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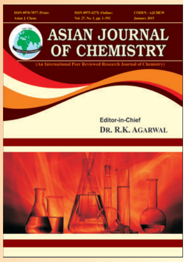

Determination of Gallium in Fly Ash by Inductively Coupled Plasma Atomic Emission Spectrometry

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The content of gallium in fly ash was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Three acids (HNO_3, HF, $HClO_4$) were used for the pretreatment of samples. RF power and carrier gas flow of ICP spectrometer were optimized. The effects of the analytical line of gallium, the amount of nitric acid and hydrofluoric acid and dissolution temperature of samples on analytical results were investigated. The detection limit of the method was 0.58 μg/g and its relative standard deviation (RSD) was 3.85 % with good precision. The recovery of this method was 94.45-105.4 %, which met the requirements of sample analysis and further validated the reliability of the method.

Keywords: ICP-AES, Three acids, Gallium, Fly ash.

INTRODUCTION

Gallium was discoverd by French chemist Buwabodelang in sphalerite extract in 1875. Accounting for 5×10^{-4} to 15×10^{-4} % in the crust, gallium is not very rare, but it can not form a relatively concentrated metal mine and it is difficult to extract, so researchers attribute scattered element to gallium. Gallium is widely used in low-melting alloy, semiconductor, superconducting materials, solid batteries, solar cells and other materials with good market prospects. Global demand for gallium is also increasing year by year, especially when GaAs is added to semiconductors and its excellent performance continues to be discovered[1,2].

Fly ash is a solid waste and contains a certain amount of gallium. Gallium in fly ash occurs in mullite and glassy containing Al_2O_3 and also its percentage increases as that of Al_2O_3[3]. Currently, the utilization of fly ash is low. According to the relevant literature[4-6], gallium can be recoverd when smelting aluminum, zinc, barium, copper, but can also be extracted from fly ash with rich gallium. Therefore, mastering content of gallium in fly ash has become the primary task of extracting gallium. Simple, rapid and accurate determination of the content of gallium in fly ash has become a major problem to solve for analysis and testing staff. There are many methods for determination of gallium and butyl rhodamine B spectrophotometric method are commonly used. However, using a variety of organic reagents with complicated extraction process, this method are not friendly to environmental protection. In recent years, inductively coupled plasma atomic emission spectrometry (ICP-AES) is used widely with good precision and accuracy,which is fully recognized[7-13]. This paper drew on the experience of previous researches[14-21], three acids *i.e.*, nitric acid, hydrofluoric acid and perchloric acid were used for the pretreatment of fly ash samples and gallium in fly ash was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), which was quick and simple with high sensitivity, low detection limit, wide linear range, high precision, good accuracy, *etc*.

EXPERIMENTAL

A Perkin Elme Optima 8000 model inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for the determination. The optimun conditions for ICP-AES are given in Table-1. Nitric acid, hydrofluoric acid, perchloric acid, hydrochloric acid were all of guaranteed reagent grade in the experiments. Deionized water was used throughout the experimental work. The containers in experiments were soaked overnight with 30 % nitric acid solution and rinsed with deionized water before use. The standard gallium solution (200 mg/L) was prepared by dissolving pure metal gallium 0.1 g in 50 mL HCl(1+1) and diluting it to suitable volume with deionized water. Gallium standard series solution (0.0, 0.1, 0.5, 1, 10 mg/L) with 5 % HCl was prepared by diluting standard gallium solution (200 mg/L).

TABLE-1
INSTRUMENT CONDITIONS FOR THE DETERMINATION OF GALLIUM

Instrument parameters	Working conditions
RF power	1300 W
Carrier gas flow	0.60 L/min
Auxiliary gas flow	0.50 L/min
Coolant gas flow	13.0 L/min
Pump speed	50.0 r/min
Vertical viewing height	12 mm

Pre-treatment of samples: The fly ash used in experiments was fine ash with its fineness of 200 mesh or more. There was a certain amount of carbon in fly ash which may affect the accuracy and precision of analytical results. Therefore, the sample needed to be ashed to eliminate the carbon. The samples were placed in a dry porcelain crucible and the crucible was placed in a muffle furnace. The temperature of the muffle furnace gradually increase from room temperature to 560 °C and then gradually increase to 630 °C after 2 h of incubation. Finally, the temperature was gradually returned to room temperature after ashing 3 h. When ashing was complete, samples were poured into a glass jar for standby which was placed in a desiccator.

