

## Determination of arsenic in grain and soil by hydride nondispersive atomic fluorescence method

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**Abstract**—Quantity of trace arsenic in grain and soil was determined by hydride nondispersive atomic fluorescence method.

Optimum conditions of measurement were selected in the experiment including the pH of the medium, reductive agent, the concentration and flowing velocity of  $\text{KBH}_4$ , rate of carrier gas and atomized temperature. The reference sample of rice C was determined and the linear relationship of the calibration curve was plotted, indicating that the method was highly precise. In the experiment of recovery rate, the method was quite satisfactory.

Based on the determination of hundreds of samples, it is proved that atomic fluorescence method is rapid, sensitive and low in interference. It is very efficient on determination of trace arsenic in soils and grains, especially in grains.

**Keywords:** soil; grain; trace arsenic; atomic fluorescence.

Arsenic is one of principal toxic elements in grains and soils. It is usually detected with DDCAg colorimetric method, but the sensitivity is relatively low. Owing to the small contents of arsenic in grains and the available arsenic in soils it is impossible to get reliable results with DDCAg method. Atomic fluorescence method can avoid the drawbacks and its interference is low. In this experiment we use atomic fluorescence method in attempt to determine the arsenic contents in grains and soils.

### EXPERIMENTAL

#### *Apparatus and reagents*

Nondispersive atomic fluorescence spectrometric model WYD-2.

Arsenic solutions:

Arsenic stock solution (As 1 mg/ml);

Standard solution S-1 (As 100.3 $\mu\text{g}/\text{ml}$ );

Soil modeling digestion solution S-2 (As 15 $\mu\text{g}/\text{ml}$ );

Grain modeling digestion solution S-3 (As 10 $\mu\text{g}/\text{ml}$ ).

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Reference sample rice-C is prepared by the Institute of Environmental Protection of Agriculture Ministry, its average value  $0.073 \pm 0.023 \mu\text{g/g}$  is analysed by twenty-three laboratories of Agriculture Environmental Cooperation Committee of China(AECCCC).

Potassium tetrahydroborate solution  $\text{KBH}_4$  (1% W/V);

Digestion mixture-nitric perchloric acid (3:1 by volume);

5% arsenic acid and thiourea mixture.

### *Procedures*

#### *(1) Samples*

The representative samples are obtained from Taihu Lake Area. The numbers of samples are:

50 samples of soil;

75 samples of dehulled rice;

75 samples of wheat grain.

#### *(2) Preparation of calibration curve*

A series of dilute standard solution ( $0.5 \mu\text{g/ml}$ ) are pipetted to 25ml volumetric flasks respectively. Add equal volume of 1:1 hydrochloric acid and 10 ml 5% ascorbic acid-thiourea solution, then dilute to 25ml (the acidity controlled at 3 mol/L). Pipet 2ml of the above solution into the hydride generator. Measure the intensity of the fluorescence and plot calibration curve.

#### *(3) Determination of arsenic in grains*

Wet digestion is used in this experiment. Accurately weigh 2.0g of ground dehulled rice or wheat grains into 50ml conical flask. Add 20ml 16 mol/L nitric acid. Soak over night. Heat to about  $160^\circ\text{C}$  until the solution has been evaporated to about 1ml. Add 15ml digestion mixture, continue heating until the solution becomes clear and the residue turns into white. The remaining solution is about 1ml. Transfer the remaining solution into 25ml volumetric flask. Then the procedures are as described in preparation of calibration curve.

#### *(4) Determination of available arsenic in soil*

Accurately weigh 5.0g of soil sample into a 50ml conical flask, then add 25ml 1mol/L hydrochloric acid, vibrate vigorously at  $25^\circ\text{C}$  for half an hour. Centrifugize and filtrate it at once. Transfer 2ml of filtrate into 25ml volumetric flask. Then the procedure is as described above.

