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Chemical Research and Development Laboratories

Technical Report

CRDLR 3160

**Methods of Microanalysis, VIb
Oxygen Determination; Evaluation of the Magnesium
Nitride Method for Fluorine-Containing Compounds**

by

Stewart S. Cruikshank

February 1963



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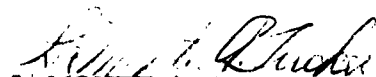
**METHODS OF MICROANALYSIS, VIb
OXYGEN DETERMINATION; EVALUATION OF THE MAGNESIUM
NITRIDE METHOD FOR FLUORINE-CONTAINING COMPOUNDS**

by

Stewart S. Cruikshank

Chemical Research Division

Recommending Approval:


LaMONTE A. TUCKER
Colonel, CmlC
Director of Weapons Systems

Approved:



S. D. SILVER
Scientific Director

**U. S. Army Chemical-Biological-Radiological Agency
CHEMICAL RESEARCH AND DEVELOPMENT LABORATORIES
Edgewood Arsenal, Maryland**

FOREWORD

The work covered in this report commenced on 21 March 1957 and the experimental part was completed on 1 May 1961 under Task 4C08-03-016-08, Analytical Chemical Research (U). The experimental data are in notebooks DO-3; DO-7; and Fluorocarbon C&H - serial designations A and B.

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DIGEST

The work leading to this report is part of a research program designed to result in improved microanalytical methods. $\downarrow$ Fluorine causes the most serious interference with oxygen determination of all the elements encountered. Inserting ~~magnesium nitride~~ ^{Mg_3N_2} in the pyrolysis tube to eliminate this interference has been recommended, and there are many references to this method in the literature.

^{Mg_3N_2} It was found necessary to modify the method given for preparing ~~magnesium nitride~~ to obtain any appreciable yield.

^{Mg_3N_2} ~~Magnesium nitride~~ when applied as recommended or with modifications does not reduce appreciably the ~~fluorine~~ interference in direct oxygen determinations.

Further experiments with magnesium nitride are believed useless and are not planned.

^{Pt} The ~~platinum~~ pyrolysis tube method devised ~~here~~ will be further developed as a means of determining oxygen in fluorine-containing compounds. $\uparrow$

CONTENTS

	<u>Page</u>
I. INTRODUCTION.	5
II. EXPERIMENTAL	6
A. Equipment, Materials, and Operation	6
B. Quartz Tube Coated With Carbon.	7
C. Magnesium Nitride Method	9
III. DISCUSSION	13
IV. CONCLUSIONS	16
LITERATURE CITED	17

METHODS OF MICROANALYSIS, VIb
OXYGEN DETERMINATION; EVALUATION OF THE MAGNESIUM
NITRIDE METHOD FOR FLUORINE-CONTAINING COMPOUNDS

I. INTRODUCTION.

Originally, oxygen present in organic compounds was determined by difference; that is, by subtracting the sum of the percentages found of all the other elements from 100%. Obviously, this is not very accurate or dependable since the sum of the errors in the other determinations is added to the oxygen value. Amounts under 1% oxygen could hardly be attempted. Sometimes another element was present which was not known and, therefore, no analysis was made for it. The percentage of the unrecognized element would be included in the oxygen value. In some instances, such as certain purification and surveillance experiments, the exact amount of oxygen present is of far more interest than the amounts of other elements present.

A hydrogenation type of direct oxygen determination was devised by ter Meulen¹ in 1934 and improved by Linder and Wirth² in 1937. This hydrogenation method has never been widely used, even though many people tried to improve it, because the results tend to be low and several common elements interfere.

The pyrolysis and conversion of all oxygen present to carbon monoxide was reported by Unterzaucher³ in 1940. In this method, the fragments of the organic molecule are led through carbon at $1,120^{\circ} \pm 5^{\circ}\text{C}$, and all of the oxygen is converted to carbon monoxide. A greater variation in the operating temperature gives a high blank. Unterzaucher reported his blank determination to be undetectable.

