Quantification of graphene materials in fibers

Weidong Li¹*, Yingjie Wang², Zhiping Mao²
¹Shanghai Institute Of Quality Inspection and Technical Research, Shanghai, China
²College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, China
*Corresponding author e-mail:13585557807@163.com

Abstract. A method for quantitative determination of graphene materials in fibers by high temperature pyrolysis - element analysis is reported. This method takes advantage of the difference between the thermal stability of fiber and graphene itself to design the corresponding temperature gradient. Firstly, the fiber matrix is removed, and then the carbon element content ratio is measured by element analyzer. This method eliminates the influence of other impurities in the fiber. The experiment is reliable, simple to operate and the relative deviation conforms to the standard range, which is of great significance for quantitative analysis of the content of graphene materials in the fiber.

1. Introduction
Graphene is a carbon nanometer material that has a similar structure to graphite, but is nanometer thick and usually has a transverse size of microns. The discovery of graphene not only enriched carbon materials, but also due to its special nanostructure and excellent mechanical, electrical, thermal and optical properties [1-2], graphene shows great scientific significance and application value. In terms of microstructure, it is a kind of two-dimension monatomic layer crystal arranged by hybridization of carbon atoms[3]. Its mono-atomic structure gives it many unique physicochemical properties, such as high modulus, high strength, high specific surface area, high-speed electron mobility and high thermal conductivity at room temperature, quantum hall effect [4]. These excellent properties make graphene have bright application prospects in many fields and become a research hotspot in the scientific community.

With the development of functionalization and industrialization of graphene, graphene has been widely applied in the research and development of textile field, and a new type of textile -- graphene textile has been born. The so-called graphene textile refers to the effective combination of graphene materials with ordinary textiles, that have one or more of the unique properties of graphene while maintaining the basic properties of the textile. For clothing added more functional, intelligent features, such as far and near infrared health care, antibacterial, deodorant, smart textiles[5-7] and so on. Currently, there are many products on the market about graphene textiles, but there are still few standards about graphene fibers. National standards are still blank, and methods for testing graphene in such fabrics have rarely been reported.

There are many quantitative methods of graphene in different substrates, such as ultraviolet Spectroscopy (vis), X-ray Photoelectron Spectroscopy (XPS), Programmed Thermal Analysis (PTA), Total Organic CarbonAnalysis (TOC), etc. [8-12]. Many universities and research institutions use the above methods to explore the content of graphene after separation, while graphene is difficult to disperse. For example, ultraviolet spectroscopy and XPS require good dispersion of samples[13], PTA
requires high requirements on testing instruments and is difficult to operate[14]. The TOC method is analyzed through trace element analysis[15]. Although its application on the fiber matrix has not been reported, it has great reference value for the experimental research in this paper.

In the early stage of the project, field emission perspective electron microscope was used to explore and establish a more accurate qualitative detection method. However, this method is limited to qualitative analysis of graphene textiles and cannot accurately detect the content of graphene in textiles or fibers.

The graphene in the graphene fibers was separated by programmed temperature cracking. According to the document, the stable cellulose fiber and synthetic fiber decomposition temperature 300°C-500°C [16-18]. Under oxygen condition, the residual rate is close to 0, However, the decomposition temperature of graphene and graphite is between 600°C and 700°C [19-21]. In addition, no loss of graphene can be achieved before this temperature. In this paper, the matrix material and graphite material are separated by means of phasing. This method is simple in experimental operation, no chemical reagent is needed in the experimental process, and the harm to human body and environment is avoided. The experimental process and result calculation are completed by instruments, and the experimental result error is small. Compared with other methods, this method is highly innovative.

2. Experimental work

2.1. Materials and medicines
The content is 100% viscose fiber, polyamide fiber, polyester fiber. Graphene powder, particles from different production companies, Unknown amounts of graphene fibers from different manufacturing companies.

2.2 Instruments and equipment
Thermogravimetric analyzer, Muffle furnace, Elemental analyzer

2.3 Sample pretreatment
100g of fiber was cut into pieces and placed in the crucible. The fiber was placed at 500°C and kept in oxygen environment for 1h. Some particles were taken into the container and recorded as sample 1 to be tested and put into use. The remaining samples were then placed in an oxygen environment at 800°C for 1h, and the remaining materials were taken out into the container and recorded as sample 2 to be tested. The two samples were then analyzed by element.

3. Characterization

3.1 Thermogravimetric Fourier infrared analyzer
Thermogravimetric analyzer is a common instrument for material composition analysis. The Fourier infrared analyzer is an instrument for the chemical functional groups of qualitative substances. In combination, the gas generated by the tga at high temperature can be introduced into the infrared analyzer through capillary tubes. By judging the composition of the gas produced by heating a certain substance at different temperatures and times, more detailed composition analysis can be made on the original sample.

