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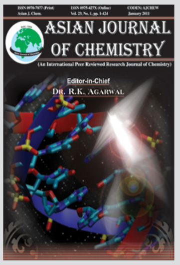

Ultrasonic Acid Digestion and Graphite Furnace Atomic Absorption Spectrometry for the Determination of Heavy Metal Ions in Tobacco

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An ultrasonic acid digestion and graphite furnace atomic absorption spectrometry method for the determination of trace amounts of heavy ions (chromium, nickel, cobalt, copper, cadmium and lead) in tobacco was studied. The tobacco samples were digested with ultrasonic assisted acid digestion. The parameters influencing ultrasonic assisted acid digestion, such as presonication time, sonication time, temperature of ultrasonic bath and different acid mixtures were carefully optimized. This procedure was applied to the determination of the analytes in tobacco samples with good results (recoveries greater than 95 % and RSD % lower than 3.5 %).

Key Words: Ultrasonic acid digestion, Tobacco, Heavy metal ions, Atomic absorption spectrometry.

INTRODUCTION

Heavy metals pollution is of great concern because their toxicity threatens the human life and the environment. Therefore, the determination of trace heavy metal ions in tobacco and tobacco additives is important[1-3]. For heavy metal determination, the quality of the analytical results mainly depends on the sample pre-treatment stages and on the detection system[4,5], particularly for determination of elements with low concentration in the samples. The most common methods used for the determination of heavy metal ions involve highly sensitive spectroscopic techniques, such as atomic absorption spectroscopy[6,7], atomic fluorescence spectroscopy[8,9], inductively coupled plasma-optical emission and mass spectrometry (ICP-AES and ICP-MS)[10-12]. These techniques generally require the destruction of the sample to render a solution of the analyte ready for analysis[13]. Also, the sample preparation step required more than 60 % of the total time to perform the complete analysis and is responsible for 20 to 30 % of the total analysis error[14,15].

Sample digestion techniques, such as microwave and conventional wet acid digestion for total metals determination have been used widely for the dissolution of elements[16-18]. Such digestion techniques require the use of concentrated acids and high temperatures and often-high pressures, to affect the total dissolution of elements from solid samples. Ultrasonic acid digestion is one of the techniques that have shown promise for speeding up and simplifying sample treatment, with minimal contamination, low reagent consumption and generation of minimal residue or waste[19,20]. In this work, the ultrasonic acid digestion and graphite furnace atomic absorption spectrometry method for the determination of trace amounts of chromium, nickel, cobalt, copper, cadmium and lead in tobacco was studied. Parameters influencing ultrasonic acid digestion such as presonication time, temperature of ultrasonic acid digestion bath and sonication time were investigated. Measurements were carried out by graphite furnace atomic absorption spectrometry.

EXPERIMENTAL

A Perkin-Elmer Model A Analyst 600 graphite-furnace atomic absorption spectrometer equipped with a Model AS-800 autosampler (Norwalk, CT) was used with monoatomic hollow cathode lamps. The ultrasonic acid digestion was carried out with a Sonicor, Model No. SC-121TH, (Sonicor Instrument Corporation Copiague, N.Y., USA) with technical specifications; timer 0-30 min, volts 220 V, 50/60 Hz, intensification frequency 35 kHz, programmable for temperature ranging from 0 to 90 °C and a total volume of 4 L. Beckman Φ-200 pH meter was used for the pH measurements.

Hydrogen peroxide (30 %), nitric acid (65 %), perchloric acid (60 %) and hydrochloric acid (37 %) were spectroscopic grades (Merck, Darmstadt, Germany). The calibration curve was established using the standard solutions prepared in 1.0 % (m/v) of HNO_3 by dilution from 1000 mg L^{-1} stock solutions (Chinese Standards Center, P.R. China).

Sample preparation: About 0.1 g of tobacco samples (particle size < 50 μm) were directly weighed into polypropylene flasks (25 mL capacity) and 1.0 mL $HNO_3 + H_2O_2$ (2:1 v/v) were added to the sample. The flasks were allowed to stand for 20 min at room temperature. Then, the flasks were immersing into the ultrasonic water bath and were subjected to ultrasonic energy at 35 kHz for 20 min. The water bath tempearture was 50 ºC. The contents of the flasks were diluted with 4.0 mL deionized water and subjected to sonication for another 2.0 min. Then, the solutions were centrifuged at 3000 rpm for 10 min. The supernatant clear solution was afforded to the AAS analysis. The blanks were also treated in the same way without samples for each experiment.