## RESULTS AND DISCUSSION

### *The optimum condition of determination*

#### *(1) Medium and acidity*

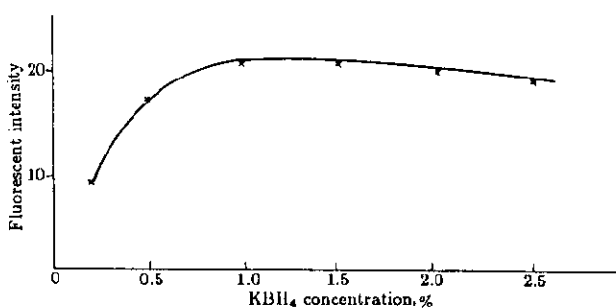
The fluorescence reading is stable when hydrochloric acid is used as medium and adjust the acidity to approximately 10%.

#### *(2) Selection and quantitation of the reductant*

Before determination, As(V) must be reduced to As(III), potassium iodide or ascorbic acid-thiourea mixture can be used as reductant. The latter which is also a masking reagent, can eliminate the interferences. So in this experiment we add 10ml of 5% ascorbic acid-thiourea mixture to 15ml of sample solution, the results are satisfactory.

*(3) Concentration and flowing rate of potassium tetrahydroborate solution*

The experiment shows when the concentration of  $\text{KBH}_4$  solution is less than 0.5%, the reaction is slow and incomplete, and the fluorescence signal is low. If the concentration is more than 1%, the noise of the flame is severe and it reduces the fluorescent signal. In this experiment, 1%  $\text{KBH}_4$  solution with the speed controlled at 1.2ml/s is used. (Fig. 1)



**Fig. 1** Relationship between concentration of  $\text{KBH}_4$  and fluorescent intensity

*(4) Flowing rate of carrier gas*

The fluorescent signal increases when the flowing rate increases. But if the flowing rate is too high, the fluorescent signal does not increase, because the hydride is incompletely atomized and diluted by the strong stream of the carrier gas. Either argon or nitrogen can be used. In this experiment nitrogen with purity of 99.999% is used and its flowing rate is 1.2L/min. (Fig. 2)

*(5) Temperature of atomizing furnace*

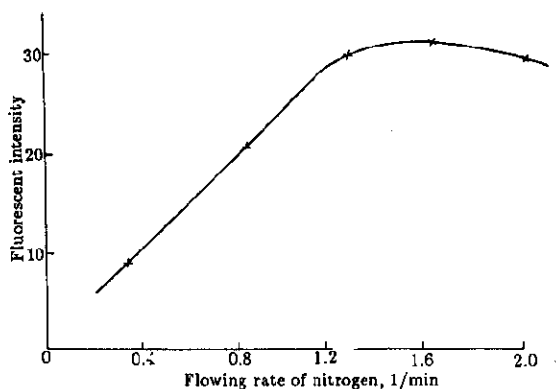
The experiment shows that when the temperature of furnace is below  $800^\circ\text{C}$ , no flame is formed, when above  $950^\circ\text{C}$  the signal decreases. Therefore,  $900^\circ\text{C}$  is chosen during determination.

*(6) Interfering elements*

Smith indicated that the interferences may be introduced by following elements: gold, nickel, bismuth, copper, antimony, tin, and tellurium, if they are present in relatively large amounts. These elements in grains and soil samples in this experiment are so small that the interference may be negligible.

*Accuracy and precision of the method*

*(1) Linearity of calibration curve*



**Fig. 2** Relationship between flowing rate of carrier gas and fluorescent intensity

The relationship between arsenic content and fluorescent intensity is shown in Table 1. It is indicated that the calibration curve is good in linearity.

