

# Determination of Total Sulfur in Food Samples by Solid Sampling High-Resolution Continuum Source Graphite Furnace Molecular Absorption Spectrometry

Nil Ozbek and Suleyman Akman\*

Department of Chemistry, Faculty of Arts and Sciences, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

**ABSTRACT:** The determination of sulfur in food samples via the rotational molecular absorption of carbon monosulfide (CS) was performed using a solid sampling high-resolution continuum source electrothermal atomic absorption spectrophotometer (SS-HR-CS-ETAAS). In the presence of plenty of carbon in the graphite furnace as well as in food samples, CS was formed in the gas phase without the addition of any molecule forming element externally. The effects of the wavelength selected to detect CS, graphite furnace program, amount of sample, coating of the graphite tube and platform with Ir, and the use of a Pd modifier on the accuracy, precision, and sensitivity were investigated and optimized. Sulfur was determined in an iridium-coated graphite tube/platform at 258.056 nm by applying a pyrolysis temperature of 1000 °C and a molecule forming temperature of 2400 °C. The calibration curve prepared from Na<sub>2</sub>S was linear between 0.01 μg (LOQ) and 10 μg of S. The accuracy of the method was tested by analyzing certified reference spinach and milk powder samples by applying a linear calibration technique prepared from aqueous standard. The results were in good agreement with certified values. The limit of detection and characteristic mass of the method were 3.5 and 8.1 ng of S, respectively. By applying the optimized parameters, the concentrations of S in onion and garlic samples were determined.

**KEYWORDS:** sulfur, solid sampling, high-resolution continuum source electrothermal atomic absorption spectrophotometer, food, molecular absorption

## ■ INTRODUCTION

Sulfur is a vital essential element for humans, animals, and plants, which is involved in the structure of many amino acids and enzymes. It is part of the amino acid methionine, which is an absolute dietary requirement. The amino acid cysteine also contains sulfur. In foods, sulfur can be found in their structure or can be added as preservative. Although harmless to healthy persons when used in recommended concentrations, sulfur in the form of sulfur dioxide can trigger an asthma-like response in sensitized individuals.<sup>1</sup> The sulfur contents of foods highly change depending on the soil, fertilizer, air, and water and their sulfur intake and accumulation properties. The average person takes in around 900 mg of sulfur per day, mainly in the form of protein.<sup>2</sup> Because sulfur is so plentiful in our bodies and in protein-based foods, no recommended dietary allowance has been established. Foods that have high sulfur contents include eggs, nuts, garlic, onions, vegetables, seafood, meat, and milk products.<sup>3</sup>

Sulfur has been determined by different methods such as inductively coupled plasma–optical emission spectrophotometry (ICP-OES),<sup>4</sup> inductively coupled plasma–mass spectrometry (ICP-MS),<sup>5–7</sup> ultraviolet–visible spectrometry (UV–vis),<sup>8</sup> X-ray fluorescence (XRF),<sup>9</sup> chromatography,<sup>10</sup> elemental analysis,<sup>11</sup> and laser-induced breakdown spectroscopy (LIBS).<sup>12</sup> Every method has its own limitations, advantages, and disadvantages such as high cost, time consumption, poor precision, and selectivity, and none of them was free of interferences.

There are various analyses of foods having high sulfur content. For example, the total sulfur contents of different onion sections were determined using an elemental analyzer.<sup>13</sup>

The whole S in whole onion was found as  $121.9 \pm 3.2 \mu\text{mol g}^{-1}$ , corresponding to  $3.90 \pm 0.10 \text{ mg g}^{-1}$ . The maximum values were determined in inner scales ( $153.1 \pm 5.1 \mu\text{mol g}^{-1}$  or  $4.90 \pm 0.16 \text{ mg g}^{-1}$ ). The average total sulfur content in bulbs of garlic was  $0.66 \text{ mg g}^{-1}$ .<sup>14</sup> In another study, total S content in garlic cloves was found to be 10.9 and 11.8  $\text{mg g}^{-1}$  for different sample preparation techniques by ICP-OES.<sup>15</sup>

Practically, sulfur cannot be determined by conventional AAS using a sulfur hollow cathode lamp (HCL) because its atomic absorption resonance line is 180.7 nm, which falls in the vacuum UV region. Sulfur was determined by electrothermal atomic absorption spectrophotometer (ETAAS) only in vacuum using a special instrumental design, which was very complicated and unsuitable for use in routine analysis. On the other hand, S was determined by conventional flame and electrothermal atomic absorption spectrophotometer sources via molecular absorption spectrum (MAS) of sulfur-containing diatomic species. The method is based on the formation of a diatomic molecule between sulfur and a molecule forming element and then measurement of the molecular absorption at one of its finely structured rotational lines using D<sub>2</sub> or an appropriate HCL having an appropriate emission line.