Atomic absorption spectrometric analysis: The graphite furnace atomic absorption spectrometric (GFAAS) analysis condition is listed in Table-1. For samples analysis, a 10 mL aliquot of the samples or standard solution was injected into the graphite cuvette for the GFAAS determination. No matrix modifier was used. The atomic absorption signals were measured with the Zeeman background corrector in operation. The measurement was repeated three times and the obtained signals were averaged.

TABLE-1
OPERATIONAL CONDITIONS FOR GFAAS

	Cr	Co	Ni	Cu	Cd	Pb
Lamp settings wavelength (nm)	357.9	242.5	232.0	324.8	228.8	283.3
Spectral band width (nm)	0.7	0.2	0.2	0.7	0.7	0.7
Lamp current (mA)	10	30	25	15	6	10
Furnace temperature (ºC)						
Drying 1 (ramp 1 s, hold 5 s)	110	110	110	110	110	110
Drying 2 (ramp 5 s, hold 15 s)	130	130	130	130	130	130
Ashing (ramp 10 s, hold 30 s)	1000	700	600	700	350	600
Atomizing (ramp 0 s, hold 5 s)	2400	2400	2300	2000	1500	1600
Clean-up (ramp 1 s, hold 3 s)	2500	2450	2450	2450	2450	2450

RESULTS AND DISCUSSION

Optimization of the ultrasonic acid digestion: In the sample digestion, the influence of the digestion solution is one of the main factors for quantitative recoveries of the analytes. Due to this important point, in this experiment, 0.1 g of sample mass (particle size < 50 μm) was used. The HNO_3-$HClO_4$-HF (2:1:1, v/v/v), HNO_3-HCl (1:3, v/v), HNO_3-H_2O_2 (2:1, v/v) and HNO_3 were used as digestion solution, respectively. The recovery values for the analyte metals were shown in Fig. 1. The results showed that the high recoveries were obtained when HNO_3-H_2O_2 used as digestion solution. Thererefore, HNO_3-H_2O_2 (2:1, v/v) was selected in this experiment.

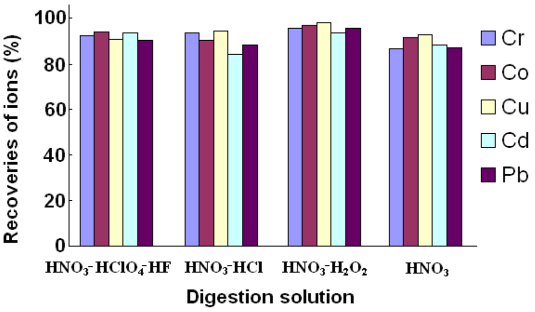

Fig. 1. Effect of digestion solution on the recoveries of heavy metals

After the treatment with acid-oxidant mixtures, the samples were kept at room temperature for different time intervals, 5 - 50 min, respectively, before being subjected to the ultrasonic bath, denoted as presonication. Optimum effects of presonication were observed at 20 min. Longer presonication has no effect on the recoveries of heavy metals under study. Thus, 20 min of presonication was used in this experiment. The results shown that for the tobacco sample, the ultrasonic acid digestion efficiency increased with the increase of sonication time from 2 to 20 min. Longer sonication time has no effect on the recoveries of heavy metals under study. Thus, 20 min of sonication time was also used in this experiment.

In this work, the 30-80 °C temperature interval of ultrasonic bath was investigated. Temperature of the extraction medium increased with increasing sonication time. The high temperature and pressure within a collapsing cavitation bubble produced by ultrasonic irradiation causes the formation of free radicals, to accelerate the reactions involved in sample digestion[21]. The results shown that the optimum amount of Cr, Ni, Co, Cu, Cd and Pb was released from the samples at 45-60 °C. Therefore, the high temperature was necessary for optimum recoveries of heavy metal from all samples as compared to the work reported at room temperature[22]. The water bath tempearture of 50 ºC was selected in this experiment.

