*Full Length Research Paper*

# A slurry sampling hydride generation atomic absorption spectrometric method for speciation analysis of trace inorganic arsenic in flours

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**A novel hydride generation atomic absorption spectrometric method is developed for speciation analysis of inorganic arsenic in flours. This method is based on the leaching of arsenic from sample slurry through the sonication followed by hydride generation in the slurry and determination of the corresponding hydrides. The content of arsenic (III) [As(III)] was determined under 1% HCl acidity condition using both inhibitory effect of 8-Hydroxyquinoline (8-HQ) on arsenic(V) [As(V)] and its enhancing effect on As(III). The content of total inorganic arsenic was determined under 5% HCl acidity condition using enhancing effect of 8-HQ on both As(III) and As(V). The method detection limit was 4.0 μg kg$^{-1}$ for As(III) and 4.5 μg kg$^{-1}$ for total inorganic arsenic. The recovery ranging from 94.3 to 107% were found for As(III) and values from 98.5 to 104% for total inorganic arsenic. The relative standard deviations (RSDs) were in the range of 4.3–4.6% and 2.2–3.3% for the determination of As(III) and total inorganic arsenic, respectively. This method was validated by using the Chinese standard method (GB/T 5009.11-2003), with good agreement for total inorganic arsenic content in real samples. The developed method was successfully applied to speciation analysis of inorganic arsenic in wheat flour and rice flour with satisfactory results.**

**Key words:** Slurry sampling, hydride generation, atomic absorption spectrometry, inorganic arsenic, speciation, flours.

## INTRODUCTION

The speciation and determination of trace arsenic (As) in food is extremely interesting. Total As content does not usually give enough information for reliably evaluating the possible health risk due to the toxicity and physiological behavior of As depended on its chemical speciation. The most toxic species found in food are arsenic (III) (As (III)) and arsenic (V) (As (V)). Monomethylarsonous acid (MMA (III)) and dimethylarsinous acid (DMA (III)) are more toxic species, but it has not yet been possible to find them in food products. Chronic toxicity of As is more relevant than acute toxicity at the concentrations studied. A half-lethal dose (LD50) for As (III) and As (V) is 14 mg kg$^{-1}$ and 20 mg kg$^{-1}$, respectively (Poison and Tattersal, 1969). Due to the toxicity of the inorganic As species, the

World Health Organisation (WHO) established a provisional tolerable weekly intake (PTWI) for inorganic As [As(III) and As(V)] at 15 μg kg$^{-1}$ body weight. Moreover, the International Agency for Cancer Research has considered this metalloid as a human carcinogen (World Health Organization, 1998). The tolerance limits of inorganic As in wheat flour and rice flour are 0.1 and 0.15 μg g$^{-1}$, respectively (Standardization Administration of CHINA, 2005). Therefore, it is of importance to generate accurate data for the occurrence of inorganic As in order to reliably assess the possible health risk.

A variety of techniques for the speciation and determination of inorganic As were reviewed and the advantages and applied field of different methods were discussed (Muñoz and Palmero, 2005; Kumar and Riyazuddin, 2007; Zhu and Qin, 2008; Rabieh et al., 2008). The extraction procedure for each method is commonly a crucial step in speciation studies, because