For this purpose, the molecular absorptions of GeS,<sup>16</sup> CS,<sup>17</sup> AlS, InS, and SnS<sup>18</sup> formed in electrothermal atomizer were utilized. The appropriate lines for GeS, CS, AlS, InS, and SnS were obtained from H<sub>2</sub> (285 and 215.2 nm), D<sub>2</sub> (257.6 nm), Fe

**Received:** February 28, 2013

**Revised:** April 25, 2013

**Accepted:** May 1, 2013

**Published:** May 1, 2013

(219.18 nm), Pt (243.7 and 241.8 nm), and W (273.6 nm) HCLs, respectively, whereas 257.6 nm was isolated from a D<sub>2</sub> lamp for CS.

However, the use of a conventional line source AAS with a suitable HCL emitting the required wavelength or isolation of the wavelength from a D<sub>2</sub> source has some drawbacks, namely, (i) only the available line(s) for the HCL rather than the most appropriate line could be used. It is problematic to select exactly the demanded wavelength, which may be the most sensitive and/or sufficiently far from the lines of other concomitants. (ii) The emission intensities of the D<sub>2</sub> isolated or the secondary lines of HCL selected for measurement of the hyperfine lines of diatomic analyte-containing molecules are low, which cause noise and high LOD. (iii) The isolated wavelength range of the source may fall partly out of the very narrow range of the rotational absorption profile for the analyte-containing diatomic molecule causing again low sensitivity and/or spectral interferences. (iv) The bandwidth of the emission line isolated from the D<sub>2</sub> lamp is broader than that of the hyperfine rotational peak of the MAS selected for analysis resulting in low sensitivity (i.e., high LOD). In addition, spectral interferences may occur due to the overlapping of the isolated emission band with neighboring absorption lines for some gaseous species originated from the sample matrix. Therefore, determinations of S, P, and halogens via MAS of their diatomic molecules using HCL and D<sub>2</sub> contain many risks, and they are practically useless.

High-resolution continuum source AAS (HR-CS AAS) is quite a new and challenging instrument that provides a resolution ( $\lambda/\Delta\lambda$ ) of 175,000 in a 0.3–1 nm range, corresponding to a bandwidth below 1.6 pm per pixel.<sup>19</sup> Therefore, it is possible to select a very narrow wavelength (a few picometers) overlapping exactly with the analytical line of the molecule by seeing its spectral neighboring environment and to take measure of spectral interferences.

By utilizing the capabilities of HR-CS-AAS instruments, a number of studies have been carried out for the determination of nonmetals using a hyperfine line selected from the structural spectrum of an analyte-containing molecule.

Huang et al.<sup>20</sup> determined sulfur in wine samples by HR-CS-AAS with a fuel-rich air–acetylene flame using a rotational line of CS molecular absorption at 258.056 nm formed in the flame. A good agreement was found between the results found by HR-CS-AAS and ICP-MS. They did not find any spectral and nonspectral interference from diverse ions and various matrices. Welz et al.<sup>21</sup> reviewed determination of phosphorus, sulfur, and the halogens using line source conventional flame and electrothermal AAS and HR-CS-AAS. Jim et al.<sup>22</sup> reported the determination of sulfur in coal slurry using low-resolution CCD spectrometer with a continuum light source coupled to platform or filter furnace vaporizers and investigated the behavior of sulfur in the furnace. Baysal and Akman<sup>23</sup> described the determination of S in coal samples by flame HR-CS-AAS and optimized the experimental and instrumental conditions. Virgilio et al.<sup>24</sup> investigated the determination of S in two microwave-assisted fungicide digests and water extracts of sulfate fertilizers by flame HR-CS-AAS and compared the analytical results obtained by different alternative wavelengths for CS and SH. Finally, Baumbach et al.<sup>25</sup> determined S concentration in some waters with electrothermal atomization HR-CS-AAS with the help of SnS.

Conventionally, prior to analysis by AAS, samples are digested mostly by mineral acids and applying heat. To avoid

many problems during digestion such as contamination, analyte loss, waste of time and chemicals, etc., samples are introduced to the graphite furnace of AAS in solid forms. Solid sampling atomic absorption spectrometry has many advantages compared to digestion, namely, (i) the risks of contamination and/or analyte loss are considerably reduced; (ii) sensitivity increases as samples are not diluted; (iii) results are obtained rapidly; and (iv) the use of corrosive or hazardous reagents is not required, resulting in both economic and environmental benefits. However, solid sampling is not free from problems due to high background absorption, calibration difficulties, weighing imperfections, sample introduction inconvenience, sample inhomogeneity, etc. However, there are many successful applications of solid sampling AAS in the literature.<sup>26–29</sup>

Resano and Florez<sup>29</sup> investigated the potential benefits of using Pd nanoparticles, in combination with Ru as permanent modifier for sulfur monitoring as CS by means of solid sampling high-resolution continuum source AAS (SS-HR-CS-ETAAS). Ferreira et al.<sup>13</sup> researched the determination of sulfur in CRMs using SS-HR-CS-ETAAS. The platform was coated with tungsten, whereas Pd was used as a modifier. Thiourea was selected as the most appropriate calibrant. The feasibility of the method for routine analysis of real samples was discussed.

