

# Determination of Total Sulfur in Agricultural Samples by High-Resolution Continuum Source Flame Molecular Absorption Spectrometry

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**ABSTRACT:** The usefulness of molecular absorption was investigated for the determination of total sulfur (S) in agricultural samples by high-resolution continuum source flame molecular absorption spectrometry. The lines for CS at 257.595, 257.958, and 258.056 nm and for SH at 323.658, 324.064, and 327.990 nm were evaluated. Figures of merit, such as linear dynamic range, sensitivity, linear correlation, characteristic concentration, limit of detection, and precision, were established. For selected CS lines, wavelength-integrated absorbance equivalent to 3 pixels, analytical curves in the 100–2500 mg L<sup>-1</sup> (257.595 nm), 250–2000 mg L<sup>-1</sup> (257.958 nm), and 250–5000 mg L<sup>-1</sup> (258.056 nm) ranges with a linear correlation coefficient better than 0.9980 were obtained. Results were in agreement at a 95% confidence level (paired *t* test) with those obtained by gravimetry. Recoveries of S in fungicide and fertilizer samples were within the 84–109% range, and the relative standard deviation (*n* = 12) was typically <5%.

**KEYWORDS:** Total sulfur, fungicide, fertilizer, flame molecular absorption spectrometry, high-resolution continuum source atomic absorption spectrometry

## INTRODUCTION

Elemental sulfur, sulfate-based fertilizers (e.g., ammonium sulfate, magnesium sulfate, and potassium sulfate), and gypsum are routinely used in intensive agriculture to enhance the yield or quality of crops.<sup>1</sup> Accurate methods of analysis for sulfur are relevant in the agribusiness field because the analysis of both custom-blended or manufactured products may check the labeled sulfur content of these commercial products.

Contents of sulfur in fungicides or sulfate in fertilizers and gypsum are usually determined by the classical gravimetric method for sulfate analysis.<sup>2</sup> After sample preparation, sulfate ions in acid medium are precipitated with barium chloride to form barium sulfate. This method is chiefly simple and adequate for samples containing high levels of sulfate, but it is time-consuming. Besides, soluble salts of barium are highly toxic and frequently used as pesticide to control rodents. Thus, this method generates large amounts of Ba-based residue, counteracting the tendency toward green chemistry.<sup>3</sup> Sulfate in agricultural samples can also be determined by spectrometry<sup>4</sup> or turbidimetry,<sup>5,6</sup> but the inherent sensitivity of both instrumental methods requires large dilution of samples, which may generate significant errors.

Among atomic spectrometric techniques, sulfur may be determined by inductively coupled plasma atomic emission spectrometry.<sup>7</sup> The difficulty of measuring absorbance of the main and secondary lines of sulfur in the vacuum ultraviolet (UV) within the 180.671–182.565 nm spectral range may be considered as the main drawbacks to the determination of sulfur by line source atomic absorption spectrometry (LS AAS).<sup>8,9</sup> However, the development of high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) has allowed further applications, such as determination of Pb in phosphoric

acid using internal standardization and multi-element determination of macro- and microelements in soils and plants.<sup>10–12</sup> Using a high-resolution double-echelle monochromator, a charge-coupled device (CCD) detector, and a xenon arc lamp continuum source, fast-sequential multi-element analyses by absorption of atoms and diatomic molecules are feasible.<sup>13–15</sup>

In air–acetylene or acetylene–nitrous oxide flames, the production of CS or SH molecules presenting fine rotating structures similar to atomic lines is the basis of existing methods for the determination of S in plant material,<sup>16</sup> wine,<sup>17,18</sup> and cast iron<sup>19</sup> by high-resolution continuum source flame molecular absorption spectrometry (HR-CS MAS). The determination of high sulfur content samples by HR-CS MAS is practicable by extending the linear working range if less sensitive lines for S are used, avoiding the need of further dilutions of samples. For routine laboratories devoted to large-scale analyses, this strategy is particularly helpful because time and costs may be significantly reduced.

