

ALUMINIUM NITRATE AS EXTERNAL ABSORBENT IN THE MICRODETERMINATION OF CARBON AND HYDROGEN IN ORGANOFLUORINE COMPOUNDS

By

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نترات الألومنيوم كمادة إمتصاص خارجي في التقدير الميكروئي للكربون والهيدروجين في المركبات العضوية الفلورينية

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في البحث المقدم تم استخدام جيل السيليكا المشبع بمحلول نترات الألومنيوم الحمضة بحمض النيتريك للتخلص من التداخلات الناتجة عن الفلور في التقدير الميكروئي للكربون والهيدروجين في مركبات الفلور العضوية . المادة المقترحة رخيصة الثمن ، متوفرة بالمعامل وسهلة التحضير .

وجد بالتجربة أن ثلاثة جرامات من المخلوط المقترح يكفي لتحليل ٢٥ عينة . تحرق العينات في تيار من الأكسجين باستخدام طريقة الحرق السريعة للأنبوبة المستقيمة الفارغة. بعد الحرق يتم مرور نواتج الاحتراق على أنابيب امتصاص تحتوي على المواد الآتية على الترتيب : فوق كلورات المغنيسوم اللامائية ، مخلوط السيليكا و نترات الألومنيوم، هيدروكسيد الصوديوم المحمل على الاسبستوس وذلك لامتصاص بخار الماء ، نواتج حرق الفلور ، ثاني أكسيد الكربون ، على التوالي .

يتم تقدير الهيدروجين والكربون وزنياً . في حالة وجود فلز يعطي أكسيد ثابت يمكن تقدير الفلز تقديراً أنياً مع الكربون والهيدروجين وكذلك الأمر في حالة وجود عنصر الكبريت أو الكلور .

Key Words: Aluminium nitrate, Carbon hydrogen determination, External absorbent, Fluorine compounds.

ABSTRACT

Silica gel loaded with saturated $Al(NO_3)_3 \cdot 10 H_2O$ solution proved to be an efficient absorbent for the elimination of the interference of fluorine in the microdetermination of carbon and hydrogen in organofluorine compounds. The reagent is cheap, readily available and easily prepared. Three grams are sufficient for 25 determinations. Samples are burnt in a flow of oxygen using the rapid straight empty tube method. The combustion products are passed through anhydrous, silica gel-aluminium nitrate, and soda asbestos absorption tubes. Carbon and hydrogen contents are determined gravimetrically. The simultaneous microdetermination of carbon, hydrogen and metal, carbon, hydrogen, chlorine or sulphur and metal are carried out successfully in fluorine containing organic compounds.

INTRODUCTION

The determination of carbon and hydrogen in organofluorine compounds has been a matter of interest in our laboratory due to the relative big number of samples submitted for analysis. In the analysis of these compounds, the fluorine decomposition products attack the tube catalyst and if not eliminated totally give rise to wrong carbon results[1]. Silicon tetrafluoride and hydrogen fluoride are the products of combustion of organofluorine compounds. Several studies concerning this problem have already been reported[2]. Internal[3] and external[4] absorbents have been suggested for the elimination of fluorine decomposition products. Other studies concerning this problem have also been reported[5, 6].

Although good results have been reported for carbon and hydrogen[7], yet the application of five absorption tubes for the elimination of fluorine interference is considered to be a disadvantage. Farag et al.[8] determined carbon and hydrogen in organofluorine compounds, using a thorium nitrate-silica gel mixture as an external absorbent and found good results. Thorium oxide was also used[9] for the analysis of fluorinated silicon compounds. Lanthanum nitrate[10] and calcium nitrate [11, 12] silica gel mixtures were claimed to be successful for the elimination of interferences due to the presence of fluorine.

In the present work, a standard absorption tube packed with a mixture of aluminium nitrate-gel has been tested for elimination of fluorine decomposition products using the rapid straight empty tube method of Korshun and Klimova[13].

EXPERIMENTAL

Preparation of the external absorbent for fluorine

Wash the silica gel grains (1.25 mm) with distilled water and dry it at 120° for two hours. Mix 25 g of it with a solution of 2.5 g Al(NO₃)₃ · 10 H₂O in 20 ml of 2M HNO₃. Decant the excess solution and allow the treated grains to dry using filter paper. Fill two-third of a standard absorption tube with the reagent, insert a short quartz wool plug and then fill the remaining empty part with anhydrous to absorb any moisture diffusible from the silica gel layer by the fast flow of oxygen.