The aim of this study was to describe a procedure for the determination of sulfur in various food samples by SS-HR-CS-ETAAS using molecular absorption of CS at a hyperfine rotational line of 258.056 nm. The experimental parameters were optimized, and the validity of the method was tested.

## EXPERIMENTAL PROCEDURES

**Instrumentation and Reagents.** All measurements were carried out using a ContrAA 700 Analytik Jena (Germany) high-resolution continuum source electrothermal atomic absorption spectrophotometer (HR-CS ET AAS), equipped with an SSA600 solid sampler and a 300 W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany). Argon (99.99%) was used as a purge gas. Iridium-coated pyrolytical graphite tubes and platforms were used for the quantification of sulfur in all samples. The experiments were performed by measuring CS absorbance at 258.056 nm. The graphite furnace program used for the determination of sulfur in this study is given in Table 1.

All chemicals were of analytical reagent grade (Merck, Darmstadt, Germany). Stock solution (1000 mg L<sup>-1</sup>) of S was prepared from Na<sub>2</sub>S (Merck) and further diluted with ultrapure water daily (TKA Wasseraufbereitungssysteme GmbH, Niederelbert, Germany). Milk

**Table 1. Optimized Graphite Furnace Temperature–Time Program for the Determination of S from MAS of CS at 258.056 nm<sup>a</sup>**

step	temperature (°C)	ramp (°C s <sup>-1</sup> )	hold time (s)	gas flow (L min <sup>-1</sup> )
1. drying	110	5	10	2.0
2. pretreatment	350	300	10	2.0
3. cooling	80	NP	2	2.0
4. sample injection	80			
5. drying	110	5	10	2.0
6. pyrolysis	1000	300	10	2.0
7. gas adaption	1000	0	5	stop
8. molecule formation	2500	2000	5	stop
9. cleaning	2700	500	4	2.0

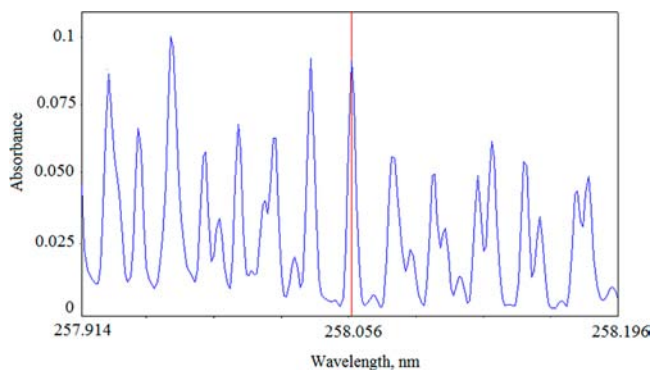
<sup>a</sup>Steps 1 and 2, thermal pretreatment of Ir; sample and Pd modifier injection in step 4; NP, no power for temperature cooling; argon gas flow rate, 2.0 L min<sup>-1</sup> in all stages except during molecule formation step.

Powder Certified Reference Material NCS ZC73015 and Spinach Certified Reference Material NCS ZC73013 were used for validation of the method.

**Procedure.** Samples were broken into pieces and, to remove contaminants on the surface, a few grams of sample was mixed with 50 mL of distilled water, shaken for about 1 min, and the wash was decanted. The samples were then dried at 100 °C for 24 h, ground using an agate mortar, and kept in a refrigerator at 4 °C in a tightly closed vessels. To cover the graphite tube and platform with Ir, 50  $\mu\text{L}$  of 1000  $\mu\text{g mL}^{-1}$  of Ir was pipetted on the platform and atomized at 1100 °C. The procedure was repeated 10 times. Prior to each analysis cycle, coated tubes were further pretreated again with Ir. For this purpose, at first, 10  $\mu\text{L}$  of 1000  $\mu\text{g mL}^{-1}$  of Ir was injected to the platform and thermally treated at 110 °C for 10 s and then at 350 °C for 10 s. The samples were then put on the pretreated platforms of the solid autosampler between 2 and 3 mg, weighed automatically in the balance of the autosampler with 0.001 mg of precision; 10  $\mu\text{L}$  of 1000  $\mu\text{g mL}^{-1}$  of Pd modifier was then injected onto the sample and transferred into the furnace. Whenever necessary, solutions were injected as 10  $\mu\text{L}$  by means of a built-in liquid dispenser of the sampler.