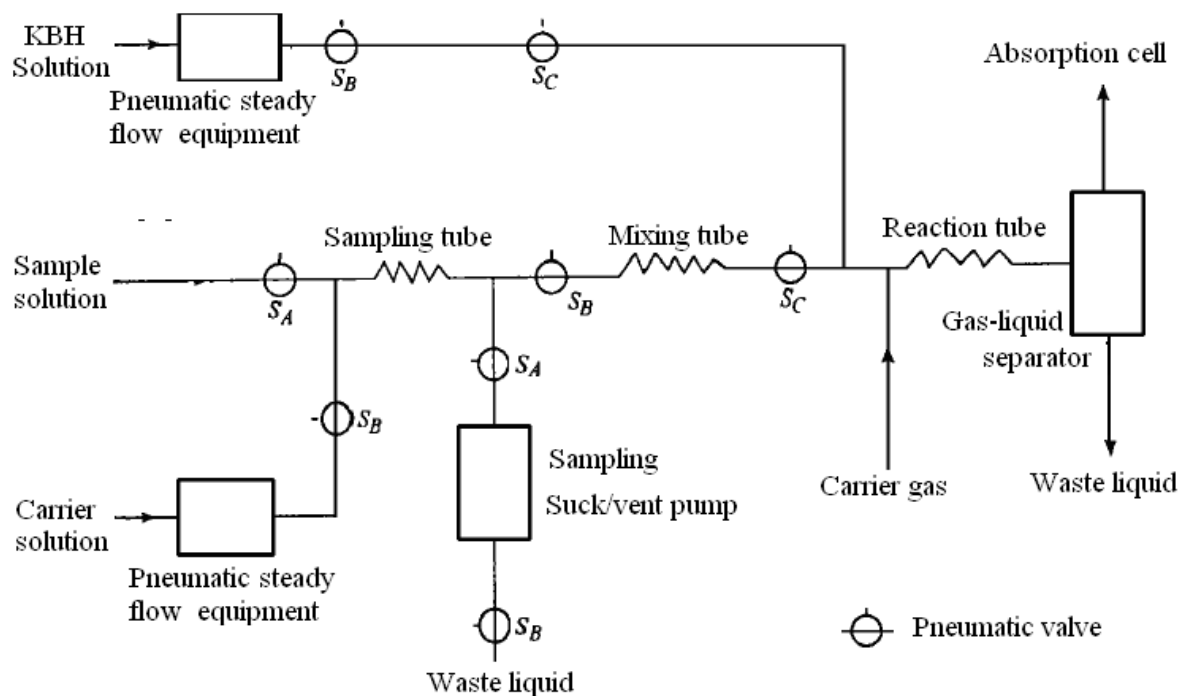\*Corresponding author. E-mail: hanwen@hbu.edu.cn.

**Figure 1.** Pneumatic steady flow injection system.

no inter-conversion of species should occur. Yuan et al. (2005) compared the different extraction methods by using different extraction solvents including water, methanol, water–methanol, water–ethanol and water–acetonitrile. Use of water–ethanol mixture as extraction solvent using microwave-assisted extraction provided good extraction efficiency without internal species conversion. The inorganic As species can be isolated from the matrix by solvent extraction with chloroform and back-extraction with hydrochloric acid (Muñoz et al., 2000), extraction with trifluoroacetic acid at high temperatures and accelerated solvent extraction with methanol (Heitkemper et al., 2001), microwave-assisted extraction (Quaghebeur et al., 2003), and ultrasonic extraction (Sánchez-Rodas et al., 2006) as well as solid phase extraction (Liang and Liu, 2007; Zhang et al., 2007). Chinese national standard method (standardization administration of China, 2003) for the determination of total inorganic As in foods adopted the extraction with 6 mol $L^{-1}$ hydrochloric acid and hydride generation atomic fluorescence spectrometry (HGAFS), with the detection limit of 40 µg $kg^{-1}$.

The slurry sampling combines the significant advantages of the solid sampling and liquid sampling (Cal-Prieto et al., 2002). The slurry sampling hydride generation method without pre-extraction were reviewed (Matusiewicz, 2003), and used for the determination of total As in different samples, such as sediments, coal and fly ash by atomic absorption spectrometry (AAS) (Vieira and Welz, 2002), plant materials by ICP-atomic emission

spectrometry (Li et al., 1998), and milk samples by atomic fluorescence spectrometry (AFS) (Cava-Montesinos et al., 2004). There are few reports for speciation analysis of inorganic As species using slurry sampling. A slurry sampling hydride generation method was developed for the determination of As(III) and total inorganic As in environmental and biological samples by their *in situ* trapping followed by graphite furnace-AAS (Matusiewicz and Mroczkowska, 2003).. Another slurry sampling hydride generation method was presented for the determination of As(III), As(V), Sb(III) and Sb(V) in milk samples by AFS based on the leaching of analytes from milk through the sonication of samples with aqua regia (Cava-Montesinos et al., 2003)..