The Unterzaucher method was investigated and discussed by Aluisse, Alber, Conway, Harris, Jones, and Smith⁴ in 1951. They recommend the method, with close control of temperature, but believe some blank is inevitable under ordinary operating conditions.

There are not very many elements which interfere with this pyrolysis method. Fluorine reacts with the quartz tube and gives high results, sulfur gives slightly high results, and phosphorus usually causes low results. Aluminum and alkaline earth metals retain oxygen as metallic oxides and alkali metals show this interference to only a small extent. Hydrogen in large amounts can interfere slightly.

Numerous modifications have been reported, such as diffusing out hydrogen liberated by pyrolysis, reacting the carbon monoxide with palladium sulfate for colorimetric determinations,^{5, 6} absorbing and weighing carbon dioxide or iodine, using platinized carbon filling, and others. None of these modifications, however, is an attempt to correct for fluorine interference.

An alternate method which is under consideration in this laboratory is the use of an all-platinum pyrolysis tube. This will eliminate all undesired oxygen from the reaction zone, even that in a relatively inert form, and thus should eliminate interference by fluorine.

II. EXPERIMENTAL.

A. Equipment, Materials, and Operation.

The train is that of the Arthur H. Thomas Co., with the modified furnace and controls described in a previous report.⁷

Benzoic acid - National Bureau of Standards

Acetanilide - National Bureau of Standards

p-Fluorobenzoic acid - British Drug House

Trifluoroacetanilide - British Drug House

m-Trifluoromethylbenzoic acid - British Drug House

Perfluorodibutyl ether - purified in this laboratory by repeated distillations

$(CF_3)_2CHCHFOC_3H_7$ - research compound, judged pure by carbon and hydrogen analysis

Teflon - commercial plastic, judged pure by carbon and hydrogen analysis

Platinum, ribbon form, approximately 0.032 by 0.001 in. - made to our order by Baker Platinum Division of Englehard Industries, Inc.

Platinum foil, approximately 0.001 in. thick

Magnesium metal, ribbon, lot 102,044 - J. T. Baker Chemical Co.

Silver metal, fine ribbon form - Arthur H. Thomas Co.

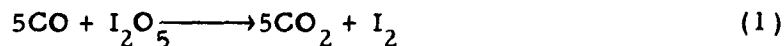
Boats, various, made of porcelain and of platinum, were tried to make magnesium nitride

Tubing, used to make magnesium nitride - Vycor

Furnace, used only to make magnesium nitride - Sargent Catalog no. 49090

In the Unterzaucher³ direct oxygen determination as used here, a sample containing about 1 mg of oxygen is weighed and then placed in the pyrolysis tube (see figure 1) with the reverse flow of helium or nitrogen passing over it. After the tube is swept free of air, the flow is changed to forward, and the cylinder burner is advanced. The sample pyrolyzes or vaporizes and passes through the carbon layer which is kept at $1,120^{\circ} \pm 5^{\circ}\text{C}$.⁷

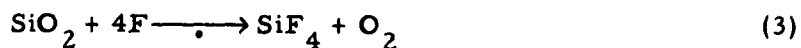
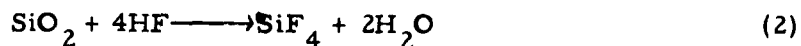
All oxygen originally present in various forms is converted to carbon monoxide by this treatment. The gases then pass through sulfuric acid and Ascarite to remove interfering pyrolysis products. The carbon monoxide then reacts with iodine pentoxide at 110°C , releasing iodine:



The iodine is absorbed in a solution of bromine and potassium acetate in acetic acid. When the solution is diluted with water, the iodine is converted to iodic acid. Formic acid is added to consume excess bromine and, after standing, potassium iodide is added to release iodine. The solution is then titrated with 0.02 N sodium thiosulfate. The results obtained with pure standards and research compounds are excellent.