A fly ash sample (0.25 g) was placed into a Teflon crucible and 10 mL of hydrofluoric acid, 3 mL of concentrated nitric acid, 1 mL of perchloric acid were added. The mixture was heated until a little solvent had remained in the electric heating plate. Then, 1 mL of $HClO_4$ was added and the temperature increase to 200 °C until a little solvent had remained. The Teflon crucible was romoved to cool and 2.5 mL of HCl(1+1) were added to make the residue dissolved completely. Then, the sample solution was transferred to tube colorimetric (25 mL) and diluted by adding deionized water until the scale mark. Finally, the content of gallium in the sample solution was determined by the ICP spectrometer.

RESULTS AND DISCUSSION

In ICP spectroscopy, there were six characteristic lines for gallium. The BEC (Background Equivalent Concentration), DL (Detection Limit), Rel Sens (Relative Sensitivity) and Intensity of the six characteristic lines were given in Fig. 1. The lower the BEC, the smaller the background interference. It was seen that the characteristic line with wavelength of 294.364 nm had the lowest BEC and DL, simultaneously, its Rel Sens and Intensity were also well. Therefore, the characteristic line with wavelength of 294.364 nm was chosen as analytical line of gallium. The spectrogram of 0.1, 0.5, 1.0 mg/L standard solution of gallium was shown in Fig. 2. It was seen that its peak shape was good, stable with high sensitivity in the wavelength of 294.364 nm by the use of synchronization background subtraction function and automatic interference factor correction method of spectrometer.

In ICP spectroscopic analysis, RF power and carrier gas flow of spectrometer were two critical parameters, which were closely associated with spatial distribution and density of electron cloud formed by exciting sample solution in spectrometer. It was shown in Fig. 3 that when RF power was increased, the intensity of gallium standard solution was also increased, which could reduce the detection limit of the analytical results.

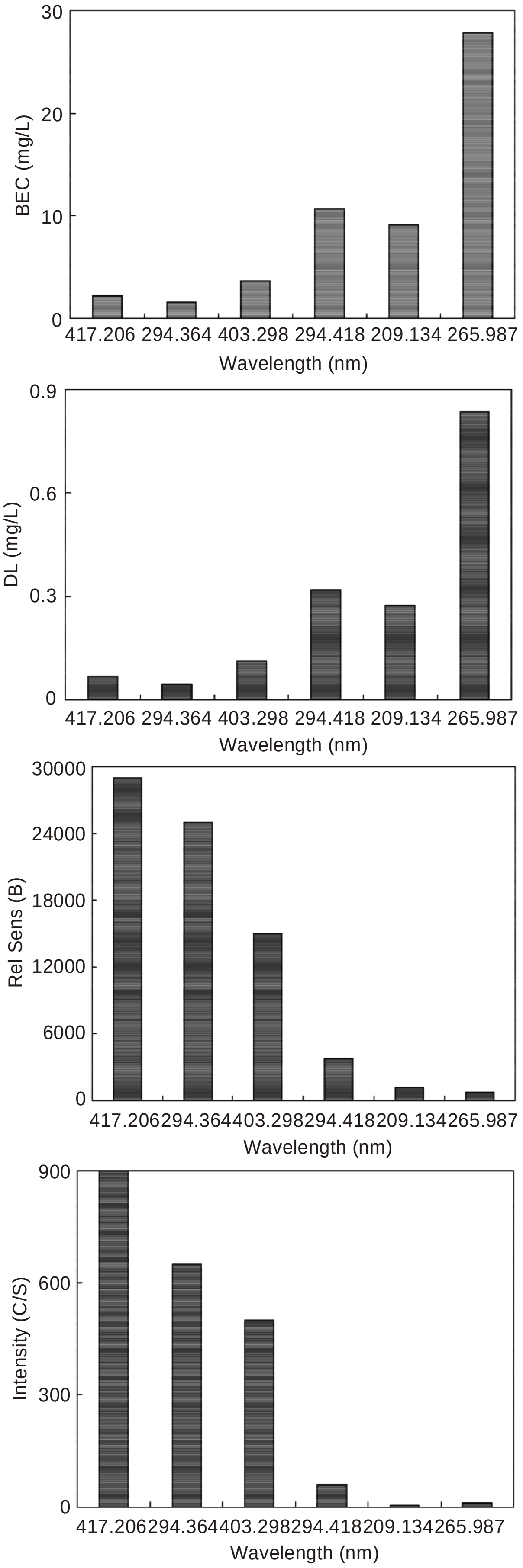

Fig. 1. BEC, DL, Rel Sens and Intensity of the six characteristic lines of gallium

