

## Determination of chlorine and sulfur in flour at ppb-level: an evaluation of sample preparation methods and detection techniques

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### Introduction

Chlorinated compounds are used in flour industry as an oxidizing and bleaching agent and to improve the quality of flour. However, some of these compounds show toxic effects to the health. On the other hand, sulfur is essential for humans, animals and plants, but at higher concentration some compounds are toxic. In general, concentration of these elements in food is relatively high. Considering that most of analytical techniques require the use of sample solution for the measurement, a previous sample preparation step is needed. Thus, sample digestion methods have been suggested such as acid digestion (generally for S), extraction, pyrohydrolysis, microwave-induced combustion and others.<sup>1</sup> However, some sample preparation methods are time consuming, with risk of analyte losses and/or contamination. Thereby, solid sampling (SS) approach is recommended in order to overcome the disadvantages of conventional sample preparation methods. Thus, in this work a SS system based on sample combustion followed by microcoulometry and fluorescence detection was evaluated for the determination of Cl and S in flour samples.<sup>2,3</sup>

### Results e discussion

A SS system (Multi EA<sup>®</sup> 5000 elemental analyzer, Analytik Jena, Germany) was employed for Cl and S determination by microcoulometry and fluorescence detection, respectively. In order to obtain maximum signal intensity with suitable accuracy and precision, some parameters such as furnace temperature (800 to 1100 °C), time of second combustion (10 to 120 s) and oxygen and argon flow rate (50 to 200 mL min<sup>-1</sup>) were evaluated. Optimized conditions of SS system for Cl and S determination were furnace temperature of 1050 °C, time for second combustion of 90 s for Cl and 60 s for S, argon flow rate of 100 mL min<sup>-1</sup> and oxygen flow rate of 100 mL min<sup>-1</sup> for Cl and 50 mL min<sup>-1</sup> for S. In order to evaluate the accuracy of proposed method, a certified reference material (CRM) of rice flour (NIST 1568a) was used and agreement with certified values ranged from 98 to 102%. The proposed method was applied for determination of Cl and S in flour samples from different raw materials such as potato (1), corn (1),

wheat (5) and whole wheat flour (1) as well as different countries such as Austria (1), Belgium (2), Brazil (3) and Poland (2). Chlorine and S concentration in flour samples ranged from 4.8 to 685 µg g<sup>-1</sup> and from 13 to 1328 µg g<sup>-1</sup>, respectively. In addition, results obtained by SS system were compared with those obtained by microwave induced combustion (MIC) system (Multiwave 3000 Microwave Sample Preparation System, Anton Paar, Austria)<sup>4</sup> followed by analytes determination by ion chromatography (IC, Metrohm, Herisau, Switzerland). Sulfur was also determined by inductively coupled plasma optical emission spectrometry (ICP OES, Optima 4300 DV, PerkinElmer, USA). It is important to point out that no significant differences were observed comparing results of SS system and MIC (detection by IC and ICP OES). The limit of detection (LOD) for Cl and S using proposed SS system was 0.9 and 0.1 µg g<sup>-1</sup>, respectively. Thus, the LOD for Cl was 2 times lower than using MIC and IC. For sulfur, LOD was 5 and 10 times lower than MIC with detection by IC and ICP OES, respectively.

### Conclusions

Solid sampling system was an excellent performance for determination of Cl and S at low concentration in flour samples. The main parameters of method were considered suitable such as good accuracy (98 to 102%) and precision (below 5%), wide range of sample mass (2 to 200 mg) was easily introduced into the system and extremely low LODs (0.9 µg g<sup>-1</sup> for Cl and 0.1 µg g<sup>-1</sup> for Cl) were achieved. Thus, proposed method is simple, once no solid standards are necessary for instrument calibration.

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