B. Quartz Tube Coated With Carbon.

It is obvious that if pyrolysis of fluorine-containing compounds releases hydrogen fluoride, or fluorine when no hydrogen is available, oxygen in the silica tube will be replaced and released:



High oxygen results have been noted by a number of investigators.^{3, 4, 8, 9} Further data are given here to show that two atoms of fluorine in an organic compound give results nearly equivalent to one atom of oxygen. However, the results are not sufficiently reproducible to correct for fluorine found by analysis. These results are shown in table 1.

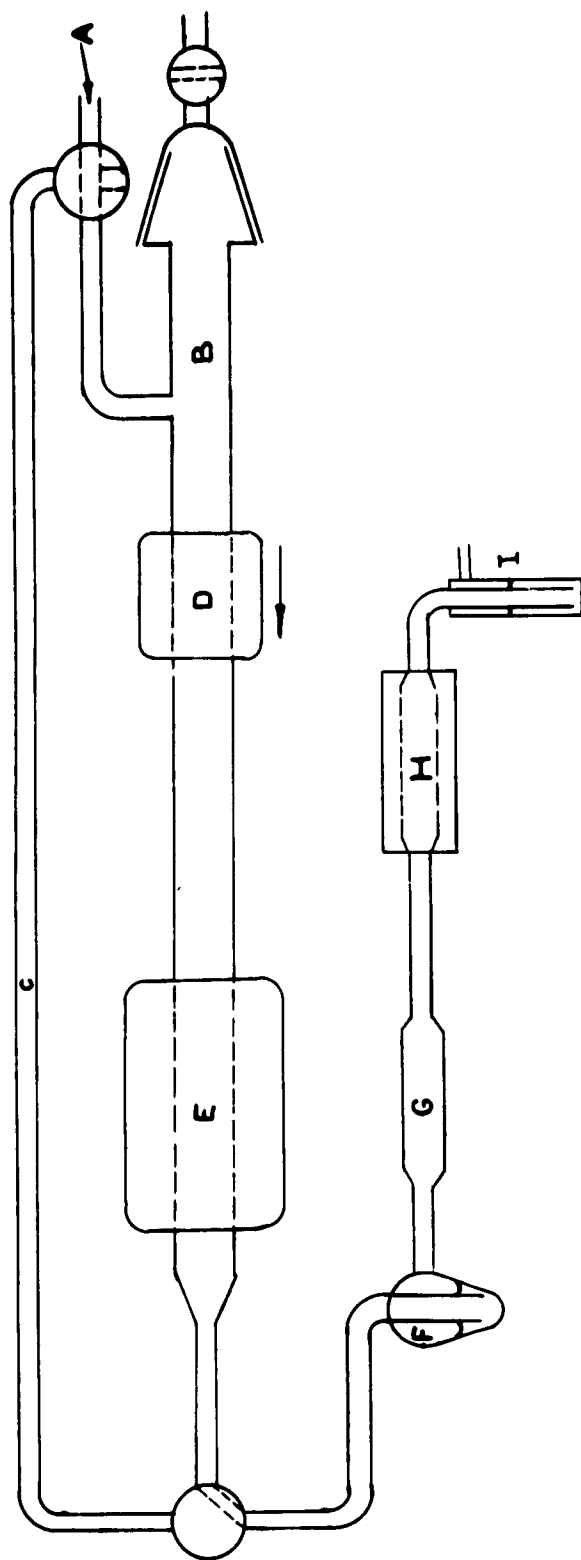


FIGURE 1

SCHEMATIC DIAGRAM FOR DIRECT OXYGEN APPARATUS

(A) Entrance for purified, dried helium or nitrogen, (B) pyrolysis tube, (C) bypass, (D) cylindrical burner operating at 1,100°C, (E) main furnace - carbon at 1,120°C ± 5°C, (F) sulfuric acid bubbler, (G) Ascarite, (H) iodine pentoxide at 110°C, and (I) absorber.

