Determination of Al in Oxalic Acid by Laser Ablation Coupled With Inductively Coupled Plasma Mass Spectrometry

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Abstract. Oxalic acid is an important reagent in industrial production. The content of metal impurities in oxalic acid affects the quality of the product. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a widely accepted method for direct sampling of solid materials for trace elemental analysis. In this work, a matrix match external calibration was used to quantify Al in oxalic acid by LA-ICP-MS. Laser ablation instrument conditions were evaluated in order to achieve the best intensity. Calibration in the range of 50-2000 ng·g⁻¹ was used. By using the optimized parameters, limit of detection was 3.41 ng·g⁻¹. The accuracy evaluated by comparison with results obtained from solution analysis by ICP-MS after sample decomposition by microwave digestion was relatively good.

1. Introduction

Oxalic acid as an important chemical material, widely used in drug production, polymer synthesis, as well as the extraction of rare earth elements and fabric bleaching industry [1]. In electronics industry, oxalic acid is mainly used in chip cleaning and etching in primary process of integrated circuit. The concentration of metal contamination is one of the purity parameter of oxalic acid and the purity of oxalic acid has high requirements in the electronics industry. In the pharmaceutical industry, oxalic acid is also a raw material for the production of tetracycline, streptomycin, vitamin B12 and Phenobarbital [2]. Excessive intake of aluminum in the human body will disturb the activity of the central nervous system, cause digestive system dysfunction and inhibit the body antioxidant system [3]. Be strict with the concentration of trace metal contamination is the requirements of the quality to drug due to the enrichment of metals in the production process.

Analytical methods to determine Al include inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS). However these analyses require a liquid sample, therefore being necessary a decomposition step for solid samples. Routine sample decomposition is time consuming, susceptible to sample contamination and analyte losses [4]. Laser sampling has received increased attention in the past few years since the technique requires minimal amounts of sample and preparation compared to solution-based methods [5]. One of the advantages of laser ablation over solution nebulization is that laser ablation creates dry plasma. This may reduce the amount of oxygen introduced into the plasma and should therefore minimize the occurrence of interfering oxide species [6-7]. This technique has been successfully
applied to the determination of geological and biological samples. Luke Bartkus et al. obtained lead concentration in 49 ancient Chilean mummy’s hair samples on the basis of external calibration curves created using three human hair certified reference material with $^{13}$C as internal standardization [8].

However, a serious problem in LA-ICP-MS analysis of high-purity materials is the quantification of the analytical results, especially if no suitable standard reference material with the same or similar matrix composition and significant number of certified trace element concentrations is available. Matrix difference can cause element fractionation that the abundances of the ions detected after m/z separation are often not entirely representative of the composition of the original sample [9]. If matrix is met, ablation, transport, atomization, and ionization of sample and standard can be considered to be nearly identical, enabling reliable quantification. The use of external calibration utilizing certified reference materials (CRMs) or matrix matching standards are the most common forms of calibration in LA-ICP-MS. Without a suitable CRM, the semi-quantitative analysis by LA-ICP-MS of an unknown sample yields the major, minor and trace element composition very quickly.

This study presents a method to detect and quantify ng·g$^{-1}$ levels in oxalic acid samples using LA-ICP-MS. This work proposed in the present study the use of a new calibration strategy, which is based on the use of samples spiked with reference solution for the direct determination of Al in oxalic acid. Method accuracy was checked by comparison of results obtained from ICP-MS and ICP-AES analysis after sample decomposition by microwave induced combustion.

2. Experimental

2.1. Instrumentation

In this experiment the laser ablation is coupled to the inductively coupled plasma mass spectrometry (OptiMass 9500, Orthogonal Time-of Flight GBC, and Australia). The mass spectrometer plasma was generated in a quartz torch. Liquid argon of 99.996% purity (BTIC, China) was used for plasma generation and assists aerosol generated by the laser into the plasma. An Nd: YAG laser system (NWR-213, USA) operated at 213 nm, was used. The LA system is equipped with a high-resolution CCD camera and an ablation chamber. Ultra-high purity grate helium was used as carrier gas for the LA system. The experimental parameters of laser ablation and mass spectrometer measurements are summarized in table 1.

Sample ablation by LA was performed in spot scan mode. Laser ablation parameters were optimized in order to achieve the best signal and precision expressed as relative standard deviation (RSD). Laser energy from 30% to 60% and carrier flow rate from 300 to 800 mL·min$^{-1}$ were evaluated.

The microwave digestion procedures were performed with a high performance microwave digestion system (Milestone ETHOS UP, Italy), equipped with PTFE advanced composite vessels (internal volume of 55 mL, maximum operating temperature of 200°C) and sensors to monitor pressure and temperature inside the reaction vessels. A balance with resolution of 0.0001 g and maximum charge of 120 g (ME104, Germany) was used for sample weighing. An automated laboratory press (SPEX 3636, America) was used for sample pressed for LA-ICP-MS analysis.
Table 1. Operational conditions for LA-ICP-MS and ICP-MS instrument

|                             | OptiMass 9500                  |
|------------------------------|--------------------------------|
| RF power                    | 1200 W                        |
| Plasma gas flow             | 10.0 L·min⁻¹                  |
| Nebulizer gas flow          | 1.0 L·min⁻¹                   |
| Auxiliary gas flow          | 0.5 L·min⁻¹                   |
| Acquisition mode            | analogue                      |
| Acquisition time            | 36 s                          |
| Sample introduction time    | 14 s                          |
| repeat time                 | 1                             |
| Troch X                     | 10 mm                         |
| Troch Y                     | -1.9 mm                       |
| Troch Z                     | -0.2 mm                       |
| NWR-213                     | 213 nm                        |
| Ablation mode               | Spot                          |
| Energy                      | 30%                           |
| Spot size                   | 60 μm                         |
| Rep rate                    | 20 Hz                         |
| Depth                       | 5 μm                          |
| Dwell time                  | 30 s                          |
| Carrier flow rate           | 700 mL·min⁻¹                  |

