Determination of Aluminum in Bamboo Pulp Black Liquor by ICP-AES

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Sodium aluminosilicate scaling in evaporators during alkali recovery is often associated with the concentration of aluminum and silicon in black liquor. The scaling problems are widespread during the utilization of non-wood raw materials. This study established a fast, reliable, and precise method to determine the aluminum concentration in bamboo black liquor by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Prior to ICP-AES measurements, black liquor samples were digested in an automatic electric heating assisted digestion system. After optimizing the digestion, ICP-AES testing showed that the recovery of the element was 96.2% to 99.9% and the relative standard deviation (RSD) was 0.07% to 0.52%. Additionally, comparative data for the concentration of analytes was obtained by flame atomic absorption spectrometry (FAAS). This technique will be useful for assessing the scaling properties of black liquor in the alkali recovery phase.

Keywords: Inductively coupled plasma-atomic emission spectrometry (ICP-AES); Black liquor; Aluminium concentration

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INTRODUCTION

Wood is the most widely used raw material in the pulp and paper industry, but its availability is limited in many forest-deficient countries. Due to the shortage of forest raw materials, non-woody fibrous raw materials are being used in the paper industry in Asia and other parts of the world (Ma and Zhang 1995). China uses a substantial proportion of non-wood raw materials such as bamboo, straws, reeds, and bagasse. However, non-wood materials generally have higher inorganic content, which can be comprised of more than 60% silica (Zhong 2002). Most silica in raw materials passes into black liquor during the alkaline pulping process. Pulp and papermaking processes are adversely affected by silica in raw materials, especially in evaporators, recovery furnaces, causticization, and lime kiln operations (Jeyasingam 1986). Thus, different techniques have been developed to remove silica from black and green liquors, including the addition of cations (bentonite and alumina) and reduced pH (Latour *et al*. 2013; Lin *et al*. 2014).

Black liquor is one of the main by-products of the pulp paper industry. In fact, it has considerable fuel value, and the residual chemicals can be used for pulping if it is used in an appropriate way. Otherwise, it can be a pollutant for some small pulp and paper mills (Zaied and Bellakhal 2009). Black liquor from bamboo pulp contains organic materials (lignin, polysaccharides, and resinous compounds of low molecular weight) and inorganic compounds (sodium hydroxide, sodium silicate, and other soluble salt ions) in an aqueous medium.

It is difficult to find a more accurate method to characterize the properties of black liquor due to its complicated chemical composition, even though TAPPI and SCAN methods are widely available. Due to the incorporation of desilication agents (sodium aluminate and aluminium sulfate) during the cooking process that affect the scaling properties of black liquor, the concentration of trace elements such as silicon and aluminum should be determined.

Atomic spectroscopy is used to quantify metal ions in many industries. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an easy, rapid, and accurate method to determine trace elements (Daskalova and Boevski 1999). ICP-AES and inductively coupled plasma mass spectrometry (ICP-MS) techniques are versatile analytical approaches for identifying the histories of individuals living in ancient and contemporary times through the determination of lead, zinc, and strontium concentrations in deciduous teeth (Webb *et al*. 2005).

The content of minor and major elements in apples, including silver, aluminum, barium, calcium, cadmium, cobalt, chromium, copper, potassium, manganese, magnesium, sodium, nickel, lead, strontium, and zinc, can be determined by ICP-AES. Additionally, barium, chromium, cadmium, manganese, lead, and zinc in atmospheric particulate matter can be identified with ICP-AES; in this case, the ICP-AES results agree well with those acquired by flame atomic absorption spectroscopy (FAAS) and direct current arc (DCA)-AES methods (Boevski *et al*. 2000). Moreover, it is a fast, reliable, and precise method for the determination of barium, zirconium, thorium, uranium, lanthanum, cerium, europium, hafnium, and gadolinium in simulated hydrogeological leaching solutions containing up to 1 mol/L $FeCl_3$ by ICP-AES (Ayranov *et al*. 2009). Up to 15 kinds of impurity elements in a vanadium-aluminum alloy have been simultaneously detected by ICP-AES, including boron, tungsten, silicon, iron, lead, tin, arsenic, nickel, chromium, cobalt, copper, phosphorus, manganese, magnesium, and molybdenum (Yonga 2011).

Furthermore, ICP-AES is used to certify the cleanliness of processing equipment by determining the lithium in validation swabs, and it can be used to determine the concentration of eight essential elements (P, K, Ca, Mg, Cu, Fe, Mn, and Zn) in brown rice grains (Ogiyama *et al*. 2008; Lewen and Nugent 2010).

