Determination of Fe in Graphene by Inductively Coupled Plasma Optical Emission Spectrometer

Yi Lu, Chen Gong, Lijun Wu, Hongchao Liu and Guojian Guo
Shandong Institute of Non-metallic Materials, Jinan, China.
Email: titi_ly@sina.com

Abstract. The Fe in graphene was determined by inductively coupled plasma optical emission spectroscopy. The effects of digestion temperature, digestion system, analyzing spectral line, RF power, peristaltic pump flow rate, and working gas flow rate on the measurement results were investigated respectively. The results show that the best digestion effect appear when the digestion temperature is 550 °C and the digestion system is 3ml hydrochloric acid combined with 1ml nitric acid. The most stable and reliable test results obtained when the analyzing spectral line is 259.941 nm, the RF power is 1400W, the peristaltic pump flow rate is 50r/min, the atomizing gas flow rate is 0.8L/min, and the auxiliary gas flow rate is 1.0L/min. The detection limit of the measurement result is 0.029mg/L, the relative standard deviation (n=6) is between 2.5% and 3.2%, and the recovery is between 96.3% and 108.2%.

1. Introduction
Graphene is a two-dimensional nanomaterial composed of carbon atoms and SP2 hybrid orbits in a hexagonal honeycomb shape. It is currently the thinnest and hardest nanomaterial known in the world. It has excellent optical, electrical, thermal, mechanical and other characteristics. Therefore, graphene has very good application prospects in the fields of semiconductors, biocatalysis, batteries, smart touch, superconductivity and so on. Fe is one of the main impurities in graphene. The presence of Fe significantly reduces the conductivity of graphene. Thus affecting the application of graphene in the fields of smart touch, superconducting fiber, semiconductor, biocatalysis and so on. Therefore, accurate determination of Fe in graphene is very meaningful. Inductively coupled plasma optical emission spectrometer (ICP-OES) has the advantages of less interference, wide linear range, and low detection limit. It has been successfully applied to the determination of Fe in food, soil and pharmaceutical samples. This paper applies this technique to the determination of Fe in graphene. The digestion method, ICP test conditions, detection limit, repeatability and recovery were investigated respectively.

2. Experiment

2.1. Materials and Instruments

2.1.1. Materials
GBW 08616 standard material with Fe concentration of (1000±2) mg/L is produced by the China Academy of Metrology. Hydrochloric acid is analytically pure and is produced by Sinopharm Reagent Group Co., Ltd. Nitric acid is analytically pure and is produced by Sinopharm Reagent Group Co., Ltd. Sulfuric acid is analytically pure and is produced by Sinopharm Reagent Group Co., Ltd. The
resistivity of ultrapure water is 18 MΩ•cm. The purity of argon is greater than 99.999%, which can provide a stable and clear plasma torch flame.

2.1.2. Instruments
The inductively coupled plasma optical emission spectroscopy uses the ARCOS type produced by SPECTRO of Germany.

2.2. Working Conditions of the Instrument
The ICP-OES conditional transmit power is 1400 W. The flow rate of atomizing gas is 0.8L/min, and the flow rate of auxiliary gas is 1.0L/min. The speed of the peristaltic pump is 50 r/min and the observation height is 12 mm. The cleaning time is 45s and the number of points is 3 times.

2.3. Sample Preparation
A 0.1 g graphene sample was weighed and placed in a crucible. Then ashing in muffle furnace at 550°C for 4h. After that, 3ml of hydrochloric acid was added to the ashed crucible and heat at 40°C for 20 min. After that, add 1ml of nitric acid and continue heating until all are dissolved. Transfer to a 50ml volumetric flask, and use deionized water to rinse the beads on the inner wall of the crucible repeatedly and transfer to the volumetric flask. Dilute to the mark with deionized water, then mix well, to be test.

3. Results and Discussion

3.1. Establishment of Working Curve
Standard method was prepared by volume method. Accurately transfer a certain volume of iron content analysis standard substance in water, and prepare a stock solution with a concentration of 50.0 mg/L. Then separately measure a certain volume of the stock solution and prepare an iron standard solution with a concentration of 1.0, 2.0, 3.0, 4.0, 5.0 mg/L. Measure the standard solution series under the best working conditions of the instrument. Figure 1 shows the calibration curve with the mass concentration of the element to be measured as the abscissa and the emission intensity of the element as the ordinate,. It can be seen from the figure that the working curve equation is $y = 72964x + 1812.6$, the correlation coefficient $r$ is 0.9998, and the correlation is very good.

![Figure 1. Working curve](image-url)
3.2. Digestion Conditions

3.2.1. Digestion temperature
Digestion temperatures have a greater influence on the digestion effect. If the temperature is too low, the digestion is incomplete. If the temperature is too high, the graphene burns too violently and easily flew out of the crucible, which also causes a low recovery. The recovery of different digestion temperatures were investigated separately in Figure 2. It can be seen from the figure that the recovery at 500-550°C is the best. Among them, 500°C is 106.2%, and 550°C is 102.5%. The recovery of 550°C is closest to 100%, which is the best digestion temperature for this study.