PROCEDURE

Assemble the apparatus as described elsewhere[8]. Exactly weigh 5-8 mg sample in a 10 mm long capsule. Decompose the sample as usual[8], using a strong burner, in a stream of pure and dry oxygen adjusted at 35 ml/min. After complete combustion, sweep for 10 min. disconnect and re-weigh the H₂O and CO₂ tubes according to the pre-

set time schedule, then calculate the hydrogen and carbon contents of the sample.

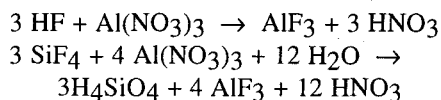
RESULTS AND DISCUSSION

The combustion products of organofluorine compounds may contain F₂, HF and SiF₄, all these products, though pass unaffected through fresh anhydrous tube, yet react in different ways with soda asbestos causing erroneous carbon figures. Fluorine differs from the other halogens in that its oxidation products can react with the silica combustion tube.

Incidentally different reports exist concerning the behaviour of silver wool, normally inserted into the combustion tube for the absorption of halogens and sulphur, towards the various fluorine-containing species. Elemental fluorine is stated[1] to be absorbed completely by silver though hydrogen fluoride reacts with silica giving rise to SiF₄, which is not retained by silver[1] and hence swept out of the combustion tube. In another work[14], it was stated that hydrogen fluoride can be absorbed quantitatively on silver heated to 500° but silicon tetrafluoride can be absorbed on magnesium oxide.

Based on previous experience gained with the four conventional rapid combustion techniques, namely Belcher-Ingram[5], flash combustion method[13], packed tube method[8] and straight empty tube method[8], the last one in addition of being most simple and economical proved to offer optimum conditions for complete decomposition and oxidation not only of partially and highly fluorinated samples but also of fluorocarbons. This is due to the combustion characteristics of the method involving sample pyrolysis inside a quartz capsule which also acts as shield protecting the main combustion tube from direct attack by fluorine combustion products.

In the present work, aluminium nitrate-silica gel mixture is selected as external absorbent for fluorine combustion products at room temperature, not only because of its higher affinity to react with fluorine ignition species, but also being a much cheaper and more common reagent when compared with others[8, 10]. The reactions involved may be as follows:



The proposed reagent was examined for the elimination of fluorine interference in carbon and hydrogen determination for nine compounds and gave rise to satisfactory results (Table 1). It is to be mentioned that one Pregl absorption tube filled with about three grams of aluminium nitrate-silica gel mixture has a capacity of 25-30 analyses.

Table 1.
Microdetermination of carbon, hydrogen and hetero element
in fluoro-organic compounds.

Compound	Calculated	Average* found	Standard deviation
4-Fluorobenzoic acid C ₇ H ₅ FO	C = 60.00	60.05	0.042
	H = 3.59	3.66	0.043
Perfluoronaphthalene C ₁₀ F ₈	C = 44.14	44.00	0.038
Trifluoroacetanilide C ₈ H ₆ F ₅ NO	C = 50.80	50.89	0.061
	H = 3.20	3.37	0.052
Fluorobenzene C ₆ H ₅ F	C = 74.99	75.14	0.064
	H = 5.24	5.35	0.041
Ethyltrifluoroacetate C ₄ H ₅ F ₃ O ₂	C = 33.81	33.98	0.061
	H = 3.55	3.64	0.035
Trifluorotoluene C ₇ H ₅ F ₃	C = 57.54	57.56	0.084
	H = 3.45	3.61	0.015
Nitro-6-fluoro-1-thio-coumarine C ₉ H ₄ NO ₃ SF	C = 48.00	48.17	0.049
	H = 1.79	1.86	0.049
	S = 14.24	14.12	0.054
2-Fluorobenzoyl chloride C ₇ H ₄ OCIF	C = 53.02	53.14	0.079
	H = 2.54	2.65	0.046
	Cl = 22.36	22.23	0.044
Aluminium fluofenamate C ₄₂ H ₂₇ O ₆ N ₃ F ₉ Al	C = 58.14	58.02	0.075
	H = 3.14	3.24	0.050
	Al = 3.11	3.26	0.065

* Average for five determinations

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