

CCA-651

543.842:543.843

Original Scientific Paper

A Combustion Tube Filling for the Determination of Carbon and Hydrogen in Fluorine Containing Compounds. I

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Received December 31, 1970

Combustion tube fillings containing titanium dioxide, tin dioxide and thorium dioxide in combination with oxidation catalyst — Körbl catalyst or copper oxide — are applied for the micro-determination of carbon and hydrogen in organic fluorine compounds.

Various samples of pure thorium dioxide and thorium dioxide on silica were examined and the measured retention capacities in mg fluorine per gram thorium dioxide are given. The capacity changes from 4.7 to 358 mg F/g ThO₂ depending on temperature and on the effective surface area of the thorium dioxide packing.

A series of standards analyzed by this procedure had a standard deviation for carbon 0.23% and for hydrogen 0.18%.

It has been found that thorium dioxide retains interfering combustion products containing fluorine but not those containing other halogens, sulphur or phosphor.

INTRODUCTION

Since many organic fluorine compounds cannot be decomposed easily, the determination of carbon and hydrogen in these compounds is rather complicated. The fluorine liberated during the combustion attacks the combustion tube and the traces of volatile silicon tetrafluoride seriously interfere with the determination.

Various combustion tube fillings have been examined and proposed as oxidation catalysts and for the retention of fluoride in the tube. In the ordinary Pregl Universal filled combustion tube the fluorine and the silicon tetrafluoride have been removed by lead chromate at 800° C¹. There have been several modifications of Pregl's method. However, lead chromate and lead oxide attack the tube and recent methods do not propose lead compounds for these purposes.

As far as we know the most frequently used methods are those of Belcher and Goulden² and Throckmorton and Hutton³.

In the former method, the silicon tetrafluoride formed during the combustion is retained in a layer of sodium fluoride maintained at 270° C. The combustion tube filling used in the latter method is a layer of magnesium oxide pellets and copper oxide maintained at 900° C. There is a number of modifications of these methods.⁴

The mineral vermiculite⁵, the magnesium-aluminium compound 3 MgO · Al₂O₃⁶, magnesium oxide with silver tungstate and zirconium dioxide⁷,

magnesium oxide or manganese oxide with silver⁷, the decomposition product of silver and lead carbonate⁹ and a cerium dioxide-mixed catalyst¹⁰ have also been found successful for the removal of fluorine containing combustion products. Generally, in all these methods the sample is first combusted in a quartz tube and the interfering gases are removed in the section of the filling kept at an elevated temperature. Only few fillings can oxidate and absorb interfering gases at the same time. When these methods were applied the combustion tube was attacked by fluorine.

Therefore, there is still a need for a convenient reagent that reacts at lower temperature and has high oxidation and retention capacities. The problem can be solved when the sample is covered with reagent and the fluorine retained in the boat.

In the present work various fillings for retention of fluorine are examined. The oxides of elements which form stable fluorides were studied. Firstly, titanium oxide, tin oxide and thorium oxide in various forms are employed to remove the interfering gases. As oxidation catalyst the decomposition product of silver permanganate is used. The results obtained with thorium oxide were satisfactory and the method for the carbon and hydrogen determination in organic fluorine compounds is given.

EXPERIMENTAL

Reagents

Copper oxide *p. a.*, in wire form 4—5 mm long.

Decomposition product of silver permanganate according to Körbl¹¹.

Silver wool for elementary analysis (W. C. Heraeus, GMBH).

Quartz wool for elementary analysis (W. C. Heraeus, GMBH).

Anhydrone for elementary analysis (W. C. Heraeus, GMBH).

Ascarite for elementary analysis (W. C. Heraeus, GMBH).

Silica gel, particle size 0.2—0.5 mm (E. Merck AG).

Titanium dioxide: Reagent 1. Titanium dioxide *p. a.* (B. D. H).

Reagent 2. Titanium dioxide prepared from $K_2TiO_2(C_2O_4)_2 \cdot H_2O$. From boiling oxalate solution titanium hydroxide was precipitated with ammonium hydroxide, filtered off, washed and ignited at 600°.

Tin dioxide, prepared from $SnCl_2 \cdot 2H_2O$. From a boiling chloride solution, tin hydroxide was precipitated with ammonium hydroxide, filtered off, washed and ignited at 1000°.

Thorium dioxide. Various samples of thorium dioxide were examined:

Reagent 1. Thorium dioxide *p. a.* (Hopkins and Williams).