![Figure 2. Effect of digestion temperature on recovery](image)

3.2.2. Digestion system
The effects of hydrochloric acid, nitric acid, sulfuric acid, hydrochloric acid combined with nitric acid, hydrochloric acid combined with sulfuric acid, and nitric acid combined with sulfuric acid on the digestion system were investigated in Figure 3. The results show that the recovery of hydrochloric acid combined with nitric acid is the best, which is the best digestion system for this study.

![Figure 3. Effect of digestion system on recovery rate](image)
3.3. ICP Test Conditions

3.3.1. Analyzing spectral lines
The excitation energy of the ICP light source is very high, which will emit a large number of spectral lines. The spectral lines of each element are subject to different degrees of interference. Therefore, the wavelength with less spectral interference and high sensitivity should be selected. Through experiments, it is found that the 259.941 nm spectral line has higher sensitivity, less interference, and best reproducibility, which is the first choice for this study.

3.3.2. RF power
When the high-frequency power changes, the intensity of the spectrum also changes. When measured at the usual observation altitude, its intensity increases with increasing power, and the background also increases. Therefore, the power is too high, the signal-to-noise ratio not only does not increase, but decreases. But too low power will cause matrix effect, and it will make the torch flame unstable and easy to extinguish. This paper examines the change of RF power in the range of 1000–1500W, and determines that the best choice for RF power is 1400W.

3.3.3. Peristaltic pump flow rate
The flow rate of the peristaltic pump directly affects the sample injection volume. The greater the pump flow rate, the higher the atomization efficiency. However, if the pump flow rate is too large, the atomization efficiency will decrease. When the pump speed is increased to a certain degree, the emission intensity of each element tends to be constant. Therefore, choosing the appropriate flow rate of the peristaltic pump can reduce the amount of sample entry as much as possible under the premise of meeting the precision of the experiment. In this paper, the relationship between the flow rate of the peristaltic pump and the emission intensity of the spectral line is investigated, and the speed of the peristaltic pump is determined to be 50r/min.

3.3.4. Working gas flow
There are three gas flow paths in the ICP-OES analyzer. They are cooling gas, auxiliary gas and atomizing gas. The auxiliary gas and cooling gas have little effect on the intensity of the spectrum, while the atomizing gas flow has a significant effect on it. The greater the atomizing gas flow rate, the more atomization will occur per unit time. Therefore, the more substances that enter the plasma, the greater the signal strength. However, the excessively high atomizing gas flow rate will reduce the torch temperature and cause the line intensity to decrease instead. Too low a cooling gas will reduce the life of the rectangular tube, and the line intensity will be reduced. The use of auxiliary gas can avoid the adhesion of carbon particles on the nozzle. Consider that the sample entering the instrument has been fully processed into an aqueous solution, and only a small amount of auxiliary gas is needed. The final determination of the atomizing gas flow rate is 0.8L/min and the auxiliary gas flow rate is 1.0L/min.

3.4. Sample Test

3.4.1. Detection limit
After applying the same pretreatment process to the blank, it was measured 10 times in succession. The detection limit of Fe element was calculated with 3 times the standard deviation. The results are shown in Table 1.

| Measured value (mg/L) | Standard deviation (mg/L) | Detection limit (mg/L) |
|-----------------------|---------------------------|------------------------|
| 0.149                 | 0.167                     | 0.176                  | 0.152                  | 0.172                  | 0.0097                 | 0.029                  |
| 0.168                 | 0.172                     | 0.154                  | 0.154                  | 0.165                  |
3.4.2. Repeatability test
The Fe element content in the three graphene samples was measured, and it was measured 6 times in parallel. The standard deviation (SD) and relative standard deviation (RSD) of the measured values were calculated respectively. The results are shown in Table 2.

| Sample | Measured value (mg/L) | Average value (mg/L) | SD (mg/L) | RSD (%) |
|--------|-----------------------|----------------------|-----------|---------|
| 1      | 16.3 15.4 16.6 15.4 15.7 16.3 | 16.0 | 0.52 | 3.2 |
| 2      | 41.5 40.8 40.5 42.3 43.2 42.9 | 41.9 | 1.11 | 2.7 |
| 3      | 275.1 278.8 269.3 273.6 282.6 263.2 | 273.8 | 6.88 | 2.5 |

3.4.3. Recovery test
The Fe element of the three graphene samples was subjected to a recovery experiment. The test results are shown in Table 3.

| Sample | Added (mg/L) | Recovery (%) | Added (mg/L) | Recovery (%) | Added (mg/L) | Recovery (%) |
|--------|--------------|--------------|--------------|--------------|--------------|--------------|
| 1      | 8            | 106.2        | 16           | 104.7        | 24           | 98.7         |
| 2      | 20           | 98.4         | 40           | 96.3         | 60           | 103.8        |
| 3      | 140          | 103.6        | 280          | 108.2        | 420          | 106.3        |

4. Conclusion
The content of Fe element in the graphene sample was realized by ICP-OES method. The detection limit of the method was determined, and the reliability of the method was verified by repeatability experiment and spike recovery experiment. The repeatability RSD of the Fe element in the different graphene samples measured is within 3.5%, and the recovery of the spike is between 96.3% and 108.2%. The results show that it is feasible to use a muffle furnace to ash graphene samples, hydrochloric acid combined with nitric acid to dissolve the ash, and ICP-OES method to determine the content of Fe in graphene samples. This method is convenient and fast, and the data accuracy is high.

5. References
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