The main purpose of this work was to develop a simple and accurate methodology suitable for rapid and sensitive speciation analysis of As(III) and total inorganic As. A new method for direct determination of As(III) and total inorganic As is developed by using slurry sampling HGAAS in the presence of 8-hydroxyquinoline (8-HQ). The proposed method was used for speciation analysis of As(III) and total inorganic As in wheat flour and rice flour using slurry sampling HGAAS.

## MATERIALS AND METHODS

The As(V) stock solution (1,000 mg $L^{-1}$, GSB G62028-90) was purchased from the national center for Analysis and testing of steel materials (Beijing, China). As(III) stock solution (1,000 mg $L^{-1}$) was prepared by dissolving 0.1320 g of $As_2O_3$ (Second Chemical Co.

Beijing) in 25 mL of 20% (m/v) KOH, neutralizing with 20% (v/v) $H_2SO_4$ (second chemical Co., Beijing), and diluting to 100 mL with 1% (v/v) $H_2SO_4$. The working standards were obtained from the stock solution after dilution with 1% (v/v) HCl. Sodium methylarsonate (MMA, GR) and sodium dimethylarsenate (DMA, GR) were purchased from Sigma-Aldrich, Inc. (Beijing, China).

The $KBH_4$ solution (1%, m/v) was prepared daily by dissolving 1 g of the reagent (Tianjin institute of chemical reagents, Tianjin) in 100 mL 0.16% (m/v) potassium hydroxide solution and last ones were filtered through a 0.45 μm nylon membrane. A 20% (m/v) KI solution was prepared by dissolving 5 g KI in 25 mL ultra pure water before use. The agar solution (1%, m/v) was prepared by dissolving 1.0 g agar (Haiyang, Guangdong, China) in boiled water. All reagents used were of the analytical purity and all solutions were prepared in double deionized water, with a resistivity of 18.2 MΩ cm obtained from a SAGA50D Water Ultrapurifier (Shanghai, China).

### Apparatus

A model WFX-1F2B atomic absorption spectrometer (Beijing Rayleigh analytical instrument corp) equipped with As hollow cathode lamp (general research institute of non-ferrous metals, Beijing, China) was employed for the measurement of the absorbance with the peak height mode. A spectral width of 0.5 nm was used for the 193.7 nm spectral line. A model WHG-102A2 hydride generator (Beijing Hanshi manufacturing institute, China) with a pneumatic steady flow injection system (Figure1) was used. The hydride generation system and its principle were described (Zhang et al., 2000). The hydride generated in a reaction coil (40 cm × 3 mm i.d) was introduced through a gas-liquid separator to an electro thermal quartz atomizer (140 mm × 8 mm i.d) by argon gas. The temperature of the quartz atomizer was controlled by adjusting supply voltage between 80 V and 130 V.

A model AFS-230 hydride generation-double-channel atomic fluorescence spectrometer (Beijing Haiguang Instrument Ltd, Beijing, China) was utilized for the determination of total inorganic As in flour samples according to the Chinese standard method (standardization administration of China, GB/T 5009.11-2003). A KQ3002B ultrasound vibrator (Kunshan Ultrasound Instrument Ltd, China) was used to stir the slurry samples.

### Slurry preparation

Wheat flour and rice flour were purchased from markets. After grinding the samples, the different diameter particles were sifted out using a sieve with corresponding aperture. Two portions of 0.5 g sample powder with ≤ 54 μm particle size were weighed accurately in 25 mL glass flasks. To one of the portions, 2.5 mL 50% (v/v) HCl and 1.25 mL 20% (m/v) KI were added and heated in water bath for tiny boiling for 5 – 10 min. After cooling, 0.25 g 8-HQ, 0.02 mL n-octanol and 7.5 mL 1% (m/v) agar solution were added, then diluted to 25 mL with deionized water to obtained final slurry with 1% (m/v) KI, 1 % (m/v) 8-HQ, 0.3% (m/v) agar and 5% (v/v) HCl. To the second portion, 0.5 mL 50% (v/v) HCl, 0.25 g 8-HQ, 0.02 mL n-octanol and 7.5 mL 1% (m/v) agar solution were added, then diluted to 25 mL with deionized water to obtained final slurry with 1 % (m/v) 8-HQ, 0.3% (m/v) agar and 1% (v/v) HCl. The two portions of slurry were then treated by sonication at 350 W for 30 min. The first slurry was used for hydride generation of total inorganic As, and the second slurry was used for hydride generation of As (III).