Reagent 2. Thorium dioxide, prepared by decomposition of thorium oxalate. From a boiling nitrate solution, thorium was precipitated with hot oxalic acid. Thorium oxalate was filtered off, washed and ignited in a quartz crucible at 1000° for 2 hours.

Reagent 3. Thorium dioxide on silica (33.3% and 9%), prepared by decomposition of thorium nitrate on silica. 5 g of silica gel was put in 10 ml of a solution containing 5.4 or 1.1 g of $Th(NO_3)_4 \cdot 5H_2O$. The mixture was temporarily shaken then evaporated and the residue was ignited at 1000° for 3 hours.

Apparatus

The apparatus I consists of a commercially available oxygen supply with a pressure reducing valve, the gas purification system, a quartz combustion tube and the absorption tubes.

The purification system consists of a junction bubbler »T« which regulates the pressure, a preheater quartz tube filled with copper oxide, a bubbler counter filled with concentrated sulphuric acid connected to an U tube filled with anhydrone.

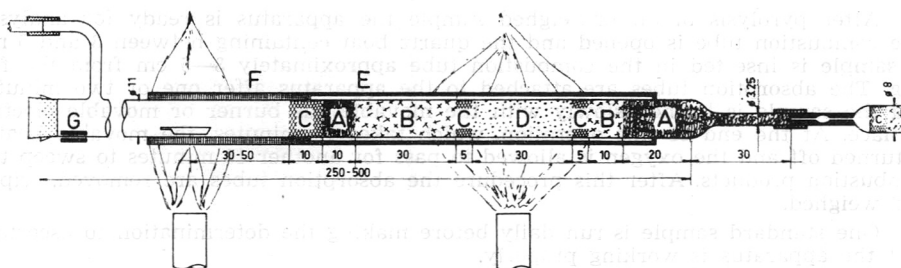


Fig. 1. Combustion system Apparatus I — A Silver wool, B Körbl catalyst, C Quartz wool, D »X Dioxide« filling, E Metal tube, F Metal net tube, G Magnet.

The combustion tube (Fig. 1) is filled starting at the capillary end with 20 mm of silver wool, 10 mm (1 g) of Körbl catalyst, of quartz wad, 10—100 mm (1—4 g) of »X dioxide« layer, another quartz wad, 30 mm (3 g) of Körbl catalyst, 10 mm of silver wool and a 10 mm quartz-wool layer. The Körbl catalyst layer is heated to 500° by the main gas burner or the main electric furnace. The second movable gas or electric burner is employed to burn the sample in the quartz boat.

The Apparatus II is a Heraeus automatic microapparatus »Standard« for the C, H, N, and O determination. The apparatus is used without the electric furnace for the lead dioxide.

The standard combustion tube (Fig. 2) is filled starting at the capillary end with 20 mm of quartz wool, a 10—30 mm (1—1,5 g) »X dioxide« layer, a quartz wad, 150 mm of copper oxide and a 10 mm quartz-wool layer. The copper oxide and the »X dioxide« layer are heated by the long electric furnace to 690 and 770°, respectively.

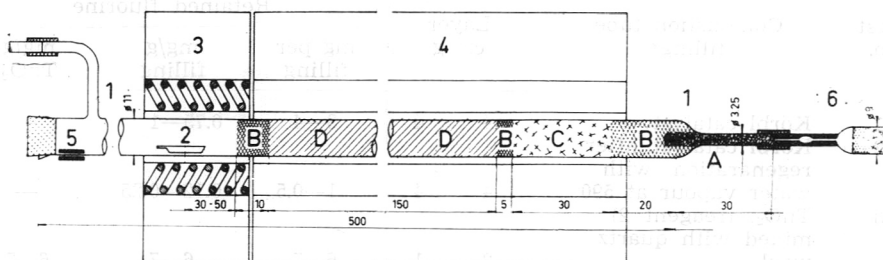


Fig. 2. Combustion system Apparatus II — 1 Combustion tube, 2 Platinum boat, 3 Movable electric furnace, 4 Long electric furnace, 5 Magnet, 6 Water absorption tube, A Silver wool, B Quartz wool, C »X Dioxide« filling, D Copper oxide.

Water, carbon dioxide and nitrogen oxide absorption tubes (standard Heraeus design tubes) are filled with anhydrone, ascarite and manganese dioxide, respectively.