## RESULTS AND DISCUSSION

**Choice of Wavelength for CS.** The method is based on the formation of diatomic CS molecule in the gas phase upon interaction of S in the sample and the carbon of graphite furnace and/or that of sample and measurement of absorption for one of its finely structural rotational lines. It is expected that the concentration of CS is proportional to that of S in the sample. Among a series of CS lines tested, the highest sensitivity was obtained at 258.056 nm, corresponding to one of the  $\Delta\nu = 0$  vibrational sequences of the electronic transition  $X^1\Sigma^+ \rightarrow A^1\Pi$  (see ref 30) (Figure 1). In addition, it was free of

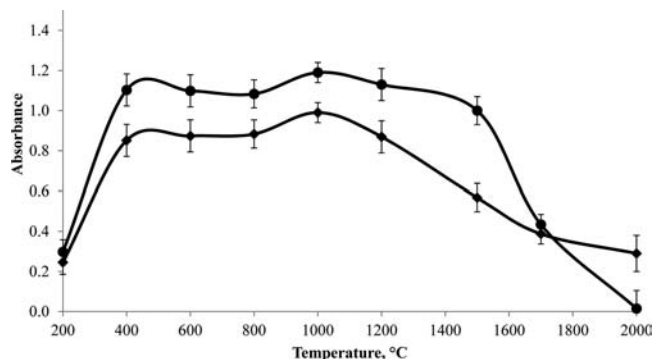


**Figure 1.** Wavelength resolved signal for CS at 258.056 nm Ir-coated tubes/platforms using palladium modifier.

spectral interferences for the samples studied (i.e., no overlapping of absorption lines from sample concomitants) and thus used as the analytical line throughout this study. In the literature, it was stated that for the determination of S in steel samples, 258.056 nm is not appropriate due to overlap of one of the secondary nonresonance Fe lines, and thus an alternative line of S at 257.958 nm was used.<sup>19,29</sup> However, because the sensitivity of the secondary Fe line is very low, its overlapping with the S line of 258.056 nm is a problem only with a huge excess of Fe such as in steel. Therefore, 258.056 nm was used in food samples without any problem.

**Pyrolysis and Atomization Curves.** The pyrolysis curves prepared from  $\text{Na}_2\text{S}$  solution and a garlic powder sample in SS-HR-CS ETAAS are given in Figure 2. Because the amounts of solid sample introduced into the furnace cannot be the same for

every sampling, all of the absorbances were normalized to 1 mg of sample.



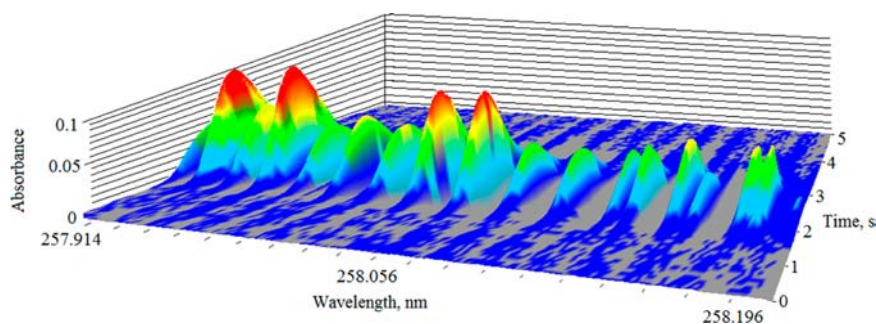
**Figure 2.** Pyrolysis curves for CS obtained by (●) injection of  $\text{Na}_2\text{S}$  containing 10  $\mu\text{g S}$  and (◆) solid sampling of garlic normalized to 1 mg.

The general behaviors of curves for solutions and solid sampling of samples were quite similar. The highest sensitivities with satisfactory precisions were achieved at a pyrolysis temperature of 1000 °C and an atomization temperature of 2400 °C, which were used in all quantifications. To stabilize the S and/or to increase the formation efficiency of CS, the effects of the permanent Ir on the results were investigated. For this purpose, the graphite tube and platform were coated as described under Experimental Procedures. Also, before every sample introduction, a pretreatment step has been applied. The solid samples were then put on Ir-coated platforms and introduced into the Ir-coated tube together with 10  $\mu\text{L}$  of 1000  $\mu\text{g mL}^{-1}$  Pd; sensitivity was increased 20%, and peak shapes for CS were improved. Therefore, all of the analyses were performed in the presence of Pd modifier using Ir-coated platforms and tubes. The time and wavelength resolved absorption (3D) spectrum for CS obtained from garlic powder in the vicinity of 258.056 nm is depicted in Figure 3. In accordance with Figure 1, the background was low, and there was no spectral overlap from the matrix with the molecular absorption line of CS at 258.056 nm.