This study reports on the evaluation of molecular lines for CS at 257.595, 257.958, and 258.056 nm and for SH at 323.658, 324.064, and 327.990 nm to extend the linear working range to achieve a simple and fast method for the analysis of agricultural samples by HR-CS MAS.

## EXPERIMENTAL PROCEDURE

**Instrumentation.** All measurements were carried out using an Analytik Jena ContrAA 300 high-resolution continuum source flame

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**Table 1. Influence of the WIA on the LDR, Angular (Slope), and Linear Correlation (*r*) Coefficients of Analytical Curves, Characteristic Concentration (*C*<sub>0</sub>), LOD, and RSD for CS at 257.595, 257.958, and 258.056 nm and for SH at 323.658, 324.064, and 327.990 nm**

$\lambda$ (nm)	LDR (mg L <sup>-1</sup> )	slope	<i>r</i>	<i>C</i> <sub>0</sub> (mg L <sup>-1</sup> )	LOD (mg L <sup>-1</sup> )	% RSD
CP						
257.595	100–2500	$3.98 \times 10^{-6}$	0.9988	1104.3	15.1	4.8
257.958	250–2000	$4.01 \times 10^{-6}$	0.9990	1096.7	22.4	5.7
258.056	250–5000	$4.13 \times 10^{-6}$	0.9991	1064.1	21.8	4.2
323.658	2000–40000	$1.52 \times 10^{-7}$	0.9984	28862.7	2558.3	5.4
324.064	2000–40000	$1.20 \times 10^{-7}$	0.9990	1502.8	1502.8	8.5
327.990	10000–40000	$3.14 \times 10^{-7}$	0.9990	955.8	955.8	4.3
CP ± 1						
257.595	100–2500	$1.12 \times 10^{-5}$	0.9990	393.9	13.4	4.9
257.958	250–2000	$1.07 \times 10^{-5}$	0.9982	412.5	22.5	5.5
258.056	250–5000	$1.10 \times 10^{-5}$	0.9992	400.3	30.0	3.4
323.658	2000–40000	$4.08 \times 10^{-7}$	0.9990	10792.8	2796.3	6.8
324.064	2000–40000	$3.35 \times 10^{-7}$	0.9992	13131.2	1701.1	8.3
327.990	10000–40000	$8.52 \times 10^{-7}$	0.9995	5167.3	775.1	3.2
CP ± 2						
257.595	100–2500	$1.66 \times 10^{-5}$	0.9991	265.0	12.6	5.6
257.958	250–2000	$1.52 \times 10^{-5}$	0.9967	288.9	39.4	5.4
258.056	250–5000	$1.47 \times 10^{-5}$	0.9836	299.7	30.6	3.7
323.658	2000–40000	$5.61 \times 10^{-7}$	0.9987	7837.7	3313.2	6.3
324.064	2000–40000	$4.98 \times 10^{-7}$	0.9989	8833.2	1806.8	7.7
327.990	10000–40000	$1.18 \times 10^{-6}$	0.9995	3740.7	918.2	3.2
CP ± 3						
257.595	100–2500	$2.06 \times 10^{-5}$	0.9985	213.7	16.0	5.9
257.958	250–2000	$1.65 \times 10^{-5}$	0.9784	267.5	36.5	4.9
258.056	250–5000	$1.58 \times 10^{-5}$	0.9780	278.3	36.1	3.8
323.658	2000–40000	$5.98 \times 10^{-7}$	0.9939	7356.6	4213.3	8.5
324.064	2000–40000	$5.88 \times 10^{-7}$	0.9977	7478.7	2243.6	7.9
327.990	10000–40000	$1.32 \times 10^{-6}$	0.9993	3321.9	1177.7	4.6

