THE DETERMINATION OF Se ENVIRONMENTAL BACKGROUND VALUE IN NATURAL RIVER WATER USING MIXED MATRIX MODIFIER-STPF

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Abstract - A method is described for the determination of the Se in river water after preconcentration by stabilized temperature platform furnace and Zeeman background correction. A mixture of platinum and ascorbic acid was proved to be an adequate and powerful matrix modifier for the determination. Thermal pretreatment temperature of 1200 °C can be used with the proposed modifier and concentration can be obtained directly via calibration curve without using the standard-addition technique. The method is sensitive, reliable and relatively simple, with the characteristic mass, detection limit and recovery, 19.5pg/0.0044A.S., 1.55 µg/L and 85.0-110.0%, respectively.

Key words: selenium, background value, mixed matrix modifier, STPF.

As an essential trace element of toxicological and physiological value to human health, selenium has attracted increasing attentions from researchers. Since the difference between the essential and the toxic level is rather narrow, precise knowledge of the selenium content in the environment is mandatory, making determination of selenium an important task for analysts.

Traces of selenium used to be determined by spectrophotometry and fluorimetry, but these two methods were labor-intensive, time-consuming, and subject to many interferences. The development of atomic absorption spectrometry (AAS) has made it possible to replace the above mentioned analytical methods to a large extent because AAS technique is relatively simple, fast, sensitive, and reasonable precise. In fact, it has become an effective means to measure trace elements such as selenium. At present, the most frequently used AAS method which has disadvantages of the same kinds as that of fluorimetric method.

Since many kinds of environmental waters, especially nature river waters, are frequently used as drinking water which is the main source for body assimilation, the significance of selenium measurement is manifest. That is why so many relevant data have been reported (1,2,3).

Selenium is analytically one of the most difficult element in graphite furnace AAS (GFAAS). Many problems have been settled partly by using matrix modification and stabilized temperature platform furnace (STPF) technique together with Zeeman background correction. But difficulties still remained for the measurement of trace selenium at sub-µg/L level in natural environmental waters (4). There are few publications concerning the direct analysis of trace selenium in this aspects.

This paper describes a method for the determination of total selenium in river water (samples collected from Jinsha River, the upper reaches of Yangzi River) using Zeeman effect background corrected STPF AAS. A mixture of platinum and ascorbic acid is used as matrix modifier with which results can be obtained via calibration curve without using the standard-addition technique.

EXPERIMENTAL

Apparatus A Hitachi 180-80 atomic absorption spectrometer was utilized for all analyses. A selenium hollow cathode lamp (Ningqiang Factory of Light Source, Hengshui, Hebei, China) was used. Pyrolytically coated graphite tubes with solid pyrolytic L'vov platforms (Hitachi Maintenance Centre) were applied throughout. The instrumental settings are given in Table 1.

Table 1. Furnace conditions and other instrumental settings

Graphite furnace:		Temp.(°C)	Hold(s)	N ₂ flow-rate (ml min ⁻¹)
1	dry	80-120	30	200
2	ash	400-400	20	200
3		800-800	10	200
4		1200-1200	10	200
5	atomise	2400-2400	7	0
6	clean	2900	3	200

Autosampler and spectrometer:			
Sample volume	20	μl ^a	
Se hollow cathode lamp light source	10	mA	
Wavelength	196.0	nm	
Spectral bandpass	1.3	nm	
Peak evaluation		peak height	

a: 10 μL of volume is injected twice, the later is sampled before atomise step begins

Reagents A selenium stock solution (1 mg/ml) was prepared by dissolving spec. pure selenium powder 0.5000g in 7.5ml HCl and 2.5ml HNO₃, and diluted with 7% (V/V) HCl to 500ml. 10 mg/ml Pt: by dissolving 0.6637g H₂PtCl₆·6H₂O in 5ml 1% HCl, and diluted to 25ml with 1% HCl. 10% (W/V) ascorbic acid: weighed out 2.5g ascorbic acid in 25ml subboiled water.

Matrix Modifier Matrix modification is an important part of the STPF technique. The addition of metals or other substance can diminish the chemical interference in water analysis, and allow using of higher ashing temperatures without losses and results in a significantly enhanced sensitivity. Nickel is the most often used metal to stabilize selenium, and very recently palladium as a recommended universal modifier(5) is also utilized in the selenium measurement by GFAAS(5,6), Nickel and Palladium are not only transition elements of the same upright row of Group VIII in the periodic chart, but also having the similar mechanism(5,7,8), the next member of this group, is rarely used for the same purpose. Nickel is a frequently determined element at trace levels which will be influenced by modifiers containing this metal ions at high concentrations in the furnace. As to palladium, it is not powerful enough to stabilize selenium even together with mognisium nitrate in the presence of a complex matrix. Slight selenium losses were observed if temperatures were above 900°C(5).

