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# Method development for the determination of manganese in wheat flour by slurry sampling flame atomic absorption spectrometry

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## Abstract

The wheat is one of the cereals more consumed in the human food in all worlds. In the form of flour it is used for preparation of breads, cookies, pizzas, cakes, and etc. This way, the knowledge of the mineral content this cereal and its flour is very important. Considering it, methods for determination of metals in these matrices are opportune and several papers have been performed.

In this paper, a slurry sampling flame atomic absorption spectrometric method for the determination of manganese in wheat flour is proposed. The optimization step was performed using univariate methodology involving the variables: nature and concentration of the acid solution for slurry preparation, sonication time and sample mass.

The established experimental conditions after optimization recommend a sample mass of 0.5 g, 2.0 mol L<sup>-1</sup> nitric acid solution and a sonication time of 15 min.

This method allows the determination of manganese in wheat flour using the standard calibration technique, with a detection limit of 0.13 µg g<sup>-1</sup>, and a precision, expressed as relative standard deviation (RSD) of 3.5% ( $n = 10$ ) for a manganese content of about 7.6 µg g<sup>-1</sup> and using a wheat flour mass of 0.5 g. The accuracy was confirmed by analyzing of three certified reference materials of rice flours.

The proposed method was applied for the determination of manganese in seven samples of wheat flour acquired in supermarkets from Salvador City, Brazil. In these, the manganese content varied of 5.2 and 7.6 µg g<sup>-1</sup>. The results showed no significant differences with those obtained after complete digestion of these samples and manganese determination also using FAAS.

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**Keywords:** Slurry sampling; Wheat flour; Manganese determination; FAAS

## 1. Introduction

Wheat is one of the cereals more consumed in the human foods. In the form of flour it is used for preparation of breads, cookies, pizzas, cakes and etc. This way, the knowledge of the mineral content this cereal and its flour is very important (Arredondo, Salva, Pizarro, & Olivares, 2003; Ranum, 2005; Sebecic & Vedrinar-Dragojevic,

2004). Considering it, methods for determination of metals in these matrices are opportune and several papers have been published (Jacob & Berndt, 2002; Shar, Kazi, Jakh-rani, Sahito, & Memon, 2002; Wang, Chen, Xie, Fan, & Wu, 2004). In the last years, a variety of analytical methods have been performed involving the direct analysis of solid samples and also slurry sampling (Kurfürst, 1997). These methods present the followings advantages: simplification of sample pre-treatment, reduced risk of sample contamination, minimization of analyte losses during the pre-treatment operations or due to incomplete release of the analyte from the solid matrix, and no hazardous or corrosive

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reagents required. Slurry sampling has been used extensively during the last years for inductively coupled plasma optical emission spectrometry (ICP OES) (Ebdon, Foulkes, & Sutton, 1997), electrothermal atomic absorption spectrometry (Amin, Kaneco, Suzuki, & Ohta, 2003; Cal-Prieto et al., 2002) and ICP mass spectrometry (Maia, Pozebon, & Curtius, 2003; Ribeiro, Vieira, & Curtius, 2004). A method using hydride generation atomic fluorescence was also recently proposed for determination of selenium in milk (Rodenas-Torralba, Morales-Rubio, & Dela-Guardia, 2005). Methods for analysis of wheat flour using slurry sampling ET AAS were performed for determination of selenium (Bendicho & Sancho, 1993) and also nickel, chromium and cobalt (Gonzalez, Gallego, & Valcarcel, 1999).

Slurry sampling methods using flame AAS (FAAS) are described less frequently in the literature (Alves, Cadore, Jardim, & Arruda, 2001; DeAlmeida, Leandro, DaCosta, Santelli, & DelaGuardia, 1997; Pereira, Berndt, & Arruda, 2002; Quaresma, Cassella, & De LaGuardia, 2004; Santos et al., *in press*), at least in part because of the limited sensitivity of this technique, and the risk of clogging the nebulizer capillary with sample particles.

Manganese is an inorganic nutrient involved in many important enzymes and/or proteins and thereby in many physiological functions of the organism. Deficiency signs include poor reproductive performance, growth retardation, congenital malformations in offspring, abnormal function of bone and cartilage and impaired glucose tolerance (Goldhaber, 2003). Several papers have been published involving the determination of manganese in food samples (Moreno-Rojas, Diaz-Valverde, Arroyo, Gonzalez, & Capote, 2004; Nergiz & Donmez, 2004; Turkekul, Elmastas, & Tuzen, 2004). In the present paper, a slurry sampling FAAS method for the determination of manganese in wheat flour is proposed. The method was applied for manganese determination in wheat flour samples acquired in supermarkets from Salvador City, Brasil.