**Linearity.** A good linearity was obtained between 0.01  $\mu\text{g}$  (LOQ) and 10  $\mu\text{g}$  of S using the molecular absorption of rotational line for CS at 258.056 nm prepared from  $\text{Na}_2\text{S}$  and applying the graphite furnace program given in Table 1. It was expected that the amounts of S in sample portions put on the platform of the solid autosampler were much lower than the upper limit of linearity. Therefore, the method was successfully applied.

**Effect of Sample Amount.** It was stated that in SS-AAS, even if the amount of analyte in the solid sample is in the linear range of the calibration curve obtained with standard solutions, the linearity is influenced, strictly speaking, decreased, by the amount of sample introduced into the furnace as well.<sup>31–34</sup>

In this study, irrespective of the analyte concentrations, when the sample portions on the autosampler platforms exceeded 3 mg, both the precision and sensitivity were reduced, resulting in elevated RSD values and deteriorated linearity, respectively. This may be attributed to improper/insufficient atomization of the analyte in the excessive pile of sample matrix on the platform and/or transportation of the analyte together with sample microparticulates during atomization. Another parameter is that the capacity of the platform is limited, and if it was



**Figure 3.** Time and wavelength resolved absorption (3D) spectrum for CS obtained from Na<sub>2</sub>S containing 0.1 S% in the vicinity of 258.056 nm using solid sampling.

excessively overloaded, some losses may occur during the transferring of sample to the balance and furnace. Nevertheless, the amount of sample should not be too low not to detect the analyte; that is, the analyte in the sample introduced into the furnace should be above the LOD. In addition, to represent the sample better, the amount of sample should be as high as possible. Therefore, an optimization of sample amount was made regarding all factors, namely, linearity, precision, capacity of the platform, and LOD of the method.

In this study, the upper limit for sample amount put into the platform did not exceed 3 mg because at higher amounts the precision was deteriorated and the sensitivity was decreased. Moreover, the platform was almost brimful above 3 mg. On the other hand, to represent the sample better, the lowest sample amount was not below 2 mg.

**Figures of Merit for S Determination.** To represent the sample as much as possible, the high sample amounts in linear range were introduced into the furnace. Therefore, all determinations were carried out using around 2–3 mg of samples, applying graphite furnace program in Table 1 and measuring the absorbance for the hyperfine rotational line of CS at 258.056 nm.

In this study, LOD was calculated as 3 times the standard deviation ( $\sigma$ ) for 10 repetitive injections of Pd modifier, that is,  $3\sigma/\text{slope}$  of calibration graph. The characteristic mass,  $m_0$ , which is a measure of sensitivity, was calculated as the amount of S corresponding to 0.0044A, that is,  $0.0044/\text{slope}$  of calibration graph. The standard deviation and the equation for the calibration curve may change slightly from day to day. Therefore, LOD and  $m_0$  values calculated on different days were not strictly the same. Analytical parameters for S determination by SS-HR-CS-MAS are given in Table 2. The maximum LOD and  $m_0$  values of different days were found as 3.5 and 8.1 ng, respectively.<sup>35</sup>

The accuracy of the method was tested using Milk Powder Certified Reference Material NCS ZC73015 and Spinach Certified Reference Material NCS ZC73013. The certified values were found in the 95% confidence limits of the mean. Finally, the S concentrations of various kinds of onion and garlic samples having different origins and properties were

**Table 2.** Figures of Merit for the Proposed Method

parameter	value
characteristic mass, $m_0$ (ng)	8.1
limit of detection (ng)	3.5
max amount of solid sample used (mg)	3
regression coefficient	$R^2 = 0.999$

determined, and the results are given in Table 3. Due to the microscale heterogeneity of the analyte in solid samples, the

**Table 3.** Determination of Sulfur Contents (Milligrams per Gram) in CRMs and Different Samples by Solid Sampling Technique ( $N = 5$  for Each Sample in Solid Sampling)

sample <sup>a</sup>	direct solid sampling <sup>b</sup>
Spinach NCS ZC 73013 <sup>c</sup> (2.14)	$4.45 \pm 0.42$ ( $H_E$ : 9.03) <sup>d</sup>
Milk Powder NCS ZC 73015 <sup>c</sup> (2.64)	$2.53 \pm 0.19$ ( $H_E$ : 4.80) <sup>d</sup>
onion 1 (2.75)	$4.79 \pm 0.41$ ( $H_E$ : 8.41)
onion 2 (2.57)	$7.34 \pm 0.42$ ( $H_E$ : 8.00)
onion 3 (2.70)	$4.89 \pm 0.43$ ( $H_E$ : 8.69)
onion 4 (2.50)	$5.66 \pm 0.52$ ( $H_E$ : 9.22)
garlic 1 (2.93)	$5.58 \pm 0.65$ ( $H_E$ : 15.54)
garlic 2 (2.54)	$5.20 \pm 0.53$ ( $H_E$ : 11.80)
garlic 3 (2.55)	$5.04 \pm 0.52$ ( $H_E$ : 12.28)
garlic 4 (2.57)	$4.13 \pm 0.37$ ( $H_E$ : 9.13)

