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GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY UTILIZING SELECTIVE ADSORPTION OF METAL IONS ONTO TUNGSTEN WIRE IN AQUEOUS SOLUTIONS

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The graphite furnace atomic absorption spectrometry (AAS) is improved by utilizing tungsten wire as an adsorbing material. This method has 20 to 50 times higher sensitivity compared to the conventional aliquot-sampling flameless AAS. Interferences of large amounts of coexisting alkali salts can be effectively eliminated.

Atomizers in flameless AAS are classified into two types. One has a closed or semiclosed structure such as graphite furnace1) and the other has an open structure such as graphite2) or metal3,4) filaments, ribbons and wires. Some kinds of pretreatments5-7) such as solvent extraction, amalgam formation and electrolytic reduction are available for separation of interfering materials and concentration of analyte ions. It is well known that various metal ions are adsorbed on metal surface8) when the metal is soaked in aqueous solutions and recently the wire loop method9) was reported for preconcentration of analyte ions.

In the present paper, simple and high sensitive AAS utilizing tungsten wire as an adsorbing material is described. Sensitivities can be remarkably enhanced and the interferences of coexisting major constituents can be effectively eliminated.

A Varian-Techtron AA1000 atomic absorption spectrophotometer with carbon rod atomizer model 63 tube type was used without any modification. Hollow cathode lamps and a D_2 lamp were from Hamamatsu TV. Co. Ltd. Argon was passed over the graphite furnace at a rate of 4 l/min.

Tungsten wire with 99.99% purity from Japan Lamp Industrial Co. Ltd. was cut in suitable length (0.5 mm diameter and generally 18 mm long) and bent in hairpin shape not to jut out from the graphite tube (3 mm in i.d., 9 mm in length).

The standard solutions were kept in acidic with 0.1 N isothermally distilled hydrochloric acid. Sample solutions with desired concentration were prepared by adding 10 ppm standard solutions with a microsyringe to deionized water. Solutions were stored in polyethylene bottles.

The general procedures in analytical work are as follows; (1) the hairpin-shaped tungsten wire is soaked in the sample solution which is stirred by a magnetic stirrer for 60 seconds and rinsed with deionized water for 3 to 5 seconds. (2) the wire is set in the graphite tube and the sample on the wire is atomized. Cleaning of the tungsten wire occurs simultaneously at this atomization stage and the identical wire is ready for use for the next run without any other aftertreatments. Mean values of three replicate runs were usually taken for each sample solution. The relative standard deviations were 0.5 to 2%.

Tungsten, molybdenum, rhenium and tantalum wires were investigated to select the most suitable one as the adsorbing material and as a result tungsten wire was chosen because of its relatively large adsorbing ability and the highest melting point among these metals.

Fig.1 shows the calibration curves for copper. For the convenience of a comparison a similar curve obtained by a conventional 5 μl-aliquot-sampling method is also shown in the same figure. [Fig.1(c)]

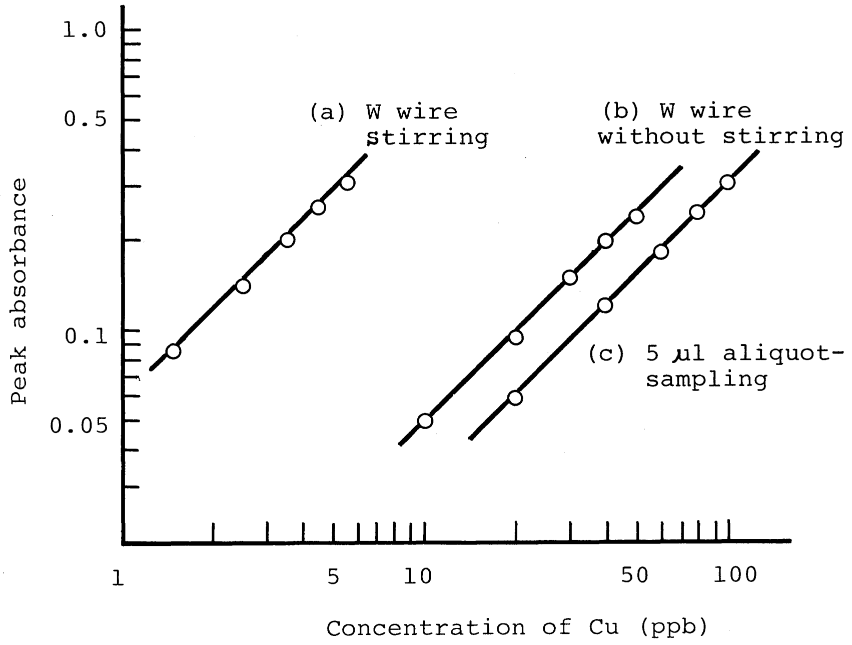

Fig.1 Calibration curves for copper

The values of the absorbance peak have good linear relationships with the concentration of copper in a reasonable concentration range. In general, stirring the sample solution resulted in a remarkable increase of analytical sensitivities (5 to 10 times) compared to stationary soaking as shown in Fig.1(a) and (b). This inclination of enhancement in sensitivities was observed for all the sample solutions investigated.