Procedure

The procedure is similar to the standard microgravimetric methods used for carbon and hydrogen determination. When the apparatus is set up, the preheater furnace is turned on and the oxygen is passed through the purification system. After about 15 minutes the oxygen is allowed to pass through the other parts of apparatus and the main furnace is adjusted to heat the combustion tube filling. The apparatus is allowed to stand 5 hours at full working temperature with a flow of oxygen 10 ml/min.

When the apparatus is used daily it takes about 30 minutes to reach the working conditions. It should not be kept at working temperature for a long time because this causes decomposition of the oxidation catalyst.

After pyrolysis of an unweighed sample the apparatus is ready for analysis. The combustion tube is opened and the quartz boat containing between 3 and 5 mg of sample is inserted in the combustion tube approximately 3—5 cm from the filling. The absorption tubes are attached to the apparatus after one or two minutes and the sample is burned slowly with the movable gas burner or movable electric furnace. At the end of this operation, which takes 15 minutes, the movable heater is turned off and the oxygen is allowed to pass for another 10 minutes to sweep the combustion products. After this procedure the absorption tubes are removed, wiped and weighed.

One standard sample is run daily before making the determination to ascertain that the apparatus is working properly.

RESULTS AND DISCUSSION

The main purpose of this study was the microdetermination of carbon and hydrogen in organic fluorine compounds at relatively low combustion tube temperatures and with a short combustion tube filling. Firstly, several series of tests were performed with a combustion tube filling containing a Körbl catalyst 40 mm layer maintained at 450—550°. The results (Table I, tests 1 and 2) show that the Körbl catalyst retained interfering combustion products in the combustion tube. However, the capacity is low and falls steeply at regeneration with water vapour at the working conditions. Regeneration at higher temperature causes decomposition of the oxidation catalyst.

TABLE I
Summary of Experimental Data

Test No.	Combustion tube filling*	Layer cm g		Retained fluorine		
				mg per filling	mg/g filling	mg/g ThO ₂
1	Körbl catalyst	4	4	3—4	0.75—1	—
2	Körbl catalyst after regeneration with water vapour at 590°	4	4	1—0.5	0.12—0.25	—
3	ThO ₂ , (reagent 2) mixed with quartz wool	2	1	6—7	6—7	6—7 ^{d)}
4	"	2	2	16	8	8 ^{a)}
5	"	2	2	13	7	7 ^{b) d)}
6	"	2	3	23	7	7 ^{a)}
7	ThO ₂ , (reagent 1) mixed with quartz wool	2	1	5	5	5 ^{a)}
8	SiO ₂	4	1.5	0	—	—
9	ThO ₂ /SiO ₂ 33% (reagent 3)	3	1.5	30	20	60 ^{a)}
10	ThO ₂ /SiO ₂ 9% (reagent 3)	3	1.5	23	15	170 ^{a)}
11	"	2.5	1	16—25	16—25	176—275 ^{a) b)}
12	"	2.5	1	12	12	137 ^{c) d)}
13	"	10.0	4	95—130	24—33	261—358

Remarks: * ThO₂ combustion tube filling contains oxidation catalyst (Figs. 1 and 2).

^a ThO₂ maintained at 600°; ^b ThO₂ maintained at 690°; ^c ThO₂ maintained at 800°; ^d Analyses performed with Apparatus II.

We have applied combustion tube fillings consisting of titanium dioxide, and thorium dioxide respectively. Unfortunately, these reagents have proved to be inadequate as to the oxidation action. When using this filling with a Körbl catalyst or copper oxide as oxidation catalysts we obtained good results.

Titanium Dioxide Filling

This filling was studied with Apparatus I. The »X dioxide« layer, reagent 1. and 2. titanium dioxide was varied from 20 to 35 mm (1—2 g TiO_2) and studied at 300°, 500°, 580° and 660°. From the results obtained it can be concluded that titanium dioxide has no influence on the C, H determination in organic fluorine compounds. It is not an oxidation catalyst and it does not remove the interfering products.

Tin Dioxide Filling

The »X dioxide« layer, 30 mm (2g) of tin dioxide heated at 300° or 500° is studied with Apparatus I. Like titanium dioxide, tin dioxide did not show the actions expected in the determination of C and H in organic compounds containing fluorine.

Thorium Dioxide Filling

Various samples of thorium dioxide and thorium dioxide on silica were examined. From the results it is obvious that thorium dioxide at 500°—700° does not retain carbon dioxide and water. However, thorium dioxide retains interfering combustion products containing fluorine. The retention capacity in mg F/g ThO_2 and the summary of all experimental data are shown in Table I.