3.2 Elemental analysis of samples
The element analyzer is composed of four parts, namely, an oxygen injection device, a high-temperature combustion furnace, a reaction tube, a mixed gas separation unit and a detector. It can simultaneously measure the content of C, H, N and S elements in the sample, and is equipped with an automatic calculation system of the instrument, with CHN and CHNS analysis mode. In this experiment, CHN model was adopted to conduct element analysis on different samples after pretreatment, and the content of graphene in the fiber was quantified by the difference of total amount of powder carbon element.
3.3 Electron microscope
SEM was used to analyze the structure and element proportion of the surface microzone before and after treatment, and to analyze the influence of heat treatment on the experimental results.

4. Result and discussion
Before using this method for quantitative analysis of samples, qualitative analysis must be conducted to determine that the fiber material is graphene material. The content of graphene in the fiber must be quantitatively detected by the thermal decomposition - element analysis technique.

The experimental results show that the quantitative limit of the method is over 2.5%, and the RSD value is 1.48%-2.50%, indicating that the experimental method meets the requirements of determining the quantitative detection method.

![Figure 1. Thermogravimetric analysis of polyester fibers mixed with pure graphene powder in different proportions](image)

Thermogravimetric analysis was observed at different addition ratios. As shown in figure 1, 100% polyester fibre in content, not the emergence of a period of 3 steps, and add the quantity in 5%, 10% and 30% when can observe an obvious weightlessness steps, using TG - FTIR spectrometry analysis under each phase cellulose decomposition of gas, in the first stage for water vapour to escape, the second phase will produce acetaldehyde, acetic acid and other chemical gases, and in the third stage only carbon oxide, fully illustrates the use of the above method can effectively remove the fiber substrate, and the full decomposition of graphite material.
Figure 2. (a-c) SEM images of residues at different stages. (d) The trend chart of carbon percentage at different stages.

Table 1. Table of quantitative test results

| Types of graphene fibers | The reference values/% | Actual measured value/% | Relative standard deviation/% |
|--------------------------|------------------------|-------------------------|-----------------------------|
| Polyester filament       | 3                      | 2.80                    | 1.52                        |
| Polyester staple         | 2.5                    | 2.20                    | 1.48                        |
| Nylon filament           | 3.5                    | 3.10                    | 2.50                        |
| Polyamide staple         | 3                      | 2.75                    | 2.43                        |

As shown in the figure above (Figure 2.), the three stages of decomposition stage 1, decomposition stage 2 and complete decomposition were observed by electron microscope.,a it was obvious that there were residual fibers, with a large number of fibers and graphite components mixed with each other(Figure2, a). As shown in, the mass loss of carbon elements in this stage was about 50%. Figure 1 shows that after b was oxidized at a high temperature of 500℃(Figure2, d), no fibrous substances could be found in the sample. After further warming, the carbon content decreased slowly, with a carbon content loss of about 15%. This process was proved to be the decomposition of high-polymerized fibers. Then, the samples were oxidized at 800℃, and the residual components were white flocculent (Figure2, d), with a carbon content of < 1%, and the main components were inorganic metal oxides. From table 1, we can conclude that the detection range of these four different types and morphologies of fibers is above 2.5%, and the standard relative deviation is between 1.5% and 2.5%.

5. Conclusion
In conclusion, we adopt the method of thermal cracking - element analysis to quantitative detection of graphene materials in fiber content, first by remove fiber muffle furnace heating, to raise the temperature again remove graphene, using elemental analyzer to determine carbon content difference before and after the experiment results show that the method had high accuracy and detection limit can be up to 2.5%, for effective supervision and detection graphene material quality has great significance on the
market. Unfortunately, the detection limit cannot be lowered to a very low level, which is challenging for the detection of low content graphene fibers.