Table 1 shows the comparison of sensitivities of conventional aliquot-sampling graphite furnace method and this method for some analytical elements. The ratio of sensitivity in the former method to that in the latter one is usually in a range of 20 to 50 for most of analytical elements. A remarkable difference in the sensitivity ratio between heavy metal ions such as copper and alkali metal ions suggests the possibility of preferential or selective adsorption of trace amounts of heavy metal ions under the coexistence of a large amount of alkali salts.

The effect of coexistence of a large amount of sodium chloride on the absorbance signal for copper is shown in Fig.2. An abrupt decrease in the absorbance signal of copper in 10 ppb solution was recognized when the concentration of sodium ion exceeded 1 ppm. However, the remarkable sensitivity increase in this method is sufficient to overcome the sensitivity decrease by the suppressive interference due to sodium ions.

The mechanism of the interference would be quite different from that of the interference by a large amount of chloride in the conventional aliquot-sampling graphite furnace AAS[10].

Table 1. Comparison of sensitivities (μg/ml/1%) of aliquot-sampling and tungsten wire methods

Element	A Aliquot-sampling	B Tungsten wire	A/B Sensitivity ratio
Ag	1×10^{-3}	2×10^{-5}	50
Cd	2×10^{-4}	7×10^{-6}	29
Co	9×10^{-3}	3×10^{-4}	30
Cr	6×10^{-3}	7×10^{-4}	9
Cu	5×10^{-3}	2×10^{-4}	25
Fe	———	———	3
K	———	———	0.5
Mg	———	———	4
Mn	2×10^{-3}	4×10^{-5}	50
Na	———	———	0.4
Ni	3×10^{-2}	1×10^{-3}	30
Pb	8×10^{-3}	3×10^{-4}	27
Zn	3×10^{-4}	8×10^{-5}	4

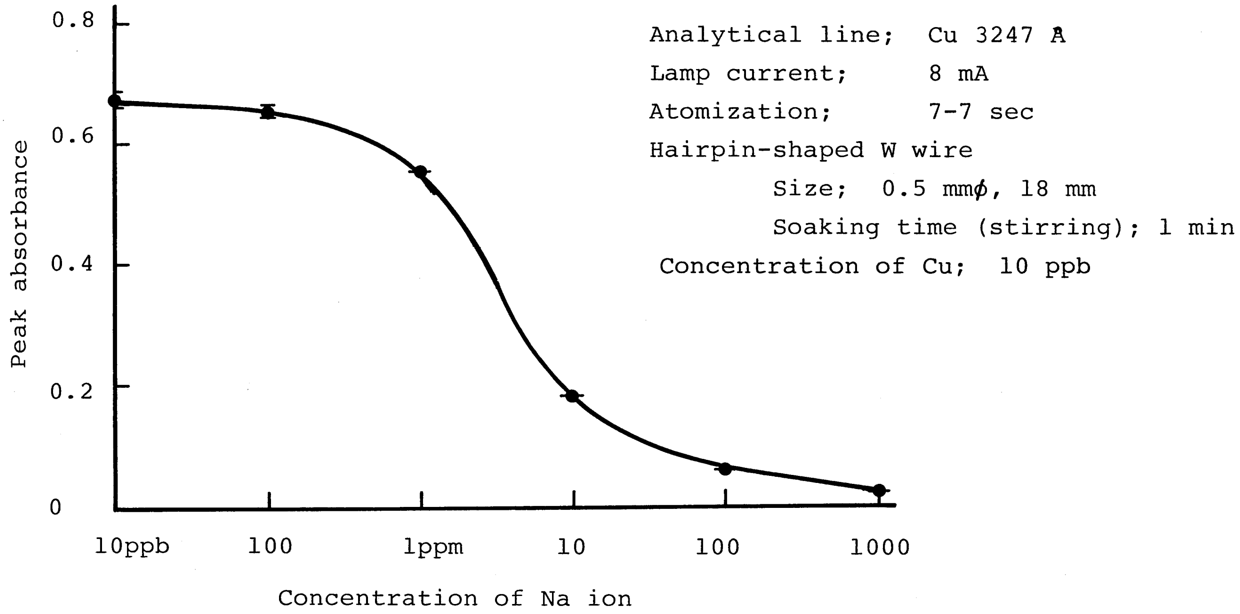

Fig.2 Effect of concentration of Na ion on the absorbance signal of copper

The amount of copper adsorbed onto the tungsten wire depends on the pH of the solution. In a strongly acidic solution the analytical sensitivity decreased because the adsorption of copper is interfered by the presence of a large amount of hydronium ions. There is, however, no significant sensitivity decrease in a pH range necessary to prevent the hydrolysis of metal ions.

The tungsten wire as far as it was used at moderate atomizing temperatures (the temperature of the atomizer is about 2400°C at 7 of the voltage setting and 10 seconds after the start of atomization[11)]) is proof against repetitive use and the deterioration of its characteristics was not observed during the use.

In the wire loop method[9)] tungsten alloy loop serves both as an adsorbing material for preconcentration and a resistance material in an electrical heating and therefore the parameters in these two functions cannot be changed independently from each other. On the other hand these two functions are definitely separated in this method because of employing a graphite furnace as a heating tool for atomization. Accordingly the optimization of the wire dimensions such as diameter, length and shape can be easily achieved irrespective of the condition of atomizing temperatures.

This analytical method would be especially usefull for the determination of a trace amount of heavy metal ions in sea water and urine which contain a large amount of alkali salts and this peculiar adsorption behavior should be applicable as a method of high degree of purification for various water soluble substances.

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