ICP-AES has the advantages of low cost, rapid analysis, wide linear range, and low detection limit (Qinghua *et al*. 2012; Carlini *et al*. 2014). Moreover, the simultaneous determination of multiple elements is a tremendous benefit of ICP-AES. Recently, the microwave digestion method has become more common because of its fast dissolution, good dissolving effect, simplicity, safe, easy control, low evaporation losses, multiple samples digestion, and good reproducibility (Alloncle *et al*. 2009; Afonso *et al*. 2010).

Only rare recent data can be found for the determination of minor and major elements in bamboo pulp black liquor by ICP-AES (Abha *et al*. 2001; Taylor and McGuffie 2007). In this report, ICP-AES was used to examine the concentration of aluminum ions in bamboo pulp black liquor, and this data was compared with data obtained by FAAS. The scaling problem in pulp and paper mills has a close correlation with the chemical ions such as silicon, calcium and aluminum. Hence, this study will aid future work, especially studies of the scaling properties of black liquor in alkali recovery systems.

EXPERIMENTAL

Materials

Bamboo black liquor was obtained by the laboratory kraft cooking process with NaOH and Na_2S as active pulping chemicals. Aluminum salt desilication agents were loaded in this cooking phase. The black liquor samples were placed into a 500-mL beaker at 20 °C.

Instrumentation

All ICP-AES measurements were carried out on an IRIS Intrepid II instrument (Thermo Fisher, USA). The specific operational conditions of the instrument are listed in Table 1. An automatic controlled electric heating digestion system was used to digest the samples. FAAS (AAnalytst 400, PerkinElmer, USA) was used to determine the aluminum concentration in the digested black liquor samples.

Table 1. ICP-AES Instrumental Parameters and Operational Conditions

Power	1200 W
Radio Frequency (RF)	27.12 MHZ
Auxiliary Gas Flow	0.2 L/min
Cooling Gas Flow	14 L/min
Nebuliser Gas	15~45 psi
Nebuliser	Pneumatic (glass concentric)
Spray Chamber	Glass cyclonic
Plasma Viewing	Axial
Replicates for Each Run	3
Wavelength of Analysis	309.27 nm

Reagents and Standards

Concentrated nitric acid (AR) was supplied by the Tianjin Tianli Chemical Reagent Co., Ltd., Tianjin, China. Hydrogen peroxide (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. A standard solution of aluminum (1000 μg/mL) was purchased from the National Center for Analysis and Testing of Nonferrous Metals and Electronic Materials, Beijing, China. All glassware was cleaned with nitric acid prior to use. Only deionised water was used.

Solvent Selection and Digestion Parameters

To determine the aluminum concentration in black liquor, it is first necessary to develop a procedure that would adequately dissolve organic materials (lignin, polysaccharides, and resinous compounds) and remain compatible with ICP-AES. Organic materials are not readily soluble in deionized water and must be dissolved in acid solution. Because ICP-AES performs well when samples are dissolved in either deionized water or dilute nitric acid, a nitric acid digestion procedure was selected.

To determine the amount of acid required to digest black liquor, 3 mL of black liquor was digested for 30 min at 90 °C with 25 wt.%, 50 wt.%, and 65 wt.% nitric acid. The 65 wt.% nitric acid solution produced the most favorable digestion. To determine the proper time period for digestion, the sample was digested for 10, 20, 30, 40, and 60 min using 10 mL of 65 wt.% nitric acid and 10 mL concentrated hydrogen peroxide (30 wt.%). All samples, digestion solutions, and blank solutions were measured in triplicate. The digestion process is illustrated in Fig. 1.

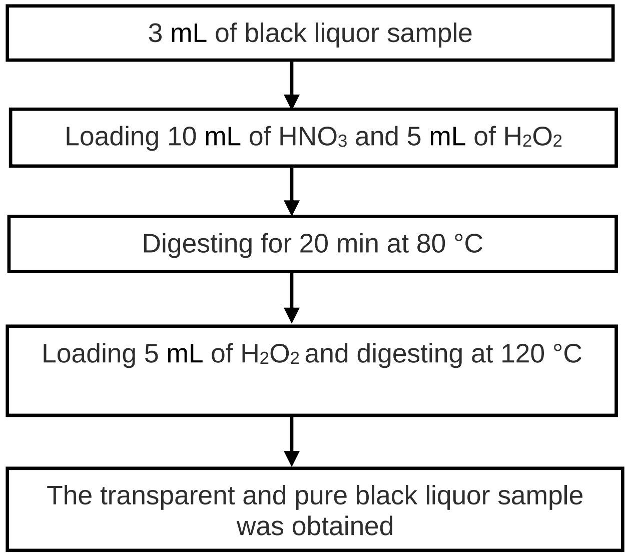

Fig. 1. Flowchart diagram of the digestion process

Preparation of Samples

Black liquor without aluminum salt silica removal agents was the control specimen, and the test samples were black liquor cooked with aluminum salt desilication agents. Digested black liquor was placed into a 100-mL volumetric flask, and 5 mL of concentrated nitric acid was added. The sample was allowed to cool completely before the contents were diluted to a final volume of 100 mL with deionized water.