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References
[1] S. Q. Lai, Y. Jin, L. J. Shi, and W. N. Du, Synthesis and Leather Application Properties of a Carboxylated Graphene Oxide Modified Waterborne Polyacrylate Leather Finishing Agent, Journal Of the American Leather Chemists Association, vol. 114, no. 6, pp. 204-215, Jun, 2019.
[2] K. Cherenack, and L. van Pieterson, Smart textiles: Challenges and opportunities Journal Of Applied Physics, vol. 112, no. 9, Nov 1, 2012.
[3] J. Kim, F. Kim, and J. X. Huang, Seeing graphene-based sheets, Materials Today, vol. 13, no. 3, pp. 28-38, Mar, 2010.
[4] M. J. Allen, V. C. Tung, and R. B. Kaner, Honeycomb Carbon: A Review of Graphene, Chemical Reviews, vol. 110, no. 1, pp. 132-145, Jan, 2010.
[5] A. J. Golparvar, and M. K. Yapici, Graphene Smart Textile-BasedWearable Eye Movement Sensor for Electro-Ocular Control and Interaction with Objects, Journal Of the Electrochemical Society, vol. 166, no. 9, pp. B3184-B3193, Apr 30, 2019.
[6] B. Mehrabi-Matin, S. Shahrokhian, and A. Iraji-Zad, Silver Fiber Fabric as the Current Collector for Preparation of Graphene-Based Supercapacitors,Electrochimica Acta, vol. 227, pp. 246-254, Feb 10, 2017.
[7] Y. J. Yun, D. Y. Kim, W. G. Hong, D. H. Ha, Y. Jun, and H. K. Lee, Highly stretchable, mechanically stable, and weavable reduced graphene oxide yarn with high NO2 sensitivity for wearable gas sensors, Rsc Advances, vol. 8, no. 14, pp. 7615-7621, 2018.
[8] K. Doudrick, N. Corson, G. Oberdorster, A. C. Eder, P. Herckes, R. U. Halden, and P. Westerhoff, Extraction and Quantification of Carbon Nanotubes in Biological Matrices with Application to Rat Lung Tissue,Acs Nano, vol. 7, no. 10, pp. 8849-8856, Oct, 2013.
[9] Y. M. Chen, X. G. Hu, J. Sun, and Q. X. Zhou, Specific nanotoxicity of graphene oxide during zebrafish embryogenesis,Nanotoxicology, vol. 10, no. 1, pp. 42-52, Jan 2, 2016.
[10] D. G. Goodwin, Jr., A. S. Adeleye, L. Sung, K. T. Ho, R. M. Burgess, and E. J. Petersen, Detection and Quantification of Graphene-Family Nanomaterials in the Environment, Environ Sci Technol, vol. 52, no. 8, pp. 4491-4513, Apr 17, 2018.
[11] K. Doudrick, T. Nosaka, P. Herckes, and P. Westerhoff, Quantification of graphene and graphene oxide in complex organic matrices, Environmental Science: Nano, vol. 2, no. 1, pp. 60-67, 2015.
[12] D. L. Plata, C. M. Reddy, and P. M. Gschwend, Thermogravimetry-mass spectrometry for carbon nanotube detection in complex mixtures,Environ Sci Technol, vol. 46, no. 22, pp. 12254-61, 2012.
[13] V.Mittal, L.Krauss,Compatibilized polyethylene thermally reduced graphene nanocomposites: Interfacial interactions and hyperspectral mapping for component distribution. Colloid Polym., vol.292,pp. 2509−2518,2014,
[14] K. Doudrick, P. Herckes, and P. Westerhoff, “Detection of carbon nanotubes in environmental matrices using programmed thermal analysis,” Environ Sci Technol, vol. 46, no. 22, pp. 12246-53, Nov 20, 2012.
[15] P. Saheli, R. Rowe, E.Petersen, O’Carroll, D. Diffusion of multiwall carbon nanotubes through a high-density polyethylene geomembrane. Geosynth. Int, vol.24, pp.184–197, 2017.
[16] Y.M.Ying, M.Y.Li, Y.H.Zhao, Determination of fixed carbon in graphite by high frequency
combustion - infrared absorption. Analytical testing techniques and instruments, vol.24, pp. 52-56, 2018.

[17] H.Q. Ling, G.H. Hu, X.Q. Hu, The thermal analysis-infrared - mass spectrometry system is used for the analysis of graphene materials, Analytical instruments, no.02, pp.65-68, 2018.

[18] H.J. Gong, S.J. Zhao, L. Wang, Study on determination of fixed carbon in graphite samples by high frequency infrared carbon sulfur analyzer, The geological, vol.31, no.03, pp.603-607. 2012

[19] Y.J. Chen, S.K. Yang, G.S. He, Thermogravimetric - infrared spectroscopy analysis of polyester stability at high temperature, Synthetic fibre industry, no.06, pp.38-40, 2000.

[20] M. Yang, X.L. Zhu, G.Z. Liang, TG-FTTR was used to analyze the pyrolysis process of Kevlar fiber, Spectroscopy and spectral analysis, vol.36, no.05, pp.1374-1377. 2016

[21] Y.C. Zhu, J. Zhu, Preliminary study on quantitative analysis method of thermal weight loss of textile fiber, Shanghai wool technology, no.03, pp.31-34, 2012