<sup>a</sup>The values in parentheses are the average mass ( $N = 5$ ) for each sample analyzed. <sup>b</sup>Average  $\pm$  SD. <sup>c</sup>Certified values for Spinach NCS ZC 73013 and Milk Powder NCS ZC 73015 are  $4.5 \pm 0.4$  and  $2.5 \pm 0.2$  mg g<sup>-1</sup>, respectively. <sup>d</sup> $H_E$  was calculated after 7% RSD (method) correction was made.

RSD values for very small amounts of portions taken from the same sample are generally somewhat higher compared to those obtained from repetitive digested samples. Because very small sample portions (<3 mg) were introduced into the graphite furnace for solid sampling analysis, it would be possible to determine the change of S concentrations in microscale in a sample. In fact, even the certified values of solid CRMs and their uncertainties are guaranteed only if at least 50 mg or sometimes 100 mg of sample portions are digested, which is much above the amounts used for solid sampling. Therefore, the overall RSD values in Table 3,  $RSD_{(\text{total})}$ , originate from the random errors of the instrumental method during measurement ( $RSD_{(\text{method})}$ ) as well as microheterogeneity of the analyte distribution in the sample ( $RSD_{(\text{analyte heterogeneity})}$ ). Using a propagation of uncertainty, the relationship between  $RSD_{(\text{total})}$  and  $RSD_{(\text{method})}$  and  $RSD_{(\text{analyte heterogeneity})}$  is  $RSD_{(\text{total})}^2 = RSD_{(\text{method})}^2 + RSD_{(\text{analyte heterogeneity})}^2$ .

The thermal behaviors and analytical characteristics of the organic standards were the most similar to those of samples. Therefore, the accuracy of the results with thiourea standard was better than those obtained using inorganic standards.

The RSDs of standard S solutions were accepted as  $RSD_{(\text{method})}$  and found between 6 and 8%. Almost the same values were obtained for the samples containing S below the LOD. Therefore, the average  $RSD_{(\text{method})}$  was taken as 7%. The

$RSD_{(\text{analyte heterogeneity})}$  for each sample was calculated from  $[RSD_{(\text{total})}^2 - RSD_{(\text{method})}^2]^{0.5}$  and then the relative homogeneity factor ( $H_E$ ) for each sample, which is described as a measure of analyte distribution homogeneity, was found from  $H_E = RSD \times (m)^{0.5}$ , where  $m$  is the average sample mass in milligrams.<sup>26,37</sup> Virgilue et al.<sup>38</sup> calculated  $H_E$  values to estimate the homogeneity of chromium distribution in medical plants. Values below 10 were interpreted as a homogeneous sample material according to Kurfürst.<sup>37,39</sup> In this study, the  $RSD_{(\text{analyte heterogeneity})}$  and  $H_E$  values for most of the samples in Table 3 were around 10% and 10, respectively, indicating a pretty homogeneous S distribution.

**Conclusion.** Determination of nonmetals by conventional atomic absorption spectrometry is not appropriate due to their atomic absorption resonance wavelengths in the vacuum UV range. However, the analyte containing diatomic molecules formed in the gas phase of flame and graphite furnaces provided new possibilities to determine nonmetals by atomic absorption spectrometry. In this study, the advantages of HR-CS-AAS and solid sampling are combined to determine S in food samples via MAS of CS formed in the gas phase without needing time-consuming sample digestion procedures. There were no analyte loss and contamination risks, which may occur during sample digestion. The procedure proposed in this study can be included in routine S determination applications. Last, but not least, it was proved that solid sampling is helpful to show the microscale heterogeneity of an analyte in a sample.

## AUTHOR INFORMATION

### Corresponding Author

\*Phone: +902122853160. Fax: +902122856386. E-mail: akmans@itu.edu.tr.

### Notes

The authors declare no competing financial interest.