TABLE 1
APPARENT OXYGEN IN FLUORINE-CONTAINING SUBSTANCES

(Quartz Tube Coated With Carbon)

Substance	F (calcd)	O (calcd)	F+O* (calcd as O)	Apparent O (found)
Teflon**	75.98	0.00	32.00	28.79
Perfluorodibutyl ether	75.32	3.52	35.24	31.56
(CF ₃) ₂ CHCHFOC ₃ H ₇	54.92	6.61	29.74	28.26
p-Fluorobenzoic acid	13.56	22.84	28.55	24.66
Trifluoroacetanilide	30.14	8.46	21.15	16.44
m-Trifluoromethyl- benzoic acid	29.98	16.83	29.45	22.51

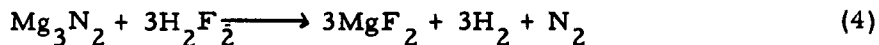
* Calculated as follows:

$$\frac{16.00}{19.00 \times 2} = 0.421; \% F \times 0.421 = \text{apparent \% oxygen because of fluorine.}$$

** Polytetrafluoroethylene, (C₂F₄)_n.

C. Magnesium Nitride Method.

Mázor⁸ describes an apparatus essentially that of Unterzaucher. In a subsequent report,⁹ a section of magnesium nitride is added immediately ahead of the customary filling and is held in place with silver wool (see figure 2). The sample burning area is carbon-coated, and the hydrogen fluoride from pyrolysis reacts with magnesium nitride to form magnesium fluoride, a compound stable below 2,260°C:



Formation of magnesium fluoride prevents subsequent reaction of hydrogen fluoride with the quartz tube.

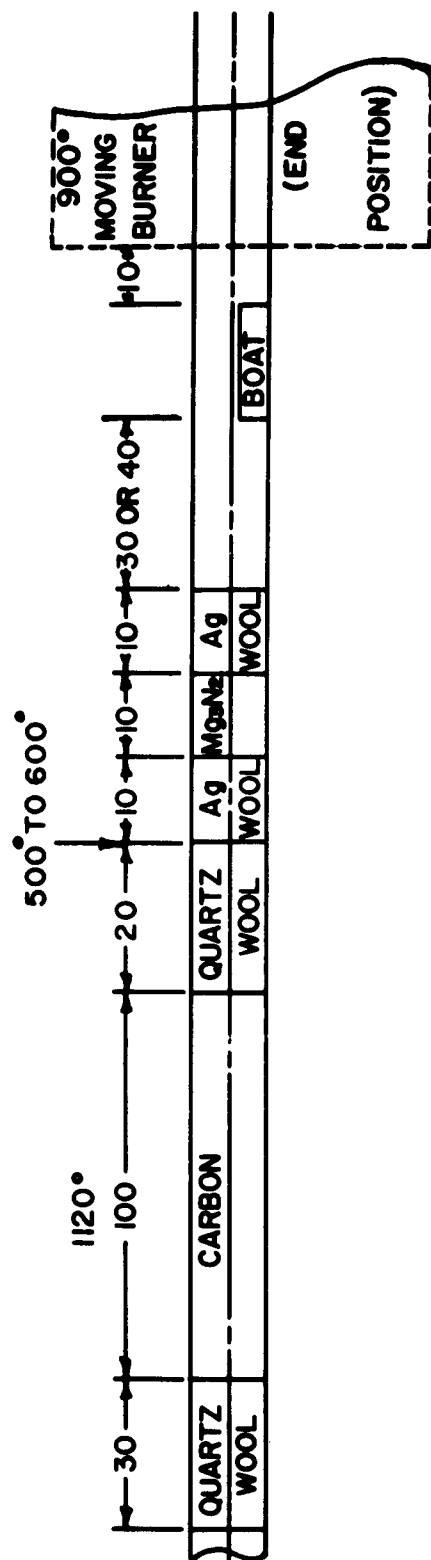


FIGURE 2

PYROLYSIS TUBE FOR FLUORINE-CONTAINING COMPOUNDS

Dimensions are in millimeters; temperature is in degrees centigrade.