## 2. Experimental

### 2.1. Instrumentation

A Varian (Mulgrave, Victoria, Australia) Model SpectrAA 220 flame atomic absorption spectrometer was used for the analysis. The manganese hollow cathode lamp was operated with a current of 5.0 mA. The most sensitive wavelength of manganese at 279.5 nm was used with a bandwidth of 0.2 nm. The flame composition was: acetylene (flow rate 2.0 L min<sup>-1</sup>) and air (flow rate: 13.5 L min<sup>-1</sup>); the burner height was 13.5 mm, and the nebulizer flow rates were around 5.5–6.0 mL min<sup>-1</sup>. The medium particle size was measured using a Shimadzu (Kioto, Japan) Superscan SS-550 scanning electron microscope. An Ultrasonic Benchtop Cleaner VWR Model 75 D (Cortland, New York, USA) was used for slurry preparation.

### 2.2. Reagents and samples

All reagents were of analytical grade unless otherwise stated. Ultrapure water was obtained from an EASYpure RF (Barnstedt, Dubuque, IA, USA). Nitric and hydrochloric acid were of suprapur<sup>®</sup> quality (Merck). Laboratory glassware was kept overnight in 10% (v/v) nitric acid. Before use the glassware was rinsed with deionized water and dried in a dust free environment.

Manganese solution (100.0 µg mL<sup>-1</sup>) was prepared by diluting a 1000 µg mL<sup>-1</sup> manganese solution (Merck) with 1% (v/v) hydrochloric acid.

The certified reference materials used for confirmation of the accuracy were: SRM 1568a rice flour (National Institute of Standard and Technology, NIST, Gaithersburg, MD, USA) and two CRM's rice flour (National Institute for Environmental Studies, NIES, Onogawa, Tsukuba, Japan).

The rice flour used for slurry preparation during the determination of the analytical features was MAIZENA<sup>®</sup> e DURYEA<sup>®</sup> (Unilever Bestfoods Brazil Ltda, Garanhuns, PERNANBUCO, Brazil).

The wheat flour samples investigated in this study were locally available brands, collected in supermarkets from Salvador City, Brazil.

## 3. Slurry preparation

The slurries were prepared by placing 0.5 g of dried sample (medium size of the particles  $\cong$  18 µm) and 50.0 mL of 2.0 mol L<sup>-1</sup> nitric acid solution in an ultrasonic bath for 15 min. Afterwards, the slurries were aspirated directly through the nebulizer for manganese determination. The blanks were prepared in the same way as the slurries using a rice flour with manganese concentration lower than the limit of quantification of this method.

### 3.1. Complete digestion of wheat flour samples

For the acid digestion, about 0.5 g of the wheat flour samples, 5.0 mL of concentrated nitric acid and 1.0 mL of hydrogen peroxide were placed in a glass vessel and heated on a hot plate (in these conditions the samples are decomposed easily). Finally the content was quantitatively transferred to 10 mL volumetric flasks and diluted with water.

## 4. Results and discussion

### 4.1. Optimization of the experimental conditions

The optimization was performed using univariate methodology, involving the parameters: nature and concentration of the acid, sonication time and sample mass. All the experiments were performed using a slurry volume of 50 mL.

During the choice of the liquid phase for slurry preparation, hydrochloric and nitric acid solutions were tested. The results demonstrated that there is no difference in the analytical signals obtained for both acids, and that maximum sensitivity is obtained at a concentration of  $1.0 \text{ mol L}^{-1}$ , which remains constant up to  $4.0 \text{ mol L}^{-1}$ . However, a concentration of  $2.0 \text{ mol L}^{-1}$  nitric acid was used for slurry preparation in all further experiments, as slurries prepared with lower acid concentrations occasionally caused blockage of the nebulizer.

The sonication time was varied from 0 to 25 min, and there was no influence from this parameter on the analytical signal obtained. However, it was observed that slurries prepared with sonication times of less than 10 min also caused occasional blockage of the nebulizer. For this reason, a sonication time of 15 min was used for all further investigations.

The sample mass for slurry preparation was varied between 200 and 1000 mg, using 50 mL of  $2.0 \text{ mol L}^{-1}$  nitric acid and a sonication time of 15 min. The results showed that the slurries could be prepared without problems using up to 0.8 g of sample. The analytical signals obtained were linearly proportional with the sample mass. A sample mass of 0.5 g was used for all further investigations.