### Procedure

Hydride generation was carried out by using 1.5 mL sample solution, 5 mL 5% or 1% (v/v) HCl, 1.5 mL 1% (m/v) $KBH_4$ and 0.02

mL n-octanol. The generated hydride was introduced through a gas-liquid separator to an electrothermal quartz atomizer by using 200 mL min$^{-1}$ carrier gas. A 110 V voltage was supplied to the electro-thermal quartz atomizer, temperature of which was about 800 °C.

A series of arsenic standards with 0.3% (m/v) agar were prepared along with analytical blank. The atomic absorption signal of As in the slurries was measured with peak height mode for the preparation of slurry standard curve. The content of As(III) in the slurry standard and blank was determined by using slurry standard curve method under 1% (v/v) HCl acidity condition in the presence of 1% (m/v) 8-HQ. The content of total inorganic arsenic was determined by using slurry standard curve method under 5% (v/v) HCl acidity condition in the presence of 1% (m/v) 8-HQ after reduction of As(V) to As(III) with 1% (m/v) KI.

### Determination of inorganic As by Chinese standard method

In order to confirm the accuracy of the slurry sampling-HGAAS method the Chinese standard method (Standardization Administration of China, 2003) was used for the determination of inorganic As in flour samples. A 2.5 g flour sample was extracted with 20 mL 50% (v/v) HCl to achieve separation of inorganic and organic As. 4 mL 50% (v/v) HCl and 1 mL KI–thiourea mixture solution were added in the extract for the determination of inorganic As in flour samples by HGAFS.

## RESULTS AND DISCUSSION

### Stability and uniformity of flour slurry

The preparation of food slurry is a key step for sampling technique. The stability and uniformity of food slurry are an important factor for precision and accuracy of this method. Frequently, the physical and chemical charac-teristics of food samples require the addition of dispersing and stabilizing reagents, which are used to wet solid materials dispersing agglomerates and/or to avoid particles settling down. Their main benefit is that they simplify the preparation of homogeneous slurry. Particle size is a widely studied factor owing to its influence on slurry stability and homogeneity, as well as on precision and accuracy. The most adequate particle size for each particular situation depends on many factors including sample homogeneity (with respect to the analyte), density and required trueness and precision for the final results (Sun et al., 2006).

The stability of flour slurry was compared by using different diameter particles. The suspended time of flour slurry with 180, 150, 88, 76 and 54 μm particles was obtained to be 5 – 30 min. Decrease of particle size prolonged the suspended time. For using particle size of 54 μm, the steady time of slurry achieved 30 min without any sample shaking, showing the good dispersion and homogeneity. In this work the particle size of 54 μm was used to slurry sampling.

Precision is highly dependent on the homogeneity of the analyte distribution in the sample and analyte partitioning between the solid and liquid phases. The

slurry stability is an important factor for measurement precision. The effects of several reagents, such as agar, glycol, xanthan gum, cetyltrimethylammonium bromide and TritonX-100 as well as ethanol on the slurry stability were investigated. Use of Triton X-100 caused foaming. Agar gave better slurry stability than other reagents. For a standard solution with agar, the absorbance value was only lower with 9% than that without agar. The effect of agar concentration on uniformity and stability of slurry with 54 µm diameter particle was investigated further. When using 0.15% (m/v) agar, the slurry could be steadied for 5 min, and the ratio of the absorbance for slurry sampling and solution sampling was obtained to be 0.87. When using 0.3% (m/v) agar, the slurry could be steadied for 3 h, and the ratio of 0.84 was achieved. When using 0.4% (m/v) agar, the steady time increased further, but the slurry was too sticky to be difficult for sampling. Therefore, a 0.3% (m/v) agar in slurry matrix was selected in further experiment.