Reagan et al. used organic compounds to act as matrix modifiers in 1976(9). Since then a great deal of research had been done on concrete analytical task and how the organic substances, mainly organic acids, worked in GFAAS. Ni Zhe-Ming et al.(10) found that in the presence of ascorbic acid, tartaric acid, citric acid or EDTA Cd, Pd, Zn and Ag could be atomised at relatively low temperatures which separated the atomic absorption signals from that of background and diminished the chemical interference. Botha et al.(11) and L'vov(12,13) reported that the carbon formed on pyrolysis of the organic acids during the heating stages had played a reductive role, allowing the determined elements to be put into a more easily atomization form. The use of metal ions in conjunction with organic substance as matrix modifiers has been introduced to the GFAAS measurements of trace selenium.

Palladium combined with ascorbic acid were used to measure selenium in serum(14). Palladium or platinum with 0.1% albumin to stabilize selenium in freeze-dried serum(8). Palladium with 1.5% albumin to determine selenium in organic matrix(15).

For this work, platinum and ascorbic acid matrix modifier was used to thermally stabilized selenium. The solutions containing 10 mg/ml Pt and 10%(W/V) ascorbic acid were individually prepared by dissolving H₂PtCl₆·6H₂O and ascorbic acid as before.

Procedure 150ml of water samples were placed into 250ml of PTFE beakers, ultra red lamps were used to vaporize solutions to small volumes (approximately 0.1ml) with a state of sub-boil maintained. Then 0.6ml of 4N HCl was added, followed by heating it for 10min on a heating plate to reduce Se(VI) to Se(IV). The solutions were allowed to cool and transferred to 5ml of colorimetric tubes. Before diluted with subboiling distilled water to volumes, 20μL of 10mg/ml Pt along with 10μL of 10%(W/V) ascorbic acids was added to act as matrix modifier. Blanks were taken through the entire procedure and diluted

in the same manner as the samples. All prepared spiking solutions were quantified directly via calibration curve, using peak height signals, by GFAAS.

The standards containing 10.0, 20.0 and 40.0 $\mu\text{g/L}$ of Se(IV), were made simultaneously with spikes from 1mg/ml of Se(IV) stock solution with the same amount of Pt and ascorbic acid added as water samples.

RESULTS AND DISCUSSION

Table II shows the results of selenium analysis in natural river waters by GFAAS and for comparison, the data obtained by fluorimetric method is also listed.

Using the above described GFAAS method, good recoveries were obtained, and equivalent results were got compared with the commonly used, but much more complex and time-consuming, fluorimetric method. The characteristic mass (m_0) calculated from the aqueous standard was 19.5pg/0.0044A.S. This is in approximate agreement with theoretically calculated value of 16pg/0.0044A.S(16). The accuracy of the method was proved by the comparison of results with that of fluorimetric analysis and by recovery experiments.

In GFAAS method of selenium determination, the element must be present as Se(IV). Therefore, it is important for total selenium measurement to reduce Se(VI) to Se(IV) as most of the selenium in drinking water is present in the form of Se(VI)(4). The method of heating the solution with 4N HCl reported by Cutter(17) is used here and proved to be a success when a recovery of 102% was obtained for 40 $\mu\text{g/L}$ of Se(VI) to be reduced to Se(IV) before GFAAS determination.

Our early work(18) had reported a method of determination selenium in blood by GFAAS, using platinum as matrix modifier in an alkaline medium. That procedure is not suitable for water analysis because water samples are often preserved under acidified conditions. Furthermore, Se(VI) is converted to

Se(IV) using HCl as reductant. For the above consideration, it is better to facilitate selenium determination in river waters under acid medium. The addition of ascorbic acid in conjunction with platinum overcame the above disadvantages and was proved to be a powerful modifier for the determination of trace selenium at $10^{-1}\mu\text{g/L}$ level in natural river waters. Thermal pretreatment temperature of 1200°C can be used without sacrifice in sensitivity. Chemical interference can be diminished effectively in the presence of this modifier. It was found that various kinds of co-existing metal ions, such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{3+} and As^{3+} etc., had almost no effect on selenium determination with the concentration multiple considered. The acidity below 10% of the solution to be measured has no influence on analytical results. In brief, the method is sensitive, reliable, and relatively simple.

Table II. Comparison of Se analysis by GFAAS and fluorimetric method

Sample	GFAAS ($\mu\text{g/ml}$)	Fluorimetric method ($\mu\text{g/ml}$) ^a	GFAAS added ($\mu\text{g/ml}$)	GFAAS found ($\mu\text{g/ml}$)	recovery (%)
B7	0.19	0.18	0.20	0.36	85.0
B14	0.25	0.24	0.20	0.47	110.0
B17	0.23	0.22	0.20	0.42	95.0
B22	0.24	0.21			
B24	0.14	0.13			
B25	0.21	0.19	0.20	0.39	90.0

a: The fluorimetric analysis were performed by Chen Yu-Ling, in the same work unit as the authors, who used 2, 3-diaminonaphthalene (DAN) as fluorimetric reagent.

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