2.2. Reagents and chemicals

All solutions were prepared using 18.25 MΩ deionized water (DIW) produced by a water purification system (Kertone, China). Aluminium stock reference solutions containing 1000 μg/mL (GSB 04-1717-2004) was used for standard preparation. The working solutions were prepared by diluting the stock solutions with 2% (v/v) HNO₃ immediately before use. The nitric acid (HNO₃) was electronic-grade.

2.3. Sample preparation

For elements quantification in oxalic acid by LA-ICP-MS, oxalic acid was used as matrix. These solutions were added to each 0.7 g oxalic acid in the concentration range 50 to 2000 ng·mL⁻¹ of Al. Solution were prepared in a mixture of 2% (v/v) of nitric acid. The corresponding analyte concentration (in ng·g⁻¹) on each Oxalic acid was provided considering the oxalic acid mass and the volume of each reference solution. Then the oxalic acid was dried at 60°C by an air dry oven (Yiheng, China). The blank was prepared by adding only the solvent into the Oxalic acid. After dried, the powered samples were grinded by using agate mortar, then pressed at 20 t for 30 s in order to form pellets of 13 mm diameter and 2 mm thickness.

3. Results and discussion

3.1. Optimization of the ablation conditions

Laser energy of 3.72, 6.07, 8.37, 10.25 J·cm⁻², corresponding to 30%, 40%, 50% and 60% of the total laser energy output, respectively, were evaluated. It was observed in Fig. 1 that the intensity was increased first and then decreased with the increase of laser energy. And the relative standard deviation (RSD) was increased. Therefore, laser energy of 3.72 J·cm⁻² was applied for subsequent experiments.
The flow rate of helium was also evaluated from 0.4 to 0.7 L·min⁻¹ in Fig. 2. It was observed that the intensity of Al increased by increasing the flow rate. The precision of the elemental signal tends to stabilize as the flow rate increases. In subsequent experiments, the flow rate of helium was fixed at 0.5 L·min⁻¹.

The pulse repetition rate can affect the amount of samples mass removed and consequently the sensitivity and precision of the results. Lower repetition rate will result in less sample ablation, therefore poorer sensitivity, but higher repetition rate will make the laser beam output unstable. Fig 3 was showed the effect of the repetition rate at 2, 5, 10 and 20 Hz on the signal intensity of Al. As can be observed, the signal intensity increased by increasing the repetition rate from 2 to 20 Hz. To get a better intensity, the pulse repetition rate was set 20 Hz in present work.
Figure 3. Effect of pulse repetition rate on the signal intensity (n=3)

3.2. Analytical performance

3.2.1. Matrix match external calibration. External calibration utilizing standard solution which match the composition of the sample, to the largest possible extent, is the another reliable method for accurate quantification in LA-ICP-MS. If this prerequisite is met, ablation, transport, atomization, and ionization of sample and standard can be considered to be nearly identical, enabling reliable quantification.

In this work, the oxalic acid powders spiked with a known concentration of the elements were used. The calibration curves were generated from the oxalic acid powders spiked with a series of known concentration of the elements in an effort to match the matrix and ablation characteristics of the other oxalic acid samples. Sample preparation is described in the preceding (2.3 Sample preparation). Calibration curves with the concentrations from 50 ng·g⁻¹ to 2000 ng·g⁻¹ for Al were performed. All signal intensities were corrected to the gas blank. Limit of detection (LOD) were calculated considering B+3s, where B is the value of the gas blank and s corresponds to standard deviation of the same blank [10]. The correlation coefficient of the calibration curve was 0.989. The limit of detection was 3.41 ng·g⁻¹.

Table 2. Result (ng·g⁻¹) of Al determination in oxalic acid samples by LA-ICP-MS and ICP-MS

| Sample    | A     | B     | C     | D     | E     | F     |
|-----------|-------|-------|-------|-------|-------|-------|
| LA-ICP-MS | 286±27| 247±50| 189±13| 219±27| 377±46| 1.39±0.90 |
| ICP-MS    | 172±5.6| 87.8±5.7| 107±6.5| 105±6.5| 150±6.5| 1.83±3.4 |

*: μg·g⁻¹

Samples were analyzed by ICP-MS after decomposition by microwave digestion system. Result of ICP-MS was used in order to verify the accuracy of the LA-ICP-MS method. It was observed that, the result of LA-ICP-MS is of nearly 1.5 to 3 times comparing with the result of ICP-MS, which can be attributed to the poor precision to low concentration and low signal intensity of the isotope monitored. But for higher concentration of Al, the accuracy of the measurement is greatly improved.

4. Conclusion

This study has demonstrated the utility of laser ablation inductively coupled plasma mass spectrometry for determination Al of oxalic acid. Matrix match external calibration in LA-ICP-MS is a possibility quantification strategy, with LOD of 3.41 ng·g⁻¹. The proposed method overcomes the limitations of the lack of standard reference material with the same matrix composition or a significant number of certified trace element concentrations in certified reference materials. Compared with the traditional
methods, the proposed method offered several benefits including shortened sample preparation time, reducing the possibility of sample contamination and decreasing the possibility of analysis.

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