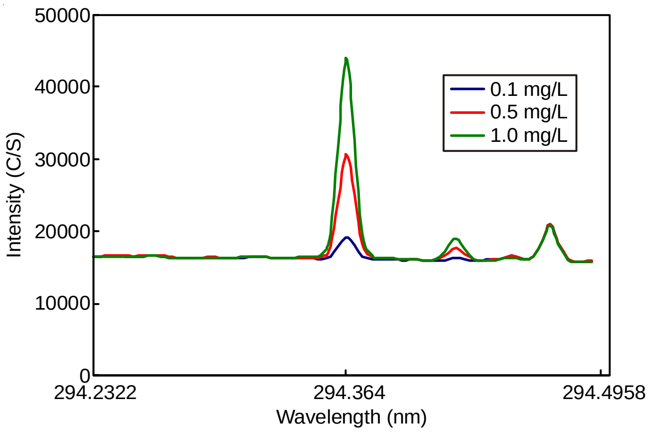

Fig. 2. Spectrogram of 0.1, 0.5, 1 mg/L standard solution of gallium

However, increasing intensity would decrease the SBR (signal backgroud ratio) of the characteristic line, which can increase the detection limit of the analytical results. Considering these two factors, the RF power of 1300 W was chosen. As shown in Fig. 3, when carrier gas flow was in the range of 0.6-0.65 L min^{-1}, the spectral intensity got the maximum. The carrier gas flow of 0.60 L min^{-1} was chosen due to the amount and cost of carrier gas.

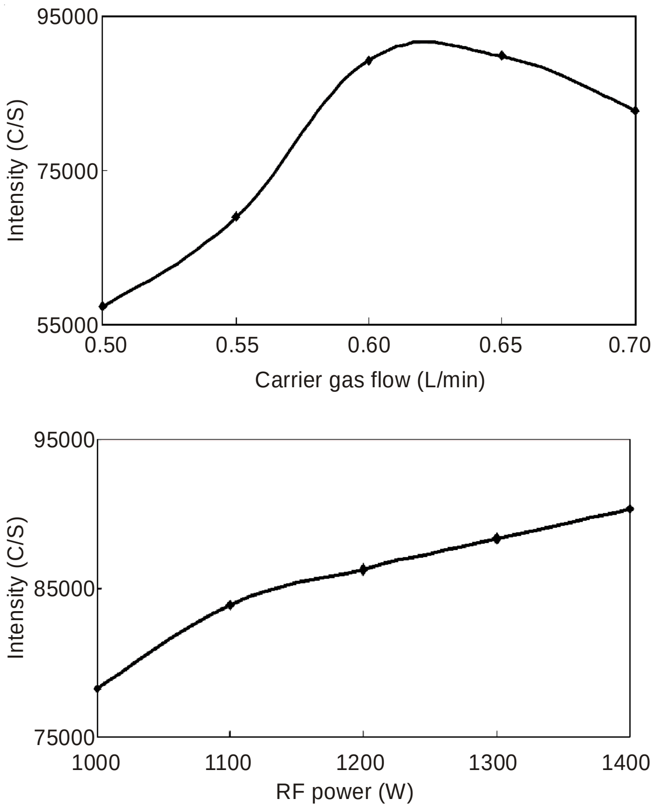

Fig. 3. Relationship between transmit power, carrier gas flow and intensity

In sample preparation, the effects of the amount of nitric acid and hydrofluoric acid on analytical results were given in Fig. 4. It was shown that the intensity of gallium was almost the same with different amount of nitric acid, but the intensity of gallium increased when the amount of hydrofluoric acid increased until it reached 10 mL. Therefore, considering the safety of the experiment (the reaction was likely to cause an explosion in the presence of HF and $HClO_4$ without HNO_3) and the reation time, 3 mL of nitric acid were taken as the best choice. When the amount of HF was in the range of 10-16 mL, the intensity of gallium was unchanged (Fig. 4), so 10 mL of HF were chosen.

