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# Determination of sulphur in various vegetables by solid sampling high-resolution electrothermal molecular absorption spectrometry

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ABSTRACT

Sulphur was determined in various vegetables via molecular absorption of carbon monosulphide (CS) at 258.056 nm using a solid sampling high resolution continuum source electrothermal atomic absorption spectrometer (SS HR-CS ETAAS). Samples were dried, ground and directly introduced into the ruthenium coated graphite furnace as 0.05 to 0.50 mg. All determinations were performed using palladium + citric acid modifier and applying a pyrolysis temperature of 1000 °C and a volatilisation temperature of 2400 °C. The results were in good agreement with certified sulphur concentrations of various vegetal CRM samples applying linear calibration technique prepared from thioacetamide. The limit of detection and characteristic mass of the method were 7.5 and 8.7 ng of S, respectively. The concentrations of S in various spinach, leek, lettuce, radish, Brussels sprouts, zucchini and chard samples were determined. It was showed that distribution of sulphur in CRM and grinded food samples were homogeneous even in micro-scale.



## 1. Introduction

Sulphur and sulphate based fertilizers are widely used in agriculture both for the improvement of the quality and yield. Sulphites and sulphur dioxide are used as a preservative in fruit and vegetable products to prevent the growth of bacteria, mold, and fungus; as an antioxidant preventing rancidity and as a chemical that attacks enzymes that cause discoloration, ripening, and rotting, usually in fruits after harvesting. It is also used in the production of wine as well as is found in ingredients like vinegar, corn syrup, corn starch, maltodextrin, dressings, and glucose syrup (Malavolta, Vitti, & Oliveira, 1997; Schnug, 1990; Virgilio, Raposo, Cardoso, Nobrega, & Neto, 2011).

According to WHO (World Health Organization, 1999), sulphur dioxide inhibits specific nerve signals, restricts lung performance and is a direct allergen. Therefore, the determination of sulphur content in agricultural samples is very important all over the world.

Sulphur or its compounds can be determined by different techniques such as gravimetric method (Vogel, 1989), spectrometric methods (inductively coupled plasma mass spectrometry (ICP-MS) (Clough, Evans, Catterick, & Evans, 2006; Yu, Kelly, Fassett, & Vocke, 2001), inductively coupled plasma optical emission spectrometry (ICP OES) (Mroczek, Werner, & Schron, 1998), UV–Vis spectrometry (Atanassov, Lima, Mesquita, Rangel, & Toth, 2000; Burakham, Higuchi, Oshima, Grudpan, & Motomizu, 2004; Hassan, Hamza, & Mohamed, 2006; Kass & Ivaska, 2001; Kurzawa, Janowicz, & Suszka, 2001; Yang, Zhang, Korenaga, & Higuchi, 1997)) and volumetric methods (Darjaa, Yamada, Sato, Fujino, & Waseda, 1998). In addition, ion chromatography (Bak, Schuhmann, & Jansen, 1993) and turbidimetry (Brienza, Sartini, Gomes Neto, & Zagatto, 1995; Krug et al., 1983) were used for the determination of sulphur and sulphate in plant samples.

All those methods have their own advantages and disadvantages. For example, the emission line of sulphur is at vacuum UV which makes the use of ICP-OES practically impossible. Determination of sulphur by ICP-MS is not free of problems as well due to high ionisation potential and polyatomic compounds of sulphur formed in the plasma.

Since the atomic absorption lines of sulphur are in vacuum UV range, it cannot be determined by atomic absorption spectrometry. On the other hand, sulphur was determined by molecular absorption of its diatomic molecules formed using AAS (Dittrich, 1980; L'vov, 1970; Parvinen & Lajunen, 1994; Resano & Florez, 2012; Welz & Sperling, 1999). For this purpose, CS, SnS was formed in the flame or graphite furnace and an appropriate line source lamp which emits on the rotational absorption line of the diatomic molecule or $D_2$ lamp were used. However, due to the problems originated from line selection, background correction, spectral

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interferences, low resolution and low spectral intensity, the conventional LS AAS is not suitable for the determination of S and halogens via molecular absorption of diatomic molecules of the analyte. On the other hand, new generation HR-CS-AAS equipped with a xenon arc continuum source and high resolution double monochromator (prims pre-monochromator and an echelle grating) and a CCD detector is capable of providing very high resolution around 1/175,000. The emission wavelength needed can be adjusted finely with high intensity. The absorption lines on and nearby of the molecule can be seen and spectral interferences can be corrected. As a result, due to the selection of needed line exactly, effective and real correction of background and spectral interferences, high intensity of emission at selected wavelength, HR CS AAS is suitable for the determination of S and halogens via measurement of the molecular absorption of diatomic molecules formed between the analyte and an element (molecule forming element) in the graphite furnace or flame. Thereby, an atomic absorption instrument, basically used for the determination of metal and metalloid can be benefited for non-metal determination.