Calibration graphs and detection limits: Under the GFAAS analysis conditions, regression equations of metal ions were established based on the standard samples injected and their absorption signals. The results are shown in Table-2. The detection limits were obtained based on three times the standard deviations of the blank. The results are shown in Table 2.

TABLE-2
REGRESSION EQUATION AND DETECTION LIMIT

Metal ions	Regression equation	Linearity range (μg/L)	Coefficient	Detection limit (ng L^{-1})
Cr	A = 0.0412 C (μg/L) + 0.0287	0.020-150	r = 0.9990	2.5
Ni	A = 0.0308 (μg/L) + 0.0321	0.016-200	r = 0.9994	2.0
Co	A = 0.0357 C (μg/L) – 0.0292	0.018-180	r = 0.9993	2.2
Cu	A = 0.0292 C (μg/L) + 0.0275	0.016-200	r = 0.9992	2.0
Cd	A = 0.0338 C (μg/L) + 0.0360	0.015-180	r = 0.9994	1.8
Pb	A = 0.0368 (μg/L) + 0.0287	0.015-180	r = 0.9990	1.8

Effect of foreign ions: In order to evaluate the possibility of selective recovery of analyte ions in the real samples, the effects of foreign ions was studued. Quantitative recoveries (> 95 %) for 5000 mg L^{-1} of Na^+, for 2000 mg L^{-1} of Mg^{2+}, for 1000 mg L^{-1} of K^+, Ca^{2+}, SO_4^{2-}, 100 mg L^{-1} for Zn^{2+}, 50 mg L^{-1} for Al^{3+} were obtained. These tolerable levels of foreign ions were enough for the quantitative separation of analyte ions from the matrix of the real samples.

Recovery of spikes from the samples: In order to estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked in samples. Good agreement was obtained between the added and found analyte content using the recommended procedure. The recovery values for the analyte ions were in the range of 93-105 %. These values were quantitative and it shows that the presented method can be applied for the determination of Cr, Ni, Co, Cu, Cd and Pb in tobacco. The relative standard deviation for the analyte ions (7 repeat determinations) were below 1.8 %.

Application to real samples: This method was applied to the determination chromium, nickel, cobalt, copper, cadmium and lead in tobacco samples. The results are given in Table-3. A standard method using wet acid microwave digestion and inductively coupled plasma mass spectrometry (ICP-MS)[23] had also been used as reference method and the result are shown in Table-4.

TABLE-3
DETERMINATION RESULTS (µg/L) OF THE SAMPLE WITH THIS METHOD

Components	Tobacco samples (µg/g)				RSD (%) (n=7)	Recovery (%) (n=5)
	YS21	YS29	YS32	YS34		
Ni	3.10	2.23	1.87	2.13	2.8	95
Co	3.77	3.37	2.40	2.95	3.2	95
Cu	8.63	9.40	11.75	9.68	2.7	96
Cr	3.10	3.55	2.23	2.53	2.9	94
Cd	0.43	0.52	0.25	0.40	3.1	97
Pb	0.98	1.12	2.38	2.43	2.6	94

TABLE-4
DETERMINATION RESULTS (µg/L) OF THE SAMPLE WITH WET ACID MICROWAVE DIGESTION AND ICP-MS METHOD

Components	Tobacco samples (µg/g)				RSD (%) (n=7)	Recovery (%) (n=5)
	YS21	YS29	YS32	YS34		
Ni	3.3 7	2.47	1.7 2	2.07	3.1	92-106
Co	3.63	3.47	2.57	3.10	3.2	94-108
Cu	8.75	9.22	11.45	9.53	3.0	93-105
Cr	2.96	3.40	2.47	2.32	3.4	92-104
Cd	0.44	0.54	0.23	0.49	3.3	93-107
Pb	0.45	0.50	0.26	0.42	3.0	92-106

Conclusion

This method offers a rapid, easy and efficient sample preparation; using a low cost and easily available routine ultrasonic bath, for determination of heavy metals in tobacco samples by GFAAS. All parameters studied (sonication time, temperature and solvent system) influence the ultrasonic acid digestion efficiency. The use of the ultrasonic acid digestion allowed the digesting of tobacco samples for heavy metals determination in a shorter time and low volume of acids mixture than required.

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