atomic absorption spectrometer equipped with a xenon short-arc lamp (XBO 301, 300 W, GLE, Berlin, Germany) operating in hot-spot mode as a continuum radiation source. This new equipment presents a compact high-resolution double-echelle grating monochromator corresponding to a spectral bandwidth <2 pm per pixel in the far UV range and a CCD array detector. High-purity acetylene (99.7% air liquid, Sertãozinho, São Paulo, Brazil) was used as fuel gas. An air–acetylene flame was used for the CS and SH production. The enthalpies of formation of CS and SH are 64.6 and 33.3 kcal mol<sup>-1</sup>, respectively,<sup>20,21</sup> and the average bond dissociation enthalpies for CS and SH are 65 and 81 kcal mol<sup>-1</sup>, respectively.<sup>22</sup> Because CS is not a free radical but a short-lived molecule, thermodynamically stable,<sup>4</sup> the SH should also be stable.

All measurements were carried out in five replicates using an injection module (SFS 6), enabling the computer-controlled aspiration of blanks, analytical solutions, and samples. The aspiration rate was fixed at 5.0 mL min<sup>-1</sup>, and the equipment was adjusted to provide the best sensitivity (burner height, 7 mm; acetylene flow rate, 110 L h<sup>-1</sup>; and air flow rate, 521 L h<sup>-1</sup>).

**Reagents and Standard Solutions.** High-purity deionized water obtained using a Millipore Rios 5 reverse osmosis and a Millipore Milli-Q Academic deionizer system (resistivity of 18.2 MΩ cm, Millipore, Bedford, MA) was used throughout to prepare all solutions. A 40 000 mg L<sup>-1</sup> S standard stock solution was prepared by dissolving 82.4338 g of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Spectrum, Gardena, CA) in water and making the volume up to 500 mL with water. This salt was standardized against

gravimetry by making a precipitate of barium sulfate and weighing the isolated pure compound. Working standard solutions containing 25, 50, 100, 250, 500, 1000, 1500, 2000, 2500, 5000, 7500, 10 000, 12 500, 15 000, 20 000, and 40 000 mg L<sup>-1</sup> S were prepared weekly by appropriate dilution of the standard stock solution.

A multi-element analytical solution containing 500 mg L<sup>-1</sup> B, Ca, Co, Cu, Fe, K, Mg, Mn, Na, P, Si, and Zn was prepared by appropriate dilution of the 1000 mg L<sup>-1</sup> single-stock standard solutions (Normex, Carlo Erba, Italy) in 1.0% (v/v) nitric acid. All solutions were stored in high-density polypropylene bottles (Nalgene, Rochester, NY). Plastic bottles and glassware materials were cleaned by soaking in 10% (v/v) HNO<sub>3</sub> at least 24 h and rinsed abundantly in deionized water before use.

**Sample Preparation.** Powdered fungicide samples were dried in a desiccator with silica gel and mineralized in triplicate in a Multiwave 3000 microwave oven (Anton Paar, Graz, Austria) equipped with 25 mL PFA vessels. A mass of 200 mg of sample was accurately weighed and transferred to a digestion vessel followed by 4 mL of concentrated nitric acid plus 1 mL of concentrated hydrochloric acid. The optimized heating program of the microwave oven involving initial power/ramp time/final power/hold time was as follows: step 1, 100 W/5 min/600 W/5 min; step 2, 600 W/5 min/1000 W/10 min; and step 3, 0 W/0 min/15 min/0 W (ventilation). After the resulting solution was cooled to room temperature, it was transferred to 100 mL volumetric flasks and the volume was made up with deionized water. Fungicides were also digested in a heating block with open vessel digestion. In this case, a mass of 400 mg