Ultrasonic agitation for slurry preparations proved useful in avoiding setting of the particles, because it can decrease sedimentation rate of particle. The flour slurry remained stable for several hours after sonicating energetically inside an ultrasound water bath at 350 W for 30 min.

**Choice of antifoam reagent**

For analysis of flour sample a mass of foams were generated in slurry sampling hydride generation process, it badly influences atomic absorption detection. When argon gas was introduced into hydride generator, a great lot of foams would badly influence hydride transgressing and transmitting, and pollute transmission tube, resulting in tailed absorption peak, and the decrease of sensitivity and precision. Antifoaming effect was investigated by comparing ethanol, isopropanol, n-octanol, and tributyl phosphate. The result showed that a great lot of foams disappeared upon addition of a 0.05 mL n-octanol in 25 mL slurry. The addition of n-octanol only could decrease the analytical signal by 4%, but enhance precision obviously.

**Effect of reagents concentration and carrier gas flow rate**

The effect of 0.25 – 2.0% (m/v) $KBH_4$ on the sensitivity was investigated. The highest absorbance was obtained when the concentration of $KBH_4$ was in the range of 0.5 – 1.2%. When $KBH_4$ concentration increased up to 2%, the intensity of the signal decreased because of the dilution of strong hydrogen gas stream. Therefore, 1% (m/v) $KBH_4$ was selected as the best condition.

The conditions of prereduction of As (V) to As (III) were another important factor in the present method. As(V) could not be reduced rapidly to its hydride quantitatively. Prereducing As (V) to As (III) was necessary for the determination of As (V) and total inorganic As. To reduce As (V) to As (III), potassium iodide was commonly used as a prereducing reagent. The time of reduction reaction also is an influencing factor. It needs a need definite time for reducing As (V) to As (III) with KI, and at the same time, $I_2$ produced by self oxidation of KI would cause interference. In order to overcome this problem, the sample solution with 1% (m/v) KI in a sealed test tube was heated in water bath for tiny boiling for 5 – 10 min to make the reaction of KI and As(V) enough and $I_2$ to be transgressed from the solution. Otherwise, before hydride generation, the reaction solution could be placed for a period of time. The higher sensitivity was observed for the longer placement time, but the placement time could not be too long to avoid the transgression of $I_2$ again. The highest absorbance was obtained by hydride generation after placement of the sample solution for 30 min.

The influence of carrier flow rate (50 – 300 mL min$^{-1}$) on absorbance was investigated. An argon flow was used to transfer generated hydride from the reaction cell to the atomizer. The absorbance increased by increasing the argon flow rate from 50 to 180 mL min$^{-1}$, probably due to the increased mass of analyte delivered to the detector by the argon carrier gas, and decreased by further increasing the argon flow rate from 220 to 300 mL min$^{-1}$. There was a platform with higher absorbance under the flow rates in the range of 180 – 220 mL min$^{-1}$. So the argon flow rate of 200 mL min$^{-1}$ was selected.

**Effect of acid medium**

Acidic medium was required for the formation of hydrides. The effects of hydrochloric acid, nitric acid and sulphuric acid on atomic absorption signal were investigated. The result showed that the higher absorbance was observed with hydrochloric acid as reaction medium. The effect of hydrochloric acid concentration from 1 to 10% (v/v) on atomic absorption signal of As is shown in Figures 2a and 3a. The highest absorbance was obtained in 1% (v/v) HCl medium for As(III) and in 5% (v/v) HCl medium during the prereduction reaction for As(V).

The reduction reaction requires the concentration of hydrochloric acid enough to assure the complete reduction within a short time. However, if the acidity was too high, a mass of hydrogen were generated and would dilute As hydride, resulting in low sensitivity.