In the procedure described, the sample burner is stopped before reaching the sample boat, contrary to usual practice, and is not advanced to the main furnace. An approximate temperature of the magnesium nitride is stated to be "several hundred degrees." More or less satisfactory results were reported on compounds containing as much as 25% fluorine.

The instructions for preparing the magnesium nitride are as follows: Fill a porcelain boat with magnesium turnings and place in a stream of nitrogen which has been freed from oxygen and moisture. Heat for 1 hour at 800° to 900°C . Allow to cool, pulverize the substance in the boat, and reheat for half an hour. The reheating is necessary to remove traces of metallic magnesium which would later absorb oxygen. The magnesium nitride must be very well protected from air and moisture. It decomposes at about $1,150^{\circ}\text{C}$.

The attempt to prepare magnesium nitride by heating magnesium metal in a stream of pure nitrogen at 800° to 900°C resulted in a very low yield, and difficulties were encountered from creeping and from reactions with the containers and the reaction tube.

Consequently, it was necessary to prepare magnesium nitride by a different procedure. Strips of magnesium were placed in a roll of platinum foil at an operating temperature of 640°C , just below the melting point of magnesium (651°C), for 40 hours. A good product was obtained, giving 28.2% nitrogen (calculated: 27.75%).

The product was placed in the pyrolysis tube with proper precautions for protection from air and moisture. With the recommended procedure followed, acetanilide (calculated: 11.84% oxygen) gave 8.4%, 0.5% and 1.0% oxygen. Teflon containing 76% fluorine and no oxygen gave 22.2% apparent oxygen.

At a later date, the entire experiment was repeated with a new combustion tube and a new preparation of magnesium nitride which was analyzed and gave 25.8% nitrogen. The results are shown in table 2.

None of these results is acceptable. Even the simple benzoic acid containing no fluorine failed.

Temperature checks showed the magnesium nitride section to be not more than 400°C . Since the burner was not advanced quite as far as the sample boat, the portion of the combustion tube between that point and the silver was at an even lower temperature. It is well known that most organic compounds can not be completely pyrolyzed at these temperatures, even in an oxygen atmosphere.

TABLE 2
APPARENT OXYGEN IN VARIOUS COMPOUNDS

(Quartz Tube With Ag-Mg₃N₂-Ag)

(Burner stopped ahead of sample boat)

Compound	F (calcd)	O (calcd)	Apparent O (found)
Acetanilide	0.00	[%] 11.84	10.15, 11.29
Benzoic acid	0.00	26.20	6.36
p-Fluorobenzoic acid	13.56	22.84	2.88
Trifluoroacetanilide	30.14	8.46	15.82

It was evident that, if this procedure was to work at all, it would be necessary to bring the sample burner over the magnesium nitride, up to the main furnace, to remove trapped decomposition products of samples.

Operating the sample burner at 700°C., well below the melting point of the silver section (961°C), gave the results shown in table 3.

TABLE 3
APPARENT OXYGEN IN VARIOUS COMPOUNDS

(Sample burner operating at 700°C passing over Ag-Mg₃N₂-Ag)

Compound	F (calcd)	O (calcd)	Apparent O (found)
Acetanilide	0.00	[%] 11.84	6.52, 10.71
Benzoic acid	0.00	26.20	18.44
p-Fluorobenzoic acid	13.56	22.84	19.45
Trifluoroacetanilide	30.14	8.46	12.73
Teflon	75.98	0.00	14.34

These results are better than those obtained by the original procedure but are still far from acceptable.

At this point, the sample burner operating at about $1,100^{\circ}\text{C}$ was accidentally run over the magnesium nitride. The silver was melted but the magnesium nitride was apparently undamaged. It was removed from the tube and evolved large amounts of ammonia when reacted with water.