The most appropriate molecule for the determination of sulphur is carbon monosulfide (CS) because it is formed in a graphite furnace or flame without adding any extra reagent (Baysal & Akman, 2011; Bechlin, Gomes Neto, & Nobrega, 2013; Heitmann, Becker-Ross, Florek, Huang, & Okruss, 2006; Huang, Becker-Ross, Florek, Heitmann, & Okruss, 2006; Huang et al., 2008; Virgilio et al., 2011). Therefore, an atomic absorption instrument, basically used for metal and metalloid element can be benefited for non-metal determination.

In this study, advantages of solid sampling technique were combined with facilities of HR-CS AAS for the determination of sulphur in various vegetables via molecular absorption of CS formed in the graphite tube. The instrumental and experimental conditions were optimised.

## 2. Experimental

### 2.1. Instrumentation

All measurements were carried out using a ContrAA 700 Analytik Jena (Analytik Jena, Jena, Germany) High Resolution Continuum Source Electrothermal Atomic Absorption Spectrometer (HR-CS ET AAS), equipped with SSA600 solid sampler. A 300 W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany) was used as a source. Ruthenium coated pyrolytical graphite tubes and platforms were used for the determination of sulphur in all samples. The experiments were performed at 258.056 nm. Argon (99.99%) was used as a purge gas.

### 2.2. Materials and reagents

Stock solutions (1000 mg $L^{-1}$) of S were prepared from thioacetamide and thiourea (Merck, Darmstadt, Germany) and further diluted with ultrapure water daily (TKA Wasseraufbereitungsysteme GmbH, Niederelbert Germany). Pd (2% Pd as $Pd(NO_3)_2$ in 5% $HNO_3$, SCP Sciences, Courtaboeuf, France) and citric acid (Merck, Darmstadt, Germany) mixture were used as a modifier. The accuracy and some optimisation tests of method were performed using Certified Reference Materials (GBW 07605 Tea, NCS ZC73013 Spinach, NCS ZC73016 Chicken and NCS DC73349 Bush Branches & Leaves (National Research Centre for Certified Reference Materials, Beijing, China)).

1000 mg $L^{-1}$ Ru (Fluka, Buchs, Switzerland), 1000 mg $L^{-1}$ W (Merck, Darmstadt, Germany) and 1000 mg $L^{-1}$ Zr (Merck, Darmstadt, Germany) were used for coating graphite tube and platforms.

### 2.3. Procedure

All the samples obtained from market were minced using a ceramic knife and washed several times with ultrapure water. The samples were then dried at 100 °C for 24 h, ground using an agate mortar throughly, and kept in a refrigerator at +4 °C in tightly closed vessels.

To cover the graphite tube and platform with Ru, 40 μL of 1000 μg $mL^{-1}$ of Ru was pipetted on the platform and atomised at 2000 °C as described elsewhere (Mior, Mores, Welz, Carasek, & Andrade, 2013). The procedure was repeated 10 times. The powdered samples were then put on the platforms of the solid autosampler below 0.5 mg, weighed automatically in the balance of the autosampler with 0.001 mg of precision. The solid samples were weighed and introduced to the furnace automatically using a SSA600 solid autosampler whereas solutions were injected by means of a built-in liquid dispenser of the autosampler. 10 μL of 0.4% Pd (w/v) prepared from $Pd(NO_3)_2$ in 5% $HNO_3$ and 10 μL of 3% (w/v) citric acid were then injected on the sample as a modifier. All determinations were performed applying a pyrolysis temperature of 1000 °C and a volatilisation temperature of 2400 °C. Linear calibration technique was applied for all quantifications.

## 3. Results and discussion

### 3.1. The choice of wavelength

The most important two critical parameters for the choice of working wavelength are (i) spectral interferences due to overlapping of absorption wavelengths of the analyte and matrix components (ii) the limit of detection (LOD) value which should be below the concentration of the analyte in the sample and depend on the sensitivity and standard deviation of the blank. From a series of absorption wavelengths for CS, 258.056 nm was found to be suitable with respect to above-mentioned criteria. In the literature, it was mentioned that one of the low sensitivity secondary lines of iron (258.045 nm) may cause spectral interferences due to overlapping with 258.056 nm of CS line (Ferreira, Lepri, Welz, Carasek, & Huang, 2010). However, since the sensitivity of iron secondary line is quite low, it would be problems only in the presence of excessive iron concentrations. The iron content of food samples studied in this study does not cause any significant interference. The sensitivity of 258.056 nm was high enough to detect the S (strictly speaking CS) in the samples. Therefore, CS line at 258.056 nm was safely used in all quantifications.

### 3.2. Pyrolysis/volatilisation curves

The pyrolysis and volatilisation (molecule forming/volatilisation) curves for CS obtained from calibration solutions and solid CRM are depicted in Fig. 1.

The sensitivities and thermal behaviours of CS obtained from thioacetamide, thiourea and a solid vegetal CRM (spinach) were not significantly different which shows that linear calibration technique using aqueous solution of thioacetamide or thiourea as a calibrant can be safely applied in all quantifications. According to the pyrolysis curves and volatilisation curves, in the presence of palladium + citric acid modifier and Ru coated furnaces/platforms, the samples and standards were pyrolysed at 1000 °C without any loss and the absorbances for CS molecules were measured at 2400 °C. The highest sensitivities were obtained when heating rate of 3000 °C $s^{-1}$ was applied in the molecule formation step.