**Table 2. Comparative Results [Mean  $\pm$  Standard Deviation (SD)] of S (wt %) in Fungicides and Fertilizers Determined ( $n = 3$ ) by the Proposed HR-CS MAS Procedure and Gravimetry, Employing Microwave Oven (MW), Heating Block (HB), and Water Extraction (WE)**

sample	HR-CS MAS			gravimetry		
	MW	HB	WE	MW	HB	WE
fungicide 1				82.4 $\pm$ 0.8	79.6 $\pm$ 0.7	
257.595 nm	80.5 $\pm$ 3.2	79.9 $\pm$ 3.3				
257.958 nm	80.3 $\pm$ 3.4	80.7 $\pm$ 2.7				
258.056 nm	80.7 $\pm$ 2.9	79.5 $\pm$ 3.3				
fungicide 2				93.9 $\pm$ 0.6	94.1 $\pm$ 0.8	
257.595 nm	92.9 $\pm$ 3.19	91.8 $\pm$ 3.0				
257.958 nm	92.2 $\pm$ 2.8	92.1 $\pm$ 2.7				
258.056 nm	92.4 $\pm$ 3.2	92.4 $\pm$ 2.8				
magnesium sulfate						13.0 $\pm$ 0.4
257.595 nm			13.6 $\pm$ 0.5			
257.958 nm			13.9 $\pm$ 0.4			
258.056 nm			13.0 $\pm$ 0.4			
potassium sulfate						17.5 $\pm$ 0.3
257.595 nm			18.3 $\pm$ 0.7			
257.958 nm			18.3 $\pm$ 0.8			
258.056 nm			18.4 $\pm$ 0.6			
ammonium sulfate						20.7 $\pm$ 0.2
257.595 nm			21.0 $\pm$ 1.0			
257.958 nm			21.0 $\pm$ 0.9			
258.056 nm			20.6 $\pm$ 1.1			

was accurately weighed and transferred to glass test tubes followed by 10 mL of concentrated nitric acid, 3 mL of concentrated hydrochloric acid, and 1 mL of 30% hydrogen peroxide (m/m). The block was heated to 130 °C and kept in this temperature for 2 h. After the fungicide digest was digested and cooled, it was transferred to 250 mL volumetric flasks and the volume was made up with deionized water.

Sulfate-based fertilizers (magnesium sulfate, potassium sulfate, and ammonium sulfate) were purchased at the local market of Araraquara, São Paulo, Brazil. After the bulk and laboratory samples were selected, a mass of 250 mg of powdered fertilizer was accurately weighed, transferred to a 100 mL beaker, and dissolved in approximately 30 mL of water. The solution was then filtered into 50 mL volumetric flasks, and the volume was made up with water.

**Analytical Procedure.** The diatomic molecular lines were evaluated by measuring absorbance at 257.595, 257.958, and 258.056 nm and 323.658, 324.064, and 327.990 nm for CS and SH, respectively. In HR-CS AAS, it is possible to apply the wavelength-integrated absorbance (WIA) over the line core, including part of the line wings to enhance sensitivity.<sup>13</sup> The influence of WIA on the linear dynamic range (LDR), sensitivity, linear correlation coefficient ( $r$ ), characteristic concentration ( $C_c$ ), limit of detection (LOD), limit of quantification (LOQ), and precision was evaluated by varying a different number of pixels used for detection: 1 pixel, central pixel (CP); 3 pixels, CP  $\pm$  1; 5 pixels, CP  $\pm$  2; and 7 pixels, CP  $\pm$  3. The LOD and LOQ for S were calculated according to the International Union of Pure and Applied Chemistry (IUPAC) recommendation.<sup>23</sup> Accuracy was also evaluated by recovery tests using fungicide digests and fertilizer solutions spiked with 500.0 mg L<sup>-1</sup> S.

## RESULTS AND DISCUSSION

**WIA Approach.** The influence of WIA on the main figures of merit was investigated by measuring absorbance at each studied

