



## Determination of Trace Lead in Cigarette Paper by Flame Atomic Absorption Spectrometry

YUPING WU<sup>1,2</sup>, QUNFANG ZHANG<sup>2</sup>, LU WANG<sup>2</sup>, ZHONGBI SU<sup>2</sup>, BING HE<sup>2</sup> and GUANGYU YANG<sup>2,\*</sup>

<sup>1</sup>Yunnan Academy of Tobacco Agriculture Sciences, Yuxi 653100, Yunnan, P.R. China

<sup>2</sup>Key Laboratory of Tobacco Chemistry of Yunnan Province, Yunnan Academy of Tobacco Science, Kunming 650106, P.R. China

\*Corresponding author: E-mail: ygyl110@163.com

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A reliable and simple method for the determination of lead in cigarette paper by flame atomic absorption spectrometry is reported. The cigarette paper was ashed with microwave ashing at 450 °C. The ashes were dissolved in nitric acid and the lead in sample solution was determined by flame atomic absorption spectrometry. Under the optimum condition, the linear range for lead is 0.05-5.0 µg/mL. The detection limit reaches 0.02 µg/mL, when the samples were added with lead, the standard recoveries were ranged from 93-97 %. The relative standard derivation of overall intra-day variation was 2.6 % and the relative standard derivation of inter-day variation was 3.2 %. This method is simple, sensitive and accurate. It can be applied for determination of lead in cigarette paper with good results.

**Key Words:** Microwave ashing, Cigarette paper, Lead, Flame atomic absorption spectrometry.

### INTRODUCTION

Lead is one of the elements that had received considerable attention, due to both its extensive use and high toxicity<sup>1-3</sup>. The determination of traces of lead in a variety of environmental samples is of great importance since lead is recognized as a cumulative poison to animals and human beings. For the determination of trace amounts of lead, usually employ atomic absorption spectrometry (AAS), cold vapour AAS, electrothermal atomization-AAS or flame-AAS<sup>4-7</sup>, inductively coupled plasma-optical emission spectroscopy (ICP-OES)<sup>8,9</sup>, chromatography (usually HPLC)<sup>10,11</sup> and photometry<sup>12,13</sup> etc.

For most of the analytical techniques, the lead should be dissolved in an aqueous solution before determination. For this reason, it is necessary to isolate the lead from the organic or inorganic matrix surrounding them prior to the analysis. It involves sample solubilization or total mineralization which can be accomplished by various wet or dry ashing procedures<sup>14-16</sup>. The dry ashing procedure is safe, few reagents are required, not labor intensive and can prepare large sample size<sup>15,17,18</sup>. However, the routine dry ashing also has its disadvantages for long time required, muffle furnaces are quite costly to run due to electrical costs, loss of volatile minerals at high temperatures.

Recent advances in microwave technology have been supplied by the chemists with simpler methods of analysis, as well as the ability to perform these analyses in a time-frame conducive to efficient plant operation. Microwave ashing is a breakthrough for quality control and rapid sample preparation<sup>18-20</sup>.

Microwave instruments greatly reduce the time required to carry out an ash analysis, with the analysis time often being less than 1 h. It is also greatly reduce energy consumption. In this manuscript, the determination of lead in cigarette paper by microwave ashing and flame atomic absorption spectrometry was studied. By microwave ashing, a large sample size (5 g) can be prepared. The content of Pb<sup>2+</sup> in sample solution is much higher than that of wet ashing or microwave digestion method. The prepared sample can be directly determined by flame atomic absorption spectrometry. The proposed method is simple, rapid and reliable.

### EXPERIMENTAL

Shimadzu AA 6300 atomic absorption spectrometer furnished with a lead hollow-cathode lamp was used. The instrument was adjusted according to the standard conditions: Lamp current 6.0 mA, wavelength 217.0 nm, air-acetylene flame (air flow rate 3.7 L/min, acetylene flow rate 1.1 L/min), the spectral band width 0.5 nm. The microwave ashing was performed on a CEM PHOENIX AIRWAVE microwave muffle furnace (1400 W ± 50 W, 15A mps) and 50 mL porcelain crucible was used.

A stock standard solution of lead (1 mg/mL) was obtained from Chinese Standard Center. The working solution used was prepared by diluting this stock solution with 5 % (v/v) nitric acid. The nitric acid used is super special grade (Merck & Co., Inc.). All solutions were prepared with ultrapure water obtained from a Milli-Q50 SP Water system. The ware used

were soaked in 5 % (v/v) nitric acid over night and then thoroughly washed with pure water.

**Preparation of sample and standard:** The cigarette paper samples (5 g) were weighed into porcelain crucibles and heated in a microwave muffle furnace. The heating process was performed by slowly increasing the temperature (25 °C/min) to 450 °C and then keeping the temperature for 40 min. After cooled, the ashes were dissolved in 10 mL of 50 % (v/v) nitric acid and evaporated to about 5 mL on an electric hot plate. The residue was transferred into 25 mL volumetric flask and diluted to the mark with 5 (v/v) nitric acid. The working standard solutions of 0.1, 0.5, 1.0, 2.0, 4.0, 8.0 µg/mL were prepared by diluting the lead stock standard solution with 5 % (v/v) nitric acid.