**Effect of 8-Hydroxyquinoline**

In our previous work, enhancing effect of 8-hydroxyquinoline on nickel was found (Sun and Suo, 2008). To improve the sensitivity and selectivity the effect of 8-HQ on absorbance for As(III) and As(V) was
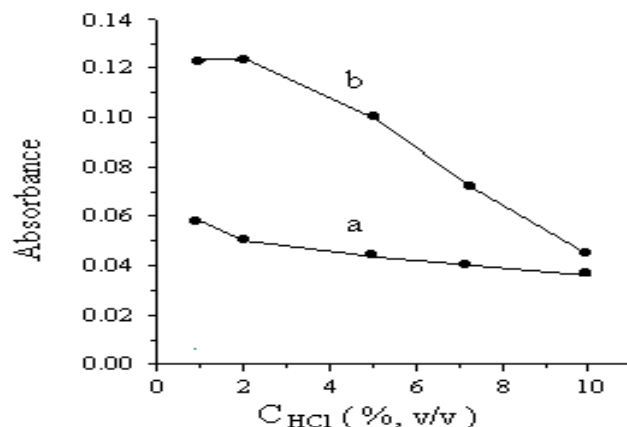
**Figure 2.** Effect of medium acidity on absorbance of As (III) in the presence and absence of 8-HQ. (a) 4 µg L$^{-1}$ As(III); (b) a+1% m/v 8-HQ; data point is the average value of three measurements with < 2% of relative standard deviation.



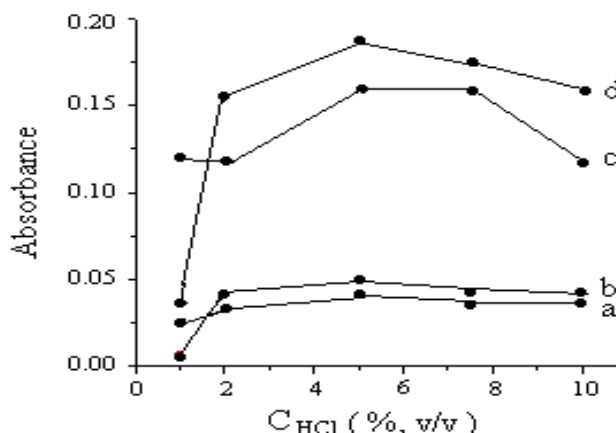**Figure 3.** Effect of medium acidity on absorbance of As(V) in the presence and absence of 8-HQ. (a) 8 µg L$^{-1}$ As(V); (b) a+1% m/v 8-HQ; (c) a+1% m/v KI; d: c+1% m/v 8-HQ; data point is the average value of three measurements with < 2% of relative standard deviation

investigated under different acidities. From Figure 2b it was shown that the absorbance for As (III) decreased gradually with the increase of HCl concentration. 8-HQ in 1 – 2% (v/v) HCl medium had obvious increasing effect, the absorbance could be increased by 108%, and the increasing extent decreased with the increase of HCL concentration. After prereduction of As(V) to As(III) with KI in 2 – 10% (v/v) HCl, KBH$_4$ was added in the obtained reaction solution for hydride generation of As(III) to investigate the effect of 8-HQ. From Figure 3c and 3d it is shown that the obviously increasing effect of 8-HQ on absorbance for As(V) which was previously reduced to As(III) through prereduction with KI in 2 – 10% (v/v) HCl medium. When the acidity of slurry was 5%, the highest

absorbance was obtained. The effect of 8-HQ concentration on the absorbance for As(V) was investigated in 5% HCl medium. The result showed that the absorbance for As(V) (previously reduced to As(III)) increased with the increase of 8-HQ concentration from 0.125 to 1.0%, and when 1.0% 8-HQ was used, the absorbance can be increased by 19%. When over 1.0%, the absorbance did not further increased. So 1% 8-HQ was used in further test.

