Determination of trace boron in human urine samples by ICP-AES using a solid sampling technique subsequent to concentration by a tailor-made boron-selective adsorbent

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Abstract A simple method for preconcentration and determination of trace boron has been developed by the conversion of common anion-exchange resins with a chelating agent, beryllon-II, and the proposed method has been successfully applied to the determination of boron in human urine samples. Beryllon-II-immobilized resin is useful for selective collection of boron in neutral pH region. The concentration of collected boron is determined by introducing the boron-sorbed resin as water-resin suspension into inductively coupled plasma-atomic emission spectroscopy(ICP-AES) apparatus without stripping procedure.

Key words : boron, human urine, ICP-AES, boron-selective adsorbent, solid sampling technique.

Introduction

Boron is an essential nutrient in higher plants[1] and might be in yeast[2] and animals[3]. There is also preliminary evidence to suggest that boron has at least a beneficial role in humans[4-15]. Recently, a boron transporter with homology to bicarbonate transporters in animal has been found in a plant[16]. On the other hand, excess boron is toxic, explaining its use in disinfectants and insecticides. ICP-AES is useful method for the determination of boron, but is not adequately sensitive for ultratrace boron. In this study, trace amounts of boron in two standard reference materials and in human urine samples were separated and concentrated by a boron-selective adsorbent and subsequently determined by ICP-AES without the elution of boron from the adsorbent.

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Materials and Methods

Preparation of boron-selective adsorbent

Tetrasodium 2-(3,6-disulfo-8-hydroxynaphthylazo) -1,8-dihydroxynaphthylene-3,6-disulfonate (Beryllon-II) was obtained from Wako Pure Chemical Industries, Ltd.(Osaka, Japan). Beryllon-II-immobilized anion-exchange resin was prepared in the following way. An anion-exchange resin(Bio-Rad, AG1-X8, 400 mesh, 10 g) was shaken with an aqueous solution of the chelating reagent(5 mmol) in an Erlenmeyer flask for 6hr. The resin was separated and washed with water and

methanol, and air-dried.

Detemination of boron

Sample solutions containing up to 0.2 mmol of boric acid were incubated with the beryllon-II-immobilized resin(50 mg) at pH 7 for 60 min. The resin was separated, washed with water and methanol, and air-dried. The beryllon-II-immobilized resin bearing boron (25 mg) was suspended into 25ml of distilled water. The water-resin suspension was introduced to ICP-AES apparatus to determine the concentration of boron.

The human urine samples were digested with nitric acid and perchloric acid by conventional method.

Results and Discussion

Beryllon-II which has 1,8-dihydroxynaphthyl moiety and four sulfonate groups is a chelating agent selective to boron as boric acid, and is immobilized easily and firmly by a strongly basic anion-exchange resin. Beryllon-II molecules were not released even in 1 mol/l of sodium chloride from the beryllon-II-immobilized resin. This finding suggests that the resin can be applied to uptake of boron even in such a high concentration of electrolyte solution as seawater. Boron was completely collected on the resin when the resin was incubated for 60min at pH7. The beryllon-II-immobilized resin bearing boron was applied to the determination of boron by direct introduction of resin-water suspension into ICP-AES apparatus. The limit of quantitation is about 1ng(10 σ) for boron.

The amounts of boron in three standard reference materials, NIST 1515(apple leaves, certified value; 27 microgram/l) and JAC 0031 (river water, certified value; 9.1 $\pm$ 0.5 microgram/l) were found 28.1 $\pm$ 1.51 microgram/l (n=3), and 9.06 $\pm$ 0.24 microgram/l (n=3), respectively. The amounts of boron in human urine samples taken from healthy male subjects were determined by the proposed method and the results were shown in Table 1.

In conclusion, the proposed method is sensitive and practical for the determination of trace amounts of boron in environmental and biological samples.

Table 1 Analytical results for boron in human urine samples.

Sample	Sample, ml	Added, μg	Found, μg/ml	Recovery, %
No. 1	50	0	0.776 ± 0.035	—
			(0.741, 0.780, 0.810)	
	50	20	1.18 ± 0.06	100.1
			(1.11, 1.16, 1.26)	
No. 2	100	0	0.361 ± 0.034	—
			(0.327, 0.359, 0.397)	
	100	20	0.573 ± 0.035	102.1
			(0.561, 0.572, 0.585)	
No. 3	50	0	1.08 ± 0.04	—
			(1.04, 1.08, 1.13)	
	50	20	1.48 ± 0.03	98.7
			(1.46, 1.48, 1.50)	

These samples were digested with nitric acid and perchloric acid and adjusted at pH7.

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