## REFERENCES

- (1) Freedman, B. J. Sulphur dioxide in foods and beverages: its use as a preservative and its effect on asthma. *Br. J. Dis. Chest* **1980**, *74*, 128–134.
- (2) Lenntech B.V. *Sulphur*; <http://www.lenntech.com/periodic/elements/s.htm> (Feb 27, 2013).
- (3) Livestrong Foundation, List of Foods High in Sulphur; <http://www.livestrong.com/article/289250-list-of-foods-high-in-sulfur> (Jan 24, 2013).
- (4) Santelli, R. E.; Oliveira, E. P.; Fátima Batista de Carvalho, M.; Bezerra, M. A.; Freire, A. S. Total sulfur determination in gasoline, kerosene and diesel fuel using inductively coupled plasma optical emission spectrometry after direct sample introduction as detergent emulsions. *Spectrochim. Acta B* **2008**, *63*, 800–804.
- (5) Amais, R. S.; Donati, G. L.; Nobrega, J. A. Application of the interference standard method for the determination of sulfur, manganese and iron in foods by inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* **2011**, *706*, 223–229.
- (6) Yang, C. H.; Jiang, S. J. Determination of B, Si, P and S in steels by inductively coupled plasma quadrupole mass spectrometry with dynamic reaction cell. *Spectrochim. Acta B* **2004**, *59*, 1389–1394.
- (7) Hassan, S. S. M.; Hamza, M. S. A.; Mohamed, A. H. K. A novel spectrophotometric method for batch and flow injection determination of sulfite in beverages. *Anal. Chim. Acta* **2006**, *570*, 232–239.
- (8) Pereira, S. F. J.; Moraes, D. P.; Antes, F. G. Determination of metals and metalloids in light and heavy crude oil by ICP-MS after digestion by microwave-induced combustion. *Microchem. J.* **2010**, *96*, 4–11.
- (9) Kowalewska, Z.; Laskowska, H. Comparison and critical evaluation of analytical performance of wavelength dispersive X-ray fluorescence and ultraviolet fluorescence for sulfur determination in modern automotive fuels, biofuels, and biocomponents. *Energy Fuels* **2012**, *26*, 6843–6853.
- (10) Koch, M.; Koppen, R.; Siegel, D.; Witt, A.; Nehls, I. Determination of total sulfite in wine by ion chromatography after in-sample oxidation. *J. Agric. Food Chem.* **2010**, *58*, 9463–9467.
- (11) Studley, S. A.; Ripley, E. M.; Elswick, E. R.; Dorais, M. J.; Fong, J.; Finkelstein, D.; Pratt, L. M. Analysis of sulfides in whole rock matrices by elemental analyzer–continuous flow isotope ratio mass spectrometry. *Chem. Geol.* **2002**, *192*, 141–148.
- (12) Musazzi, S.; Golinelli, E.; Perini, U.; Barberis, F.; Zanetta, G. A. Elemental analysis of coal by means of the laser induced breakdown spectroscopy (LIBS) technique. *SAS, IEEE* **2012**, 1–3.
- (13) Benítez, V.; Mollá, E.; Martín-Cabrejas, M. A.; Javier López-Andréu, F.; Downes, K.; Terry, L. A.; Esteba, R. M. Study of bioactive compound content in different onion sections. *Plant Foods Hum Nutr.* **2011**, *66*, 48–57.
- (14) Muradic, S.; Karacic, D.; Mahmutovic, O.; Mutovic, F.; Sofic, E.; Kroyer, G. Total sulphur and organosulphur compounds in garlic and ramsons plant organs at the end of vegetative period. *Planta Med.* **2010**, *76*, 12.
- (15) Wang, J.; Yi, H.; He, C.; Li, H. Sample preparation method for the determination of total sulfur in plant materials. *Commun. Soil Sci. Plant Anal.* **1999**, *30*, 599–603.
- (16) Dittrich, K.; Vorberg, B. Molekülabsorptionsspektrometrie bei elektrothermischer verdampfung in einer graphitrohrküvette: Teil 8. Untersuchung der GeS-Molekülabsorption und Bestimmung von S-Species durch Lichtabsorption von GeS-Molekülen. *Anal. Chim. Acta* **1983**, *152*, 149–161.
- (17) Tittarelli, P.; Lavorato, G. Determination of sulphur in fuel oils by absorption spectrometry of electrothermally generated carbon sulphide molecules. *Anal. Chim. Acta* **1987**, *201*, 59–65.
- (18) Parvinen, P.; Lajunen, L. H. J. Determination of sulphur by tin, aluminium and indium monosulphide molecular absorption spectrometry using sharp line irradiation sources. *Anal. Chim. Acta* **1994**, *295*, 205–210.
- (19) Welz, B.; Vale, M. G. R.; Florek, S.; Okruss, M.; Huang, M. D.; Becker-Ross, H. High-resolution continuum source atomic absorption spectrometry—theory and applications. In *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; Wiley: Hoboken, NJ, 2010.
- (20) Huang, M. D.; Becker-Ross, H.; Florek, S.; Heitmann, U.; Okruss, M. Direct determination of total sulfur in wine using a continuum-source atomic-absorption spectrometer and an air-acetylene flame. *Anal. Bioanal. Chem.* **2005**, *382*, 1877–1881.
- (21) Welz, B.; Lepri, F. G.; Araujo, R. G. O.; Ferreira, S. L. C.; Huang, M.-D.; Okruss, M.; Becker-Ross, H. Determination of phosphorus, sulfur and the halogens using high-temperature molecular absorption spectrometry in flames and furnaces – a review. *Anal. Chim. Acta* **2009**, *647*, 137–148.
- (22) Jim, G.; Katskov, D.; Tittarelli, P. Sulfur determination in coal using molecular absorption in graphite filter vaporizer. *Talanta* **2011**, *83*, 1687–1694.
- (23) Baysal, A.; Akman, S. A practical method for the determination of sulphur in coal samples by high-resolution continuum source flame atomic absorption spectrometry. *Talanta* **2011**, *85*, 2662–2665.
- (24) Virgilio, A.; Raposo, J. L.; Cardoso, A. A.; Nobrega, J. A.; Neto, J. A. G. Evaluation of solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry for direct determination of chromium in medicinal plants. *J. Agric. Food Chem.* **2011**, *59*, 2197–2201.
- (25) Baumbach, G.; Limburg, T.; Einax, J. W. Quantitative determination of sulfur by high-resolution graphite furnace molecular absorption spectrometry. *Microchem. J.* **2013**, *106*, 295–299.
- (26) Kurfürst, U. *Solid Sample Analysis*; Springer-Verlag: Berlin, Germany, 1998.
- (27) Vale, M. G. R.; Oleszczuk, N.; dos Santos, W. N. L. Current status of direct solid sampling for electrothermal atomic absorption spectrometry – a critical review of the development between 1995 and 2005. *Appl. Spectrosc. Rev.* **2006**, *41*, 377–400.