The high enhancement effect of 8-HQ was probably due to the fact that 8-HQ improved the physical properties of solutions, such as viscosity and surface tension etc. Otherwise, from Figures 3b and 3d it is can be seen that, 8-HQ in 1% HCl medium  without  and with

the prereduction has strong control effect on As(V), resulting the absorbance decreased to 0.006 and 0.027, respectively. Therefore, use of 8-HQ as inhibiting agent can overcome the interfere of As(V) to As(III). This was probably due to the formation of an ion-associate of As (V) with 8-HQ (Deng et al., 2001).

Based on above result, it is indicated that the determination of As (III) can be achieved using both inhibitory effect of 8-HQ on As(V) and enhancing effect of 8-HQ on As(III) under 1% HCl acidity condition. And the determination of total inorganic As can be achieved using enhancing effect of 8-HQ on both As (III) and As (V) under 5% HCl acidity condition with prereduction.

## Interference studies

The direct determination of As(III) and total inorganic As in water samples was achieved using HGAAS without prereduction of As(V), and no interferences from methylated arsenic species, mutual hydride-forming, and transition elements in the determination of As(III) and total As were observed (Kumar and Riyazuddin, 2008). Otherwise, selective medium reactions were investigated for selectively generation hydrides of each As species (Bermejo-Barrera et al., 1998; Quináia and Rollemberg, 2001). Total inorganic As (As (III) and As (V)) can be determined by using $KBH_4$ under higher HCl acidity after pre-reduction with KI, and DMA could not be determined under the same conditions. It is suggested that DMA could not be reduced by KI and $KBH_4$ in the test conditions.

The use of 8-HQ as a masking reagent did not modify the valences of As in the sample and had a low blank value. In our work the influences of common interferents on the atomic absorption signals were investigated in the presence of 8-HQ using the recommended conditions. The tolerance content of foreign ions is suggested as the interferent content reducing the analyte signal by 10%. The effect of MMA(V) and DMA(V) (10 µg $L^{-1}$, each) on As(III) and As(V) (10 µg $L^{-1}$, each) was investigated further, respectively. The result showed that no interference from MMA(V) and DMA(V) was observed during the determination of As(III) under 1% HCl acidity condition in the presence of 8-HQ, and during the determination of As(III) and As(V) under 5% HCl acidity condition in the presence of 8-HQ.

Otherwise, 50 mg $L^{-1}$ K and Na; 40 mg $L^{-1}$ Ca and Mg; 25 mg $L^{-1}$ Al and V; 10 mg $L^{-1}$ Mn, Fe and Zn; 5 mg $L^{-1}$ Pb, Cu and Bi; 1mg $L^{-1}$ Sb and Se have no influence on the determination of 10 µg $L^{-1}$ As in the presence of 8-HQ. In real samples, the contents of the foreign ions were much lower then the tolerance content, so that there was no interference for the determination of As(III) alone and total inorganic arsenic.

## Analytical performance

The calibration curve was conducted by determining a series of standard solutions with 0.3% m/v agar for direct determination of As by slurry sampling HGAAS. Standard addition method was used to evaluate the accuracy by comparing the slopes of calibration curve for this method and standard addition method. The obtained slope value was 0.01997 ± 0.00189 (SD, n = 3) for this method and 0.02004 ± 0.00180 (SD, n = 3) for standard addition method. The slope ratio of the two curves was close to 1, so the slurry sampling standard curve can be used directly for the determination of As in real samples with advantage of convenience. The linear equation for As(III) was A = 0.02131C + 0.0027, with the correlation coefficient (r) of 0.9996, and the linear equation for total inorganic arsenic was A = 0.01997C + 0.0088, with the correlation coefficient (r) of 0.9988, where A is the absorbance and C is the analyte concentration (µg $L^{-1}$).The instrumental detection limit (LOD) is given as equal to the mean of the blank signal for ten replicates plus three times the standard deviation of the blank for ten replicates, and it was 0.080 µg $L^{-1}$ for As(III) and 0.089 µg $L^{-1}$ for total inorganic As. For 0.5 g sample, the method detection limit was 4.0 µg $kg^{-1}$ for As(III) and 4.5 µg $kg^{-1}$ for total inorganic As. Thus, the developed methodology is adequate for the speciation analysis of ultra-trace inorganic As in flour samples.