It is very probable that hydrofluoric acid formed during combustion reacts with thorium dioxide. However, the main reaction is the retention of silicon tetrafluoride on thorium dioxide.

Some tests were performed at higher temperatures. It is most probable that SiF_4 decomposes in the hot zone, forming SiO_2 and this causes a decrease in the effective surface of thorium dioxide filling and thus a decrease in the capacity. Apparently, the thorium dioxide surface area as well as the temperature play an important role in this process.

The attempts to regenerate the thorium dioxide with water vapour failed since after the regeneration the filling was inactive. However, thorium dioxide after saturation with fluoride can be easily dissolved in an acid solution and thorium can be precipitated again with oxalic acid.

A series of samples with different constituents is analysed with Apparatus I. The »X dioxide« layer was 30 mm reagent 3 ($\text{ThO}_2/\text{SiO}_2$ 9% or 33%) heated to 600°. The results for carbon and hydrogen are presented in Table II. All analyses were carried out using the procedure described. Taking into account all results obtained, the standard deviation for carbon is 0.23%, for hydrogen 0.18%. Furthermore, a number of samples $(\text{R}_2\text{R}'\text{NH})_2\text{NbOF}_5$, $(\text{R}_2\text{R}'\text{NH})\text{TaOF}_4$ and $(\text{R}_2\text{R}'\text{NH})_2\text{TaF}_6$ where $\text{R} = \text{C}_8\text{H}_{17}$, $\text{R}' = \text{CH}_2\text{CH}_2\text{OH}$, were analysed. Good carbon and hydrogen results were obtained. With a 100 mm layer of thorium dioxide/silicium dioxide (9 or 33%) about 110 mg of fluorine can be removed or about 150—200 analyses can be performed with one filling.

Using the apparatus II we tried to analyze several organic compounds containing Cl, Br, J, S and P respectively. It has been found that the interfering combustion products are not removed on the layer of thorium dioxide.

TABLE II
Analyses of Different Compounds

Sample	Carbon		Hydrogen		Fluorine Calcd. %	Results No.
	Calcd.	SD	Calcd.	SD		
	%		%			
Sucrose C ₁₂ H ₂₂ O ₁₁	42.10	0.185	6.48	0.146	—	14
<i>o</i> -Fluorotoluene C ₇ H ₇ F	76.34	0.266	6.41	0.215	17.25	37
<i>p</i> -Fluorobenzoic acid C ₇ H ₅ FO ₂	60.01	0.242	3.60	0.175	13.56	26
Trifluoroacetanilide C ₈ H ₆ F ₃ NO	50.81	0.256	3.19	0.118	30.14	12
Trifluoroacetic acid C ₂ HF ₃ O ₂	21.07	0.112	0.89	0.100	49.99	4
<i>m</i> -Trifluoromethylbenzoic acid C ₈ H ₅ F ₃ O ₂	50.54	0.228	2.65	0.263	29.98	5
1-[Thenoyl-(2')]-3,3,3-tri- fluoroacetone C ₁₀ H ₅ F ₃ S	43.25	0.175	2.27	0.146	25.66	10
Overall standard deviation		0.23		0.18		

Acknowledgment. The authors are indebted to Mrs. B. Matijević for technical assistance.

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IZVOD

**Određivanje ugljika i vodika u organskim supstancama koje sadrže fluor.
Punjenje cijevi za spaljivanje. I***M. Tonković i Š. Mesarić*

Titan dioksid, stanum dioksid i torium dioksid u kombinaciji s Körblovim katalizatorom ili bakrenim oksidom kao oksidansom, upotrijebljeni su za punjenje cijevi za spaljivanje za mikroodređivanja ugljika i vodika u organskim supstancama koje sadrže fluor.

Ispitivana je sposobnost zadržavanja fluora na različito pripremljenom torium dioksidu i torium dioksidu na silicium dioksidu kao nosaču. Kapacitet vezanja je 4,7—358 mg F/g ThO₂, a ovisi o temperaturi i površini torium dioksida. Standardna devijacija određivanja je 0,23% za ugljik i 0,18% za vodik.

Nađeno je da torium dioksid zadržava produkte spaljivanja koji sadrže fluor, ali ne i one koji sadrže druge halogenide, sumpor ili fosfor.

ODJEL FIZIČKE KEMIJE
INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB

Primljeno 31. prosinca 1970.