It was decided to try magnesium nitride again, holding it in place with layers of platinum ribbon and passing the sample burner over it at the normal operating temperature of $1,100^{\circ}\text{C}$ (see figure 3). In this manner, pyrolysis of the sample should have been complete. The results are shown in table 4. The magnesium nitride appeared undamaged when removed and tested.

TABLE 4
APPARENT OXYGEN IN VARIOUS COMPOUNDS

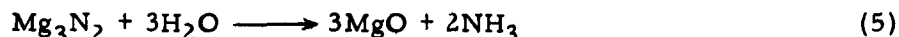
(Sample burner operating at $1,100^{\circ}\text{C}$ passing over $\text{Pt-Mg}_3\text{N}_2\text{-Pt}$)

Compound	F (calcd)	O (calcd) %	Apparent O (found)
Acetanilide	0.00	11.84	0.17
Benzoic acid	0.00	26.20	2.31
p-Fluorobenzoic acid	13.56	22.84	8.03
Trifluoroacetanilide	30.14	8.46	7.68
Teflon	75.98	0.00	9.16
Acetanilide (repeated)	0.00	11.84	0.28, 0.97

III. DISCUSSION.

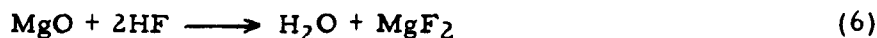
When the possible causes for failure are evaluated, it would be surprising indeed for the magnesium nitride method to give acceptable results on a variety of compounds, either containing fluorine or not containing fluorine.

It is well known that organic compounds containing oxygen, when pyrolyzed in an inert atmosphere, decompose to give varying amounts of water, carbon dioxide, carbon monoxide, and some oxides of other elements present. The relative amounts of water and other oxides are dependent on the temperature of pyrolysis and the nature of the compound. The water formed can react with magnesium nitride to form magnesium oxide, which is stable at temperatures over 3,000°C.

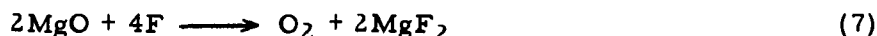


Hence, low results may be expected on compounds containing oxygen but no fluorine.

It is also clear that magnesium oxide may be present in the nitride section, either as an impurity in the reagent or from reaction with a pyrolyzed sample. Hence, if a sample containing fluorine is run, the pyrolysis products can release previously bound oxygen:



or



Thus, an oxygen value may be expected even when no oxygen is present in the sample.

It would seem possible that, in a compound containing oxygen and enough fluorine, oxygen, if bound as magnesium oxide (equation 5), might be immediately (equations 6 and 7) or simultaneously released (equations 5, 6, and 7) to give correct oxygen results. These reactions may be operative at the same time to some extent, but any consistency appears to be lacking.

Coating the area of sample burning with carbon appears to be of doubtful value. Only occasionally can results that are approximately correct be obtained. It is believed that reaction of hydrogen fluoride or fluorine with quartz takes place in the area of sample burning in spite of carbon coating. Indeed, if carbon coating were entirely effective, there should be no need for magnesium nitride. In our experiments, the area inside the main furnace, as well as the area of sample burning, has been coated with a glossy film of carbon free from visible irregularities. Reaction of fluorine with quartz past the main furnace should cause no error.

This work with magnesium nitride has not confirmed the results of Mázor.⁹

After the results of these experiments were reported,¹⁰ another investigator¹¹ corroborated the findings described in this report. He also stated that he had tried sprinkling magnesium nitride directly on the sample without any success.

IV. CONCLUSIONS.

1. Magnesium nitride when applied as recommended or with modifications does not reduce appreciably the fluorine interference in direct oxygen determinations.
2. Further experiments with magnesium nitride are believed useless and are not planned.
3. The platinum pyrolysis tube method devised here will be further developed as a means of determining oxygen in fluorine-containing compounds.

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