**Table 1** Relationship between arsenic content and fluorescent intensity

Concentration, $\mu\text{g/ml}$	0	0.025	0.050	0.075	0.10
Intensity	0	11.5	25.0	32.0	43.0
Regression equation	$y = 426x + 1$				
Relative coefficient, $r$	0.996				

**Table 2** Determination of arsenic in S-1, S-2, S-3 solutions

Solution	No. of measurement	Mean	<i>S.D.</i>	<i>C.V.</i> , %	Proper value	Mean of AECCC	95% C. L.
S-1	5	101.3	0.8	0.8	100.3	100.8	99.9-101.7
S-2	5	15.0	0.3	2.0	15.0	14.9	14.7-15.2
S-3	5	10.3	0.1	0.97	10.0	9.97	9.71-10.2

(2) *Determination of standard solution S-1 and modeling digestion solutions S-2 and S-3.*

The results obtained from this three solutions are given in Table 2. Values of three solutions are very close to their proper values and within the 95% confidence limit of twenty-three

laboratories of AECCC. The variation coefficient of 5 determinations of 3 solutions are between 0.8—2.0%. It is indicated that the results are accurate and reliable.

(3) *Determination of arsenic in rice C*

In Table 3, the arsenic contents of rice C are extremely low and the values are within 95% confidence limit of AECCC. The standard deviation is 0.0034 and the variation coefficient is 4.02%.

**Table 3** Arsenic content in reference sample rice-C

Sample	1	2	3	4	5	6	7	8	9
Content, $\mu\text{g/g}$	0.085	0.078	0.084	0.091	0.086	0.083	0.080	0.083	0.084
Mean, $\mu\text{g/g}$	0.085								
S.D.	0.0034								
C.V., %	4.02								
Mean value of 23 laboratories of AECCC	0.073 $\mu\text{g/g}$								
95% confidence limit of AECCC	0.054—0.092								

**Table 4** Recovery of arsenic from ground dehulled rice

Sample		Arsenic content, $\mu\text{g/g}$	Added, $\mu\text{g/g}$	Found, $\mu\text{g/g}$	Recovery, %	Ratio mean,	C.V., %
Shanghai	1	0.375	0.400	0.768	98.3		
	2	0.396	0.400	0.779	95.8		
	5	0.386	0.400	0.773	96.8	100.2	3.7
Jiangsu	2	0.169	1.000	1.190	102.1		
	3	0.169	1.000	1.215	104.6		
	4	0.129	1.000	1.165	103.6		

(4) *Recovery test*

This test is carried out with six dehulled rice samples, 0.4 or 1.0  $\mu\text{g/g}$  of arsenic is added

individually. The Table 4 shows the recovery rates are between 95.8—104.6%, the average value is 100.2% and variation coefficient is 3.7%.

*Background values of arsenic in wheat and dehulled rice and soil available arsenic content from Taihu Lake Area*

There are hundreds of samples. Each sample is measured twice. In measuring each batch of samples (10 samples), reference sample rice C is measured simultaneously as control.

**Table 5** Background values of arsenic in grains and soil available content from Taihu Lake Area

Kind of samples	Source of samples	No. of samples	Mean $\mu\text{g/g}$	<i>S.D.</i>	Range of background value
Dehulled rice	Taihu	71	0.185	0.101	0.084—0.285
	Shanghai	28	0.178	0.079	0.099—0.257
	Jiangsu	22	0.181	0.117	0.064—0.298
	Zhejiang	18	0.178	0.096	0.079—0.277
Wheat	Taihu	70	0.063	2.063	0.031—0.131
	Shanghai	13	0.044	0.288	0.013—0.153
	Jiangsu	46	0.087	0.056	0.031—0.142
	Zhejiang	10	0.092	0.076	0.016—0.167
Soil available As	Taihu	46	1.15	0.641	
	Shanghai	14	1.61	0.442	
	Jiangsu	17	0.918	0.600	
	Zhejiang	15	0.980	0.617	

Table 5 shows that the background values of arsenic in grains in Taihu Lake Area are below the allowable threshold  $0.7\mu\text{g/g}$  of standard food hygiene. So they are safe to human and animal.

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### CONCLUSION

Under the optimum conditions, the calibration curve is in linear relationship, the values of three standard solutions are very close to their proper contents, the mean value of reference sample rice C is in good coincident with that recommended by AECCC, with its 95% confidence. The recovery rate of arsenic is 95.75–104.6%.

The analytical results show that the method is simple, rapid and sensitive. It may be negligible from interference and is broad in linear, especially is effective in determination of trace arsenic in grain.

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