksidaciju potrebno je mijenjati nakon 150—200 analiza.

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ZAGREB

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