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Analytical Methods

Determination of total sulfur concentrations in different types of vinegars using high resolution flame molecular absorption spectrometry

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Total sulfur concentrations in vinegars were determined using molecular absorption of carbon monosulfide (CS) determined with a high-resolution continuum source flame atomic absorption spectrometer. The molecular absorption of CS was measured at 258.056 nm in an air–acetylene flame. Due to non-spectral interference, as well as the different sensitivities to some sulfur compounds, all sulfur species were oxidized to sulfate using a HNO_3 and H_2O_2 mixture and the analyte addition technique was applied for quantification. The limit of detection (LOD) and limit of quantification (LOQ) were 11.6 and 38.6 mg L^{-1}, respectively. The concentrations of sulfur in various vinegars ranged from ⩽LOD to 163.6 mg L^{-1}.

1. Introduction

Vinegar is an acidic liquid that is produced by fermentation of wine (or, strictly speaking, ethanol) or fruit pulps and juices with the help of bacteria. It consists mainly of acetic acid, water and other trace chemicals to give flavor and taste (Nakayama, 1959). Vinegar is commonly used as a condiment, a preservative, an antiseptic and a cleaning agent. Annual vinegar production in Turkey is more than 35,000 tonnes and increases year-by-year. Grape vinegar is the most commonly used in Turkey as well as globally.

Generally, grapes are treated with sulfur dioxide during production and transportation to prevent mold and decay. When these grapes are used for vinegar, sulfur compounds can still be present. In addition, sulfur compounds, mainly sodium metabisulfite ($Na_2S_2O_5$), are added to vinegars as preservatives for their antibacterial and antioxidant properties. In an acidic matrix, sodium metabisulfite releases sulfur oxides. In vinegars, sulfur can be present as free sulfur dioxide in the forms of H_2SO_3, HSO_3^- and SO_3^{2-} as well as bound to compounds, such as phenols, acetaldehyde and sugar. Sulfate also occurs in vinegars through oxidation of free sulfur dioxide as well as from other sources. The sum of free and bound SO_2 makes up total SO_2. The bound SO_2 is inactive and has no antimicrobial efficacy whereas free sulfur dioxide has antioxidant, bactericide and antiseptic characteristics (Quirós, Herrero, García, & Díaz, 2012).

Sulfur can cause allergic reactions, leading to anaphylaxis, or respiratory reactions, such as asthma (Metcalfe, Sampson, & Simon, 2009). Because of its negative health effects, the addition of sulfur as a preservative is authorized according to defined standards. According to the US Environmental Protection Agency (US EPA), sulfur dioxide between 50 and 100 mg L^{-1} is allowed in grape juice and wine vinegar (International for the USDA National Organic Program ICF, 2011; U.S. EPA, 2007). According to EU Regulation (EC) No. 1333/2008, the maximum should be expressed as SO_2 content of not more than 10 mg kg^{-1} or 10 mg L^{-1} (Council of the European Union, 2011). In Turkey, the maximum allowable sulfur dioxide concentration, as a preservative in vinegar set by regulation, is 170 mg L^{-1} (Republic of Turkey Ministry of Food Agriculture & Livestock, 2004).

There are several methods for the determination of sulfur, such as flow injection turbidimetry (Brienza, Sartini, Neto, & Zagatto, 1995), inductively coupled plasma-atomic emission spectrometry (Santelli, Oliveira, de Carvalho, Bezerra, & Freire, 2008), inductively coupled plasma-mass spectrometry (Heilmann, Boulyga, & Heumann, 2004), X-ray fluorescence spectrometry (Kendall, Schoenwald, Siao, & Hendricks, 1995) and chromatography (Bak, Schuhmann, & Jansen, 1993). Each method has advantages and disadvantages with respect to cost, precision, selectivity, limit of detection and simplicity.

Since the atomic absorption lines of non-metals are in the vacuum UV range, they cannot be determined by conventional AAS.

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Following the availability of commercial HR-CS AAS, non-metals including sulfur have been determined based on the molecular absorption of diatomic molecules formed with another element, a so-called "molecule forming element", in a flame or graphite furnace. Sulfur is commonly determined at one of the rotational absorption lines of CS. Generally, carbon is chosen as a molecule forming element because it is found abundantly both in the flame and the graphite furnace as well as in the sample matrix. Thus, it is not necessary to add it to the sample, externally.

Since LOD values in the graphite furnace are lower than those in flame, in most studies, the former was used as an atomizer. However, in the graphite furnace, the sensitivities of sulfur compounds in standards and samples as well as their thermal behaviors, such as conversion efficiencies of sulfur to CS and volatilities of sulfur compounds, are not always the same, causing dissimilar pyrolysis curves prior to the molecule formation step and also inaccurate results (Huang, Becker-Ross, Florek, Heitmann, & Okruss, 2005). Therefore, a systematic study would be needed to optimize instrumental conditions for the graphite furnace as well as selection of an appropriate calibrant with similar sensitivity and thermal behavior to those of the analyte in the sample. In case of the flame atomizer, since the sample is not thermally treated prior to the molecule formation, such problems (i.e. removal of the volatile compounds at lower temperatures) do not occur. Moreover, non-spectral interferences, due to reactions with sulfur, are less likely in the flame environment. Finally, optimization and analysis using the flame technique are faster and more practical than the graphite furnace.