## Recovery experiments

Recovery studies were conducted on wheat flour and rice flour samples spiked with different concentration of As(III) and As(V). The results are summarized in Table 1. The recovery values ranging from 94.3 to 107% were found for As(III) spiked in the range of 25–150 µg $kg^{-1}$ with relative standard deviations (RSDs) of 1.0 – 2.5%, and the recovery values from 98.5 to 104% were obtained for As(V) spiked in the range of 50 – 150µg $kg^{-1}$ with RSDs of 1.2 – 2.8%. It is indicated that lack of losses or contaminations during sample preparation and specially that added As species remain unchanged.

## Sample analysis

Wheat and rice flour are most foodstuff. The content of As (III) and total inorganic As in these flours was determined by slurry sampling HGAAS with slurry standard curve method. The results are listed in Table 2, along with the content of As(V) obtained by the difference between total inorganic As and As(III). The relative standard deviation (RSD) is in the range of 4.3 – 4.6% for three determinations of As(III) and 2.2 – 3.3% for three determinations of total inorganic As.

The feasibility of the method for the determination of

**Table 1.** The results of recovery experiment (n=3).

| Sample | As (III) added ($\mu g \cdot kg^{-1}$) | Average recovery (%) | As(V) added ($\mu g \cdot kg^{-1}$) | Average recovery (%) |
|---|---|---|---|---|
| Wheat flour | 25 | 106 | 50 | 102 |
| | 50 | 106 | 100 | 104 |
| | 100 | 107 | 150 | 101 |
| Rice flour | 50 | 94.3 | 50 | 100 |
| | 100 | 102 | 100 | 98.5 |
| | 150 | 104 | 150 | 104 |

**Table 2.** Speciation analysis of inorganic arsenic in flours.

| Sample | This method | | | | | Chinese standard method |
|---|---|---|---|---|---|---|
| | As(III) * ($\mu g\ kg^{-1}$) | RSD** (%) | Total inorganic As* ($\mu g\ kg^{-1}$) | RSD** (%) | As(V)* ($\mu g\ kg^{-1}$) | Total inorganic As* ($\mu g\ kg^{-1}$) |
| Wheat flour | *** | | 67±1.5 | 2.2 | 67±1.5 | 65±3.5 |
| | *** | | 60±1.2 | 2.5 | 60±1.2 | 59±1.5 |
| Rice flour | 56±2.6 | 4.6 | 76±2.5 | 3.0 | 20±2.6 | 77±3.0 |
| | 49±2.4 | 4.3 | 67±2.2 | 3.3 | 18±2.4 | 68±2.3 |

*Average ± SD, ** n=7, ***not detected.

total inorganic As in these samples was evaluated by the Chinese standard method (GB/T 5009.11-2003). Statistical analysis using t-test (n = 7) showed no significant difference (p = 0.05) between the total inorganic As values obtained using the two method by 7 measurements for each sample. Based on these test results, it is shown that the proposed method is reliable for the determination of As (III) and total inorganic As. From the analytical results it is shown that the contents of total inorganic As obtained by this method and Chinese standard method are coincident, which lower than the tolerance limit of the inorganic As established in Chinese National Standard.

## Conclusion

8-HQ has both inhibitory effect to As(V) and enhancing effect to As(III) under 1% HCl acidity condition, and enhancing effect to both As(III) and As(V) under 5% HCl acidity condition. Based on these characteristics hydride generation in slurry of food sample can be used for speciation analysis of As(III) and total inorganic As by atomic absorption spectrometry. From the analytical results it is shown that the contents of total inorganic As obtained by this method and the standard method are coincident, which lower than the tolerance limit of the inorganic As established in Chinese national standard. The proposed procedure is accurate, precise and low

time consuming. This approach provides a viable alternative to the conventional HGAAS technique for speciation analysis of As(III) and total inorganic As in food samples.

## ACKNOWLEDGEMENTS

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