wavelength for CS and SH in a different number of pixels and plotting absorbance versus the S concentration within the 25–40 000 mg L<sup>-1</sup> range. All figures of merit are summarized in Table 1. The trend in Table 1 reveals that, in general, the CS lines furnished better sensitivity than those observed for SH lines. The precisions of measurements [calculated as percent relative standard deviation (% RSD)] for CS were to some extent higher than those obtained for SH. The difference in sensitivity between CS and SH lines may be explained by the higher characteristic concentration (analyte concentration that results in an absorbance signal of 0.0044) for CS, or else, analytical lines for CS present a higher absorption coefficient than those for SH. CS is not a free radical but a short-lived molecule, which is thermodynamically stable, although chemically highly reactive.<sup>4</sup> Electronic transitions for CS and SH are  $\sigma-\pi^*$  and  $\pi-\sigma^*$ , both allowed by spin. However, the orbital of C and S allows for better spin-orbit coupling, making their electronic transitions more likely. Indeed, vibration transitions are more pronounced for CS than those for SH.<sup>13</sup> Spectrum details in the air-acetylene flame with bands of CS and SH show that the signal/noise ratio (SNR) is much higher for CS than that observed for SH.<sup>13</sup> Therefore, the uncertainty of measuring SH species is higher than that observed for CS. However, for CP  $\pm$  3 pixels, linear correlation coefficients better than 0.9980 were consistently obtained for all lines evaluated. Because the increase of the number of pixels from 1 (CP) to 4 (CP  $\pm$  3) did not significantly improve the quality of results, the number of pixels was selected as 1 (CP). For a typical 200 mg amount of fungicide digested and diluted up to 100 mL, the final concentration of S is around 1600 mg L<sup>-1</sup>. For ca. 250 mg of sulfate-based fertilizers containing S levels within 12–22 wt %, the final concentrations of S are in the 600–1100 mg L<sup>-1</sup> interval. In these situations, the linear dynamic ranges observed

**Table 3. Concentrations of S (Mean  $\pm$  SD;  $n = 5$ ) Expressed in  $\text{mg L}^{-1}$  and Recovery Percentages in Fungicide Digests Analyzed by HR-CS MAS**

sample	wavelength (nm)	[S] found after addition		recovery (%)
		0 $\text{mg L}^{-1}$	500 $\text{mg L}^{-1}$	
fungicide 1	257.595	412.1 $\pm$ 27.7	895.6 $\pm$ 35.4	97
	257.958	357.9 $\pm$ 28.7	873.2 $\pm$ 57.3	103
	258.056	333.1 $\pm$ 34.1	877.3 $\pm$ 45.8	109
fungicide 2	257.595	399.6 $\pm$ 13.1	818.5 $\pm$ 16.3	84
	257.958	328.1 $\pm$ 9.3	874.7 $\pm$ 16.1	109
	258.056	326.0 $\pm$ 10.2	853.4 $\pm$ 17.0	106
magnesium sulfate	257.595	408.5 $\pm$ 23.9	899.2 $\pm$ 29.6	98
	257.958	362.8 $\pm$ 31.1	889.4 $\pm$ 42.8	105
	258.056	351.9 $\pm$ 24.7	867.1 $\pm$ 39.2	103
potassium sulfate	257.595	396.3 $\pm$ 19.9	858.2 $\pm$ 20.6	92
	257.958	359.8 $\pm$ 15.8	893.5 $\pm$ 39.7	106
	258.056	347.0 $\pm$ 23.1	851.9 $\pm$ 26.3	101
ammonium sulfate	257.595	401.3 $\pm$ 23.3	909.8 $\pm$ 30.9	102
	257.958	349.4 $\pm$ 29.5	891.3 $\pm$ 47.2	108
	258.056	348.9 $\pm$ 28.9	866.1 $\pm$ 35.4	103

for CS lines at 257.595 nm (100–2500  $\text{mg L}^{-1}$ ), 257.958 nm (250–2000  $\text{mg L}^{-1}$ ), and 258.056 nm (250–5000  $\text{mg L}^{-1}$ ) were suitable for this analytical application. Lines for SH at 327.990 nm led to the worst sensitivity (10 000–40 000  $\text{mg L}^{-1}$ ) and was unworkable in analysis of fungicides for S determination. It should be commented that working standard solutions presenting sulfur concentrations higher than 10 000  $\text{mg L}^{-1}$  reduced the sample flow rate from 5 to 4  $\text{mL min}^{-1}$ , inducing transport effects.<sup>10</sup> Indeed, these concentrated solutions gradually clogged the slot of the burner head. The lower concentration of calibration curves at lines 323.658 and 324.064 nm was 2000  $\text{mg L}^{-1}$ . This value impairs the selection of both lines for the analytical task proposed in this work.