An additional experiment was carried out in order to investigate the extraction efficiency for manganese from the wheat flour samples, using the proposed method, i.e.  $2.0 \text{ mol L}^{-1}$  nitric acid and a sonication time of 15 min. The absorbance obtained for the slurry was  $0.0170 \pm 0.0002$ . The absorbance obtained for the liquid phase of the same slurry after centrifugation for 10 min and filtration was  $0.0147 \pm 0.0002$ , demonstrating that the extraction process of manganese under these conditions was not complete ( $\cong 86\%$ ). Hence it was necessary to use the slurry for complete recovery and not the liquid phase only.

#### 4.2. Analytical features

The limit of detection (LOD) and quantification (LQ) were determined considering the standard deviation(s) of the blank (prepared in the same way as the samples as slurry using 0.5 g of MAIZENA® rice flour). The LOD and LQ obtained were 0.13 and  $0.44 \mu\text{g}$  of manganese per gram of wheat flour.

The precision calculated from 10 consecutive measurements of the slurry of a wheat flour sample with a manganese content of  $7.6 \mu\text{g g}^{-1}$ , expressed as relative standard deviation (RSD), was 3.5%.

The calibration equations using aqueous standards ( $A = 0.1831 C_{\text{Mn}} + 0.0013$ ), and for the analyte addition in wheat flour ( $A = 0.1834 C_{\text{Mn}} + 0.0084$ ) and rice flour ( $A = 0.1855 C_{\text{Mn}} + 0.0002$ ), exhibited very similar slopes, and the correlation coefficients were all  $>0.999$ . These results demonstrated that manganese in wheat flour samples can be directly determined using the standard calibration technique. The accuracy of the method was further

Table 1  
Manganese determination in rice flour CRM

Rice flour CRM	Certified value ( $\mu\text{g g}^{-1}$ )	Slurry method ( $\mu\text{g g}^{-1}$ )
NIST 1568a	$20.0 \pm 1.6$	$19.2 \pm 0.6$
NIES 1-a	$34.7 \pm 1.8$	$34.3 \pm 0.6$
NIES 1-c	$40.1 \pm 2.0$	$38.3 \pm 0.3$

Results expressed as interval confidence (at the 95% level). Observation number = 3. NIST: National Institute of Standard and Technology; NIES: National Institute for Environmental Studies.

Table 2  
Manganese determination in wheat flour samples ( $n = 3$ )

Sample	Complete digestion ( $\mu\text{g g}^{-1}$ )	Slurry method ( $\mu\text{g g}^{-1}$ )
1	$5.8 \pm 0.3$	$5.8 \pm 0.2$
2	$5.1 \pm 0.1$	$5.2 \pm 0.7$
3	$5.8 \pm 0.4$	$6.0 \pm 0.8$
4	$7.8 \pm 0.5$	$7.6 \pm 0.5$
5	$5.4 \pm 0.1$	$5.5 \pm 0.3$
6	$7.1 \pm 0.1$	$7.3 \pm 0.6$
7	$5.9 \pm 0.4$	$6.2 \pm 0.1$

Results expressed as interval confidence (at the 95% level). Observation number = 3.

confirmed by manganese determination in three certified reference materials (CRM) of rice flour. The results expressed as confidence interval (at the 95% level) are shown in Table 1. The statistical comparison by *t*-test showed no significant difference between the manganese values obtained with the proposed method and the certified value for both CRM.

#### 4.3. Application

The proposed method was applied for the determination of manganese in seven locally available powdered wheat flour samples, collected in supermarkets from Salvador City, Brazil. The results expressed as interval confidence (at the 95% level) are summarized in Table 2. The manganese content found in these samples was between 5.2 and  $7.6 \mu\text{g}$  per gram of wheat flour. These samples were also analyzed after complete digestion (using nitric acid and hydrogen peroxide) and manganese determination by FAAS, and the results also are shown in Table 2. The *t*-test exhibited no significant difference between the manganese values obtained with the slurry method and those after complete digestion. The results achieved are close of data published in the literature (Santos, Lauria, & Silveira, 2004).

#### 5. Conclusions

The method proposed has limit of detection, precision and accuracy necessary for the determination of manganese in wheat flour samples. The use of the standard calibration technique with aqueous solutions makes the procedure quite simple and fast. The manganese content

found in the wheat flour samples are close of data published in the literature.

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