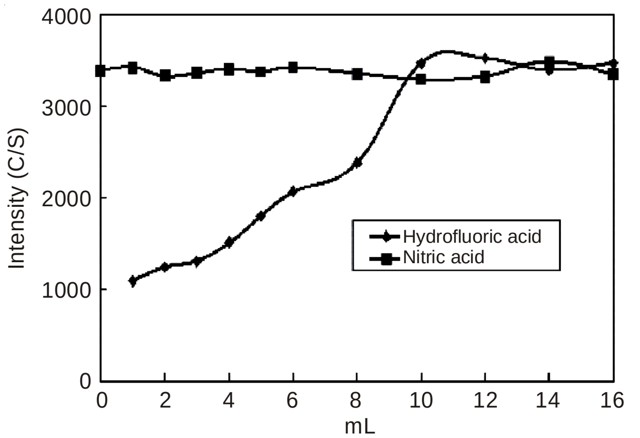

Fig. 4. Relationship between the amount of nitric acid and hydrofluoric acid and intensity

In addition, the effect of dissolution temperature on content of gallium was given in Fig. 5. It was seen that when the temperature increased, the content of gallium decreased. With the temperature rising, part of the acid evaporated before reacting completely to make incomplete dissolution of fly ash, which led to a low measurement result. As a result, 130-150 °C was chosen as the best dissolution temperature. Finally, the influence of the addition of hydrochloric acid on analytical result in sample preparation was also investigated. After hydrochloric acid was added to dissolve the sample, the content of gallium was low (Table-2). It was described that gallium in the sample reacted with HCl to produce $GaCl_3$ that was easy to volatile when temperature rising, which impacted the determination of gallium. Therefore, three acids (HNO_3, HF, $HClO_4$) were selected for the pretreatment of samples.

TABLE-2
COMPARISON OF SAMPLE RESULTS BETWEEN THREE-ACID-DISSOLUTION AND FOUR-ACID-DISSOLUTION (n = 8)

Sample dissolution method	Content of galliun in the sample (μg/g)
Three-acid-dissolution	26.71
Four-acid-dissolution	22.60

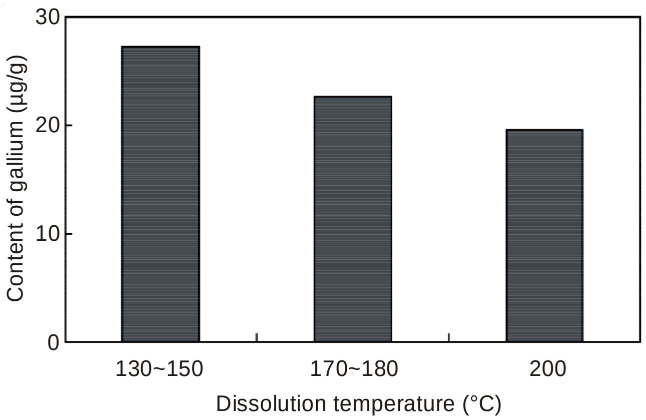

Fig. 5. Relationship between dissolution temperature and content of gallium

A blank sample was measured 10 times in the optimal working conditions of ICP spectrometer and its standard deviation was calculated. The detection limit of the method was 0.58 μg/g, three times of the standard deviation. The fly ash samples were pretreated as above method and determined by ICP-AES for ten times (Table-3). It was seen that the average content of gallium in the samples was 26.88 μg/g and the relative standard deviation was 3.85 % with good precision. The recovery experiments of the method were given in Table-4. The recovery of this method was 94.45-105.4 %, which met the requirements of sample analysis and further validated the reliability of the method.

TABLE-3
PRECISION EXPERIMENTS OF THIS METHOD

Number	Intensity (C/S)	Content of galliun (μg/g)
1	3270.6	26.04
2	3399.5	27.05
3	3140.6	26.56
4	3365.7	26.78
5	3472.7	27.62
6	3176.8	25.30
7	3750.2	28.82
8	3471.2	27.61
9	3230.8	25.73
10	3425.8	27.26
Average	3370.4	26.88
RSD (%)	-	3.85

TABLE-4
RECOVERY EXPERIMENTS (n = 11)

Number	Measured value	Standard addition	Total value	Recovery (%)
	ω (μg g^{-1})			
1#	26.23	20	47.11	104.4
2#	27.26	20	48.34	105.4
3#	27.96	20	46.85	94.45

Conclusion

In this study, the trace gallium in fly ash samples was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The fly ash samples were dissolved by three acids (HNO_3, HF, $HClO_4$). The method was optimized by adjusting working conditions of the instrument, the amount of acids, dissolution temperature of samples, *etc*. As is shown in the experimental results, the method is simple, rapid, accurate, which fulfils the requirements of sample analysis and is suitable for rapid determination of trace gallium of fly ash.

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