**Interference Studies.** The influence of the presence of some potential interfering elements were evaluated by measuring at the selected lines the absorbance of working standard solutions containing 500  $\text{mg L}^{-1}$  B, Ca, Co, Cu, Fe, K, Mg, Mn, Na, P, Si, and Zn. The apparent concentration of sulfur (calculated using the absorbance measured for the interfering species alone) observed for all tested elements at 257.595 nm was around 20  $\text{mg L}^{-1}$  S. For the line 323.658 nm, the interference as a result of Ca, Cu, Fe, K, Mn, Na, P, Si, and Zn was significant, because apparent concentrations up to 2800  $\text{mg L}^{-1}$  occurred. It should be commented that the concentration of foreign ions correspond to those that may occur in final digests if they were present in original workable samples. The interference of foreign species on sulfur determination at wavelengths of 257.958, 258.056, and 324.064 nm were insignificant because apparent concentrations of sulfur lower than 3  $\text{mg L}^{-1}$  were obtained. However, the line at 324.064 nm led to poor precision (RSD of ca. 8.5%). After the concentration range of calibration curves, expected concentrations of sulfur in workable samples, dilution factor adopted in the sample preparation method, precision, and selectivity are taken into account, the wavelengths of 257.595, 257.958, and 258.056 nm were elected as optimum for analyzes of samples.

**Analysis of Real Samples.** After the optimum lines were evaluated and selected, a procedure was developed and applied to

the determination of S in commercial fungicide and fertilizer samples. Using the CS lines at 257.595, 257.958, and 258.056 nm, WIA corresponding to CP, and aspiration rate of the nebulizer at 5.0  $\text{mL min}^{-1}$ , analytical curves in the 100–2500  $\text{mg L}^{-1}$  (257.595 nm), 250–2000  $\text{mg L}^{-1}$  (257.958 nm), and 250–5000  $\text{mg L}^{-1}$  (258.056 nm) concentration ranges were always obtained with a linear correlation coefficient better than 0.9980. Samples were analyzed by the proposed HR-CS MAS method and gravimetry<sup>2</sup> as comparative techniques (Table 2). Results for S determination were in agreement with those obtained by gravimetry at the 95% confidence level (paired *t* test). The determined contents of S varied from 79.5 to 92.9 wt % for fungicides and from 13.0 to 21.0 wt % for fertilizers, and these contents were comparable to labeled values by manufacturers. The performance of the procedure for fungicide preparation based on microwave-assisted digestion in closed vessels was checked using an alternative digestion based on the heating block with open vessels. The trend in Table 2 reveals that results obtained by both sample preparation procedures are in agreement at the 95% confidence level. Accuracy measurements were also carried out using recovery tests for fungicide digests and fertilizer extracts (Table 3) spiked with 500.0  $\text{mg L}^{-1}$  S. Recoveries for fungicides varied within the 84–97% (257.595 nm), 103–109% (257.958 nm), and 106–109% (258.056 nm) intervals. Recoveries for fertilizers varied within the 92–102% (257.595 nm), 105–108% (257.958 nm), and 101–103% (258.056 nm) intervals (Table 3). The RSDs ( $n = 12$ ) were 4.8% (257.595 nm), 5.7% (257.958 nm), and 4.2% (258.056 nm) for a fertilizer extract containing 915  $\text{mg L}^{-1}$  S. The LODs were 15.1, 22.4, and 21.8  $\text{mg L}^{-1}$  for lines at 257.595, 257.958, and 258.056 nm, respectively.

The developed procedure for S determination in agricultural samples by the formation and measurement of CS molecules in an air–acetylene flame by HR-CS MAS is feasible in routine analysis, being a good alternative to current procedures. A lower amount of residue may be generated, and more samples can be analyzed per hour, as compared to gravimetry.

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