Until now, sulfur was determined by flame HR-CS AAS (HR-CS FAAS) in foods (Ozbek & Baysal, 2015; Zambrzycka & Godlewska-Żyłkiewicz, 2014), coal samples (Baysal & Akman, 2011), plant leaves (Oliveira, Gomes Neto, Nóbrega, & Jones, 2010), agricultural samples (Virgilio, Raposo, Cardoso, Nóbrega, & Gomes Neto, 2011), petroleum products (Kowalewska, 2011) and by graphite furnace HR-CS AAS (HR-CS GFAAS) in food samples (Gunduz & Akman, 2014; Ozbek & Akman, 2013), biological samples (Ferreira, Lepri, Welz, Carasek, & Huang, 2010), coal samples (Mior, Morés, Welz, Carasek, & de Andrade, 2013) and airborne particulates (Ozbek & Baysal, 2016). Moreover determination of sulfur in water samples was done by molecular absorption of SnS by HR-CS GFAAS (Baumbach, Limburg, & Einax, 2013). Sulfur determination methods, based on molecular absorption of carbon monosulfide (CS) using high resolution-continuum source atomic absorption spectrometers, were extensively reviewed (Butcher, 2013; Resano, Flórez, & García-Ruiz, 2014; Welz et al., 2009). The aim of this study was, therefore, to develop and optimize a procedure for the determination of total sulfur in vinegars based on molecular absorption of CS using HR-CS FAAS, and to discuss the effects of different sulfur species on the CS sensitivity and elimination of errors due to interference.

2. Experimental

2.1. Instrumentation

An Analytik Jena ContrAA 700 High-Resolution Continuum Source Flame Atomic Absorption Spectrometer (Analytik Jena, Jena, Germany) equipped with an air–acetylene-flame, 300 W xenon short-arc lamp (XBO 301, GLE, Jena, Germany), a high-resolution double monochromator with a prism pre-monochromator, a high-resolution echelle monochromator and a charge coupled device (CCD) array as a detector was used. The molecular absorption of CS was measured at 258.056 nm (central pixel ± 1). All measurements were made in at least three replicates. Samples were prepared using Eppendorf pipettes in polyethylene wares.

2.2. Reagents

High-purity water (resistivity 18.2 MΩ cm) obtained by a TKA reverse osmosis and a TKA deionizer system (TKA Wasseraufbereitungsysteme GmbH, Niederelbert, Germany) was used in solution preparations and dilutions. The reagents used in this work were of analytical grade (HNO_3, 65% (w/w), Merck, Darmstadt, Germany·H_2O_2, 30%, Carlo Erba, Italy).

The sulfur standards, potassium pyrosulfate ($K_2S_2O_7$), potassium sulfate (K_2SO_4), magnesium sulfate heptahydrate ($MgSO_4$-·$7H_2O$), sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), sodium thiosulfate ($Na_2S_2O_3$), sodium sulfite (Na_2SO_3), sodium persulfate ($Na_2S_2O_8$) and sodium metabisulfite ($Na_2S_2O_5$) were obtained from Merck (Darmstadt, Germany). The waste water standard reference material SPS-NUTR-WW2 (which includes 10.0 ± 0.1 $\mu g\ mL^{-1}$ of F^-, 50.0 ± 0.5 $\mu g\ mL^{-1}$ of Cl^-, 7.5 ± 0.08 $\mu g\ mL^-$ of PO_4^{3-}, 5.0 ± 0.05 $\mu g\ mL^{-1}$ of NO^{3-} and 100 ± 1 $\mu g\ mL^{-1}$ of SO_4^{2-}) was provided by LGC Standards (Teddington, UK).

Different types of vinegars (grape, apple, balsamic, pomegranate and fig), produced in 2015 by different factories, were purchased from markets in Istanbul. The samples were chosen from amongst the most commonly consumed brands in Turkey.

2.3. Procedure

The analyte addition technique was applied to determine sulfur in vinegar. Standards were prepared from sodium metabisulfite daily. Vinegars were analyzed seven days after opening the bottle. In order to convert the sulfur forms to sulfate, 0.20 mL of H_2O_2 (30%) and 0.20 mL HNO_3 (65%) were added to 5 mL of vinegar and the mixture was made up to 10 mL with distilled water or standards. In order to prepare the analyte addition graph, three solutions were used. While the first was made up to volume with distilled water, the others were made up to volume with 20 mg L^{-1} and 50 mg L^{-1} of sodium metabisulfite, respectively. For each sample type (grape vinegar, apple vinegar etc.), different standard addition graphs were developed since their matrices were different from one another. After standing for 30 min, the solutions were aspirated into the fuel-rich air–acetylene flame. The results were evaluated as the mean of triplicate analysis.

3. Results and discussion

3.1. Selection of atomizer

In this study, the flame technique was selected because it was anticipated that the sulfur concentrations in most of the vinegars samples would be higher than the LOD. Sulfur determination, even in a flame, is not completely free of problems. It has been reported that the sensitivities of CS obtained from different compounds might not always be the same (Huang et al., 2008). However, the problems are less significant and their elimination is less troublesome compared to the graphite furnace.

3.2. Selection of wavelength

The primary CS lines, 257.593, 257.959 and 258.056 nm, are well documented in the literature with respect to sensitivity (Ferreira et al., 2010; Huang, Becker-Ross, Florek, Heitmann, & Okruss, 2006; Huang et al., 2005; Virgilio et al., 2011). The highest sensitivity was obtained at 258.056 nm, corresponding to one of the $\Delta\nu = 0$ vibrational sequences of the electronic transition $X^1\Sigma + \rightarrow A^1\Pi$ (Kowalewska, 2011). The wavelength resolved absorption spectrum of a vinegar sample in the vicinity of 258.056 nm is shown in Fig. 1. No molecular and atomic absorption signal