Experimental Procedure

Following calibration of the instrument, aluminum standard solutions were used to determine the linearity of the method. A series of samples were spiked and digested (Fig. 1) to determine the accuracy of the digestion procedure. After digestion, the samples were allowed to cool and diluted to a final volume of 100 mL with deionized water. The samples were then analyzed by ICP-AES and FAAS. The relative standard deviation (RSD) was exported by the computer control system of the ICP. The recovery P of the element was calculated as follows,

$$P = \frac{C_2 - C_1}{C_3} 100\% \tag{1}$$

where P is the recovery, c_1 is the concentration of the sample, c_2 is the concentration of the sample after adding the standard reagent, and c_3 is the volume of standard added.

RESULTS AND DISCUSSION

Linearity

The linearity of the method was analyzed with five standard solutions containing 0 to 5.0 μg/mL aluminium (Table 2). The linearity study demonstrated acceptable linearity and recovery for aluminum, with a correlation coefficient of 0.9988.

Table 2. Linearity of Aluminum Standards

Prepared Concentration of Al (μg/mL)	Measured Concentration of Al (μg/mL)
0	0.000
1.0	1.041
2.0	2.119
3.0	2.999
4.0	3.999
5.0	4.987
Correlation Coefficient = 0.9988	

Accuracy

Because the tested black liquors were cooked with different amounts of aluminum salt desilication agents (0.09 wt.% to 0.65 wt.%), their residual aluminum contents were unequal. Consequently, black liquor samples 1 to 5 had different aluminum concentrations (Table 3). For each sample, six independent replicates of digestion and ICP-AES were performed. The relative standard deviation showed that the method was precise, and the recoveries of the samples were all acceptable (Table 3).

Table 3. Precision of the Measurement (n = 6)

Element	Wavelength (nm)	Sample	Average (μg/mL)	Standard Deviation (μg/mL)	RSD (%)	Recovery (%)
Al	396.125	1	3.791	0.003	0.0739	96.25
		2	3.963	0.007	0.1707	98.56
		3	5.014	0.010	0.2046	99.89
		4	5.266	0.020	0.3878	98.20
		5	9.306	0.049	0.5225	99.47

FAAS Analysis

To verify the precision of the ICP-AES technique, FAAS measurements of the aluminum in samples 1 through 5 were performed (Table 4). The average aluminum concentration in each sample was close to the ICP-AES measurement. The FAAS technique had a favorable precision with an RSD of 1.37% to 1.40%. These results demonstrated that the ICP-AES technique accurately determines the aluminum concentration in bamboo pulp black liquor.

Table 4. FAAS Measurements (n = 6)

Sample	Average (μg/mL)	Standard Deviation (μg/mL)	RSD (%)
1	5.569	0.0761	1.37
2	5.664	0.1266	2.23
3	7.205	0.0095	0.13
4	7.576	0.1026	1.35
5	9.842	0.1377	1.40

Analysis of Samples

Five batches of digested black liquor samples were analyzed for their aluminum concentration. The aluminum concentration in black liquor produced from the cooking phase was below 10 μg/mL, with desilication agents in the range of 0.09 wt.% to 0.65

wt.%. The RSD obtained from ICP-AES measurements was below 0.5225%, indicating that the ICP-AES technique is a satisfactory method to determine the aluminum content in bamboo pulp black liquor. Compared with the FAAS technique, the data obtained by these two methods basically agree with each other, regardless of some errors. The average concentrations of the aluminium determined by these two techniques were between 3.791 and 9.842 μg/mL, and the data was similar in the parallel experiments.

The absorbance values in the organic phase (calculated by the FAAS technique) are greatly dependent on the kind of atom bound to the metal. Thus, in spite of the accuracy obtained by the two methods for black liquor samples, there were some discrepancies. Another possible reason for these discrepancies is the use of a calibration curve. In sum, the ICP-AES technique can be applied to the analysis of aluminum concentration in pulp black liquor.

CONCLUSIONS

1. ICP-AES saves time and effort and reduces environmental pollution. It exhibits the superior properties of small matrix effect, good stability, high sensitivity, high analysis speed, and good accuracy.
2. ICP-AES was used to determine the aluminum content of bamboo pulp black liquor. The method was optimized and validated for samples after assisted digestion.
3. The method exhibited good accuracy, with the standard deviation in the detected concentration ranging from 0.003 to 0.049 μg/mL, and good recovery (96.25% to 99.89%). There were no statistically significant differences between the aluminium concentrations measured by ICP-AES and FAAS.

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