(28) Welz, B.; Vale, M. G.; Borges, D. L.; Heitmann, U. Progress in direct solid sampling analysis using line source and high-resolution continuum source electrothermal atomic absorption spectrometry. *Anal. Bioanal. Chem.* **2007**, *389*, 2085–2095.

(29) Resano, M.; Florez, M. R. Direct determination of sulfur in solid samples by means of high-resolution continuum source graphite furnace molecular absorption spectrometry using palladium nanoparticles as chemical modifier. *J. Anal. At. Spectrom.* **2012**, *27*, 401–412.

(30) Kowalewska, Z. Feasibility of high-resolution continuum source molecular absorption spectrometry in flame and furnace for sulphur determination in petroleum products. *Spectrochim. Acta B* **2011**, *66*, 546–556.

(31) Resano, M.; Garcia-Ruiz, E.; Crespo, C.; Vanhaecke, F.; Belarra, M. A. Solid sampling graphite furnace atomic absorption spectrometry for palladium determination at trace and ultratrace levels. *J. Anal. At. Spectrom.* **2003**, *18*, 1477–1484.

(32) Coskun, N.; Akman, S. Direct determination of manganese in vitamin–mineral tablets using solid sampling electrothermal atomic absorption spectrometry. *Talanta* **2004**, *64*, 496–500.

(33) Baysal, A.; Ozbek, N.; Akman, S. A practical solid sampling method for the determination of lead in chewing gum by electrothermal atomic absorption spectrometry. *Food Chem.* **2010**, *123*, 901–904.

(34) Atilgan, S.; Akman, S.; Baysal, A.; Bakircioglu, Y.; Szigeti, T.; Óvári, M.; Zárny, G. Monitoring of Pd in airborne particulates by solid sampling high-resolution continuum source electrothermal atomic absorption spectrometry. *Spectrochim. Acta Part B* **2012**, *70*, 33–38.

(35) Ure, T. A. M.; Butler, R. P.; L'vov, B. V.; Rubeska, I.; Sturgeon, R. International union of pure and applied chemistry analytical chemistry division commission on spectrochemical and other optical procedures for analysis terms related to electrothermal atomization. *Pure Appl. Chem.* **1992**, *64*, 253–259.

(36) Kelly, A. G.; Wells, D. E.; Freyer, R. J. Sampling strategy to detect a change in concentration of trace organic contaminants in marine sediment. *Sci. Total Environ.* **1994**, *144*, 217–230.

(37) Kurfürst, U. Statistical treatment of ETA-AAS (electrothermal atomization - atomic absorption spectrometry solid sampling data of heterogeneous samples. *Pure Appl. Chem.* **1991**, *63*, 1205–1211.

(38) Virgilio, A.; Nóbrega, J. A.; Rêgo, J. F.; Neto, J. A. G. Evaluation of solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry for direct determination of chromium in medicinal plants. *Spectrochim. Acta B* **2012**, *78*, 58–61.

(39) Kurfürst, U.; Pauwels, J.; Grobecker, K. H.; Stoeppler, M.; Muntau, H. Microheterogeneity of trace elements in reference materials: determination and statistical evaluation. *Fresenius' J. Anal. Chem.* **1993**, *345*, 112–120.