Simple procedure for determination of the carbon content in silica-supported materials

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ABSTRACT

A simply and accurate analytical method was developed to determination the carbon content in silica-supported materials. The principle of this method was to oxidize sample by a strong oxidant like potassium dichromate to produce carbon dioxide and this gas is absorbed into an alkaline solution for subsequent titration. The repeatability and the recovery of this method fell into the required range (% RSD <1.3 % and 98-102 % in recovery) of AOAC International. The chloride content of up to 100 mg did not give any influence. The developed procedure was applied to determine the carbon content in octadecyl-modified silica samples.

Keywords: *Carbon, wet oxidation, silica-supported materials*

INTRODUCTION

Currently many silica-supported materials are widely used in various applications [1-3]. To evaluate characterizations of the material, its compositions are usually determined. Of elements to be determined, carbon is the most popular since it presents in all organic compounds.

Methods of sample combustion for determination the carbon content have been developed since 1970s with high recovery and repeatability. The principle was to oxidize carbon compounds to produce carbon dioxide and capture it in an absorbent towards weight or volumetric methods [4-6]. So far, modernly instrumental methods have been applied to carbon analysis such as NMR or using elemental analysis technique. These methods are rapid and accurate, however their tremendous disadvantage is too expensive to equip for all laboratories.

In this work a method of wet combustion for determination of the carbon content in silica-supported materials was developed and evaluated. The method was also applied to our 10 research samples.

MATERIALS AND METHODS

Materials

$K_2Cr_2O_7$ and NaOH were products of Merck. H_2SO_4, H_3PO_4 and HCl were purchased from Labscan. Silica (particle diameter 40-60 µm, mean pore diameter 60 Å, specific surface area 500 m^2/g), was purchased from Scharlau. Trimethoxyoctadecyl silane (TMOS) 90 % and stearic acid (98.5 %) were obtained from Sigma-Aldrich. Ten research samples of octadecyl-supported silica material were prepared by silanization [7].

Apparatus

Apparatus for determination of the carbon content is illustrated in Fig. 1.

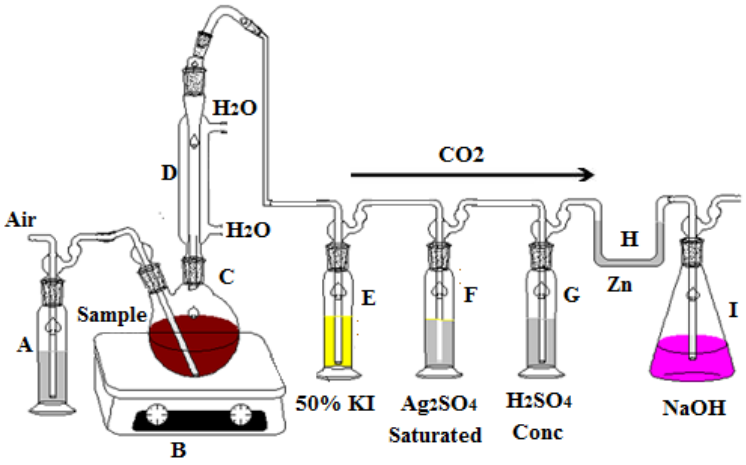

Figure 1. Apparatus for determination of carbon content

The aeration vessel A (25 cm in height, 4 cm in diameter) is connected to on air compressor and a quarter is filled with CaO to remove carbon dioxide from the incoming air. The vessel A is connected to 250-mL two-neck flat bottom flask C to contain sample and oxidation reagents. The electric stove B can heat up to 400 $^{\circ}$C. When the digestion flask C is heated, CO_2 as well as acid fume, Cl_2… are resulted in. The condenser D (25 cm in height, 4 cm in diameter) is attached to the flask C to condense the acid fume. The next is the trap chain with 4 traps. Among them traps E, F and G are the same aeration vessel (25 cm in height, 4 cm in diameter). The trap E is half filled with 50 % aqueous solution of potassium iodide to absorb chloride by-products. The trap F is also half filled with saturated solution of Ag_2SO_4. Trap G contains not more than one third concentrated H_2SO_4 for absorbing the humidity. Any acid fume escaping the trap G is captured at the U tube H (40 cm in length, 1 cm in diameter) containing 2-cm height Zn particles. Finally, the conical flask I containing NaOH is connected to the system to absorb the resulted CO_2.

Procedure

To the CO_2 absorbing flask I, add 25 mL of 1.0 M NaOH solution and 2-3 drops of phenolphthalein (1 % in ethanol) and place it in the position in the system.

To the digestion flask C, add a precise amount of silica-supported materials that contain 15-120 mg of carbon, continuously add 4-5 g of $K_2Cr_2O_7$ and approximately 30 mL of H_2SO_4:H_3PO_4 mixture (3:2) (v/v), respectively. Immediately assemble it to the position in the system.

Turn on the incoming air at the velocity of 1 mL/min and use “check leak” solution to check all the joints to make sure that there are no gaps.

Successively heat the digestion flask C at about 150 $^{\circ}$C for 1 h and then at 200 $^{\circ}$C for 30 min.

Unbind the flask I off the system, rinse its aeration tube several times with de-ionized water and titrate it with 1 M HCl solution until the solution converts from pink to colorless.

Blank sample is prepared as the procedure above with sample as silica.