## RESULTS AND DISCUSSION

**Sample ashing:** The influence of temperature on the samples ashing was studied. For this purpose, 5 g of sample was ashed at different temperature (300, 350, 400, 450, 500, 550, 600, 650 and 700 °C). The results showed that the cigarette paper sample can be ashed completely when the temperature reaches 450 °C. However, the recovery of lead decrease obviously when the temperature above 650 °C because the higher temperature can cause the lead losses. Therefore the ashing temperature of 450 °C was selected in this experiment.

The effect of ashing time on the sample ashing was studied. It was found that the sample can be ashed completely at 450 °C for 35 min. Stretch the ashing time up to 150 min cannot cause the lead loss. Therefore, the ashing time of 40 min was selected in this experiment.

The effect of sample size on the sample ashing was studied. It was found that the sample can be ashed completely when the sample size below 8 g. An increase in the ashing temperature or stretch the ashing time is needed when the sample size above 8 g. Therefore, the sample size of 5 g was selected in this experiment.

**Calibration graphs and detection limits:** Under the FAAS analysis conditions, the regression equation of Pb(II) was established based on the standard samples injected and their absorption signals. The results showed that the linearity range for lead was obeyed in the range of 0.05-5.0 µg/mL and the linear regression equation obtained was:  $A = 0.00217 + 0.0484 C$  (µg/mL),  $r = 0.9996$ .

The limit of detection (LOD) of this method for the determination of lead was studied under the optimal experimental conditions. The limit of detection was obtained<sup>21</sup> from  $CLOD = K_b S_b m^{-1}$ , where  $S_b$  is the SD of the blank measurements (ten replicates),  $m$  is the slope of the linear calibration graph and  $K$  is a confidence factor equal to 3. The limit of detection of the method was found to be 0.012 µg/mL.

**Interference study:** The influence of matrix ions on the recovery of Pb<sup>2+</sup> was investigated. The results showed that 10000-fold of alkaline and alkaline-earth ions, chloride, nitrate, hydrogen, 5000-fold of carbonate, 1000-fold Zn(II), Fe(II), Ni(II), Pd(II), V(III), 500-fold Mn(II), Cu(II), Hg(II), Al(III), Mo(VI), Co(II), Cr(III), Ag(I), 100-fold Cd(II), Hg(II) did not interfere the determination. This method is highly selective for Pb(II) and interferences did not occur.

**Method precision and recovery:** The measurements of intra-day and inter-day variability (determination of the same samples for seven times) were utilized to evaluate the precision of the developed method. The results shown that the relative standard derivation of overall intra-day variations were less than 2.6 % and the relative standard derivation of inter-day variations were less than 3.2 %. This method is high precision.

The recovery tests were carried out by adding lead standard to the samples (three different concentrations of markers: 0.5, 1.0 and 5.0 µg). The sample was prepared as above sample preparation procedure and afforded to FAAS analysis. The results shown that the recoveries ( $n = 5$ ) were ranged from 93-97 %. This method is high recovery.

**Application to real samples:** The method was applied to the determination of lead in cigarette paper. The results (deducted the reagents blank) were given in Table-1. A standard method using graphite furnace atomic absorption spectrometry (GFAAS) and microwave digestion had also been used as reference method and the result were also shown in Table-1. The results showed that the determination results of this method are agreed with that of GFAAS method. The precision of method is higher than that of GFAAS method.

## Conclusion

In this method, the microwave ashing was used as sample preparation method. The dry ashing procedure is safe, few reagents are required, not tedious process and can prepare a large amount of sample. This method also can avoid the disadvantage of long time required for the routine dry ashing procedure. Only about 1 h is needed for ash a set of samples. Compared to the routine dry ashing procedure<sup>22-24</sup>, more than 50 % of time was saved. By microwave ashing, a large amount of sample can prepared. The content of Pb<sup>2+</sup> in sample solution (5 g sample to 25 mL of measured solution) was much higher than that of wet ashing or microwave digestion method (0.5 g sample to 25 mL of measured solution). The trace lead in sample can directly be determined by flame atomic absorption spectrometry without any preconcentration. This can avoided the disadvantage of low sensitivity for FAAS. In a word, this method is simple, rapid and reliable. It can be applied to the determination of lead in cigarette paper with good result.

TABLE-1  
DETERMINATION RESULTS OF THE WATER AND BIOLOGICAL SAMPLES

Samples	GFAAS method			Present method		
	Found (mg/kg)	RSD % (n = 5)	Recovery (%)	Found (mg/kg)	RSD % (n = 5)	Recovery (%)
HTLY-1	0.688	5.2	94	0.667	3.2	95
HTLY-5	0.963	4.8	96	0.904	2.8	96
HTLY-22	1.26	4.2	102	1.14	2.5	94
HTLY-44	2.75	3.9	93	2.62	2.6	95

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