Calculation

$$m_C\,(mg) = (V_{Bl} - V_S) \times C_{HCl} \times 12$$

And

$$C\,(\%) = \frac{(V_{Bl} - V_S) \times C_{HCl} \times 12}{m\,(g) \times 10}$$

Where:

m_C: Weight of carbon in sample specimen (mg)

V_{Bl}: Volume of HCl solution to titrate absorption solution of blank sample (mL)

V_S: Volume of HCl solution to titrate absorption solution of sample (mL)

C_{HCl}: Concentration of HCl solution (M) after calibrating with standard oxalic acid

m: Weight of sample specimen (g)

RESULTS AND DISCUSSION

Precision and trueness

Determinations were carried out to examine the precision of this method. Since the goal of this development was to determine the carbon content in silica-supported materials, those usually are saturated chains of 3, 8 or 18 carbons bonded to the silica surface, and there is no standard material, stearic acid was selected as the standard for the method validation.

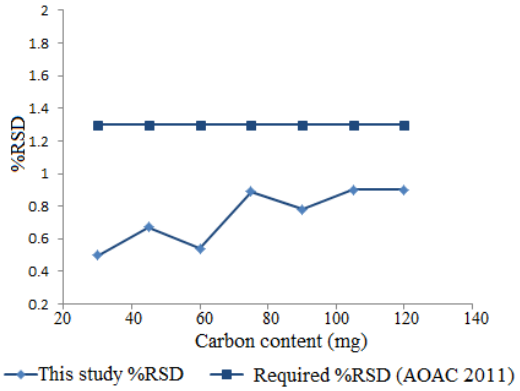

Figure 2. Comparision of % RSDs at different carbon amounts between our method and the AOAC regulation (n=5)

The standards with various carbon contents from 30 to 120 mg were analyzed five times independently for each level. All % RSD at different carbon levels were lower than those required by AOAC International (Fig. 2).

Trueness

The precision validation part of these experiments, the recovery of this method was calculated through the ratio of practical and theoretical carbon amount. The results showed that recovery of the whole procedure is in the range from 98 to 102 % which is required by AOAC International [8].

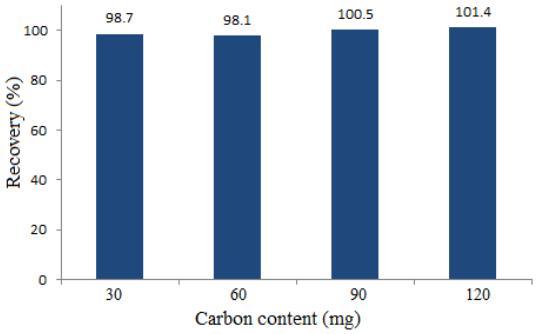

Figure 3. Recovery of carbon content at different amounts

As a result it can be stated that this method was accurate since both the precision and trueness complied with the international regulation.

Chloride interference

Chloride is considered the interference in wet combustion method. Because some silica-supported materials may contain chloride, its effect was investigated. The influence of increasing amounts of chloride (up to 100 mg) added as sodium chloride to the ca. 30 mg of carbon containing standard samples are presented in Table 1. It can be concluded that the chloride mass of less than 100 mg did not have effect on the carbon content since both recovery and % RSD values fell into the required range of AOAC international.

Table 1. Repeatablity and recovery of the method

Added chloride (mg)	Carbon (%)		Recovery (%)	RSD (%)
	Theoretical value	Experimental value		
25	76.0	75.7	99.6	0.68
50	76.0	76.4	100.5	0.98
75	76.0	77.1	101.4	0.11
100	76.0	77.3	101.7	1.15

When the contents of the digestion flask are heated, chloride is converted to CrO_2Cl_2, which is deposited in on the cooler part of the flask and condenser. However when the digestion mixture is brought to boiling, CrO_2Cl_2 disappears since it decomposes at 180-190 °C which is lower than the boiling point (210 °C) of the mixture, and releases Cl_2 [5]. This Cl_2, traces of CrO_2Cl_2 and HCl fume react with the contents of "chlorine and acid fume" traps (E and F). Therefore, chloride by-products could not reach the CO_2 absorbing part to affect it.

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

Determination of real samples

10 samples (S1–S10) were synthesized they are octadecyl containing material on silica support with trimethoxyoctadecyl silane reagent. Experiments were optimized so that the reaction yield was the highest. Table 2 showed the carbon content of resulted products when some conditions such as temperature, catalyst were changed.

Table 2. Carbon content in some synthesized samples

Sample No	Carbon (%)	Sample No	Carbon (%)
S1	6.4	S6	11.2
S2	7.8	S7	12.8
S3	8.5	S8	13.2
S4	10.2	S9	14.2
S5	10.8	S10	14.6

CONCLUSION

In this study, a simple and accurate analytical method for determination of the carbon content in silica-supported materials was developed and validated. With high trueness, precision as well as cheap cost the method could be applied to all laboratories. This method can also be used for determination of the carbon content in different types of sample without further development [4-6].

Phương pháp đơn giản xác định hàm lượng carbon trong các vật liệu trên nền silica

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TÓM TẮT

Một phương pháp phân tích đơn giản và chính xác đã được phát triển cho việc xác định hàm lượng carbon trong các vật liệu trên nền silica. Nguyên tắc chung của phương pháp là sử dụng chất oxy hóa mạnh như $K_2Cr_2O_7$ để oxy hóa mẫu, tạo ra khí CO_2. Khí CO_2 sinh ra được hấp thu vào dung dịch kiềm và chuẩn độ lại để xác định hàm lượng carbon. Độ lặp lại và hiệu suất thu hồi của toàn bộ quá trình ở trong khoảng yêu cầu của AOAC International (% RSD < 1,3 % và độ lặp lại 98-102 %). Hàm lượng chlorine lên tới 100 mg không gây ảnh hưởng đến kết quả. Quy trình này được áp dụng để xác định hàm lượng carbon trong các mẫu trong nghiên cứu tổng hợp vật liệu silica biến tính octadecyl.

Từ khóa: *carbon, oxi hóa ướt, vật liệu trên giá mang silica*

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