

## AOAC Official Method 2016.xx

### Determination of Total Sulfur in Fertilizers by High Temperature Combustion

Proposed First Action 2015

(Applicable for measuring total sulfur concentration in solid and liquid inorganic fertilizers in the range of 1 – 100% with an LOD and LOQ of 47 and 106 µg S, respectively. [to be determined by MLV])

*Caution: Elemental analysis using combustion includes the risk of burn as some instrument components operate hot. Even after switching off the instrument, some components stay hot for long periods of time. Serious burns can occur if working inappropriately inside the instrument. Follow manufacturer specific operating instructions for safest handling.*

See Table 1 for interlaboratory study results that support the acceptance of this method.

**Table 1.** Interlaboratory study results for total sulfur in fertilizer and pure chemical standards.

Material	Expected S (%)	No. of Labs <sup>a(b)</sup>	Mean (%)	Recovery <sup>c</sup> (%)	RSD <sub>r</sub> (%)	RSD <sub>R</sub> (%)	HorRat
2011-05	1.56	x (y)	0.01	95.0	1.0	1.5	0.5
2011-08	6.39						
2011-06	11.95						
2011-01	13.22						
2011-07	7.76						
(NH <sub>4</sub> )SO <sub>4</sub>	24						
S 12-508	90						
Cysteine	26.72						
Sulpomag 12-1773	22						
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub> 12-591	26						
K <sub>2</sub> SO <sub>4</sub> KY12289	18						

<sup>a(b)</sup> a = number of labs retained after eliminating outliers, (b) = number of labs removed as outliers

<sup>c</sup> c = when applicable

#### A. Principle

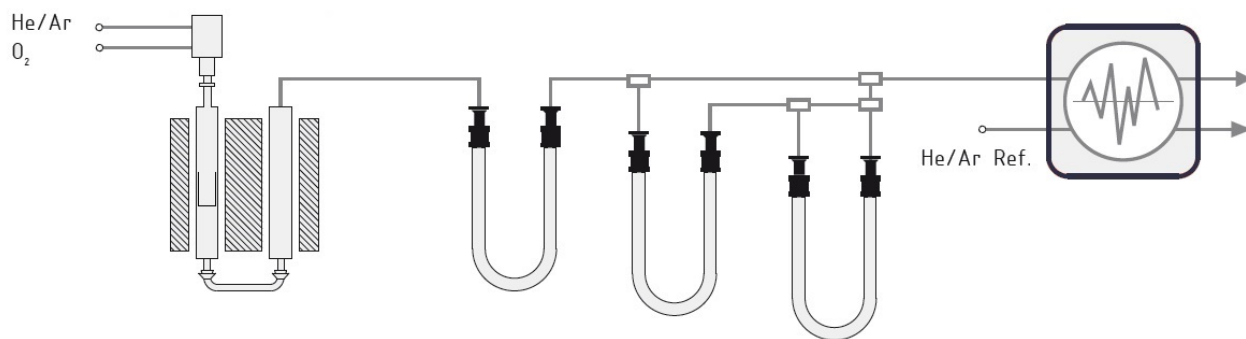
This procedure involves conversion of sulfur (S) species from fertilizers and chemical standards into SO<sub>2</sub> through combustion at a temperature >1100°C followed by measurement with thermal conductivity detection (TCD) or infrared (IR) detection reported as weight/weight percentage (w/w %). In the case of thermal conductivity detection and where simultaneous measurements of additional elements, such as carbon (C), hydrogen (H), or nitrogen (N), are performed an intermediate SO<sub>2</sub> separation by thermal adsorption/desorption is necessary. In accordance, this method allows simultaneous conformation to AOAC Method 993.13, *Nitrogen in Fertilizers by Combustion*, when using thermal conductivity detection. (1)

#### B. Apparatus and Materials

Total sulfur measurements can be performed via two variable apparatus types depending on detection method of choice.

(a) Apparatus A: Combustion followed by thermal conductivity detection —

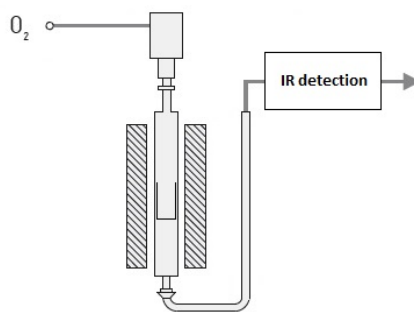
For Apparatus A type instruments, shown in Figure 1, sulfur as  $\text{SO}_2$  is determined by TCD with helium or argon carrier gas allowing for multi-element analysis. With this setup the test portion should be introduced into the combustion zone in a way such that atmospheric contamination is removed. Oxygen is added over the test portion at a temperature  $>1100^\circ\text{C}$  converting all elements to their fully oxidized gaseous specie. A catalyst, such as tungsten (IV) oxide ( $\text{WO}_3$ ), inside the combustion tube is used to aid oxidation. Following combustion, gases pass through a reducing environment and halogen scrubber in order that  $\text{NO}_x$  species be converted to  $\text{N}_2$  and removal of halogen contaminants, respectively. Other resulting combustion gas components  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{SO}_2$  are scrubbed or adsorbed on analyte-specific thermal adsorption/desorption columns.  $\text{N}_2$  is not adsorbed and flows directly to the thermal conductivity detector. Each  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{SO}_2$  are desorbed sequentially following the previous elements complete measurement by the TCD allowing for clear separation of the analyte species. Scrubbing materials may be used to remove each  $\text{CO}_2$  and/or  $\text{H}_2\text{O}$  if determination of either C and/or H is undesired. Software processing will convert the  $\text{SO}_2$  peak signal into a w/w percentage.



**Figure 1.** Typical multi-element measuring combustion system using adsorption/desorption separations and TCD.

*(b) Apparatus B: Combustion followed by infrared detection —*

For Apparatus B type instruments, shown in Figure 2, sulfur as  $\text{SO}_2$  is determined by a sulfur-specific IR detector with oxygen carrier gas. The test portion is introduced into the combustion zone where oxygen in combination with a temperature  $>1100^\circ\text{C}$  converts  $\text{S} \rightarrow \text{SO}_2$ . A catalyst, such as tungsten (IV) oxide ( $\text{WO}_3$ ), inside the combustion tube is used to aid oxidation. The gas stream is dried before entering the detector. With this apparatus type, variable amounts of  $\text{CO}_2$ ,  $\text{NO}_x$  and/or halogen combustion products may influence the results of  $\text{SO}_2$  measurement by the IR detector. Software processing will convert the  $\text{SO}_2$  peak signal into a w/w percentage. For best results using this apparatus type follow special instructions in Section D.



**Figure 2.** Typical sulfur only measuring combustion analyzer using  $\text{SO}_2$ -specific IR detection.

- (c) *Analytical balance* — resolution to 0.01 mg
- (d) *Test portions containers* — typically tin foil
- (e) *Hand pellet press* — for pelletizing powder materials
- (f) *Capsule sealing press* — for making a gas-tight cold seal on tin capsule holding liquid materials

## C. Reagents

- (a) *Helium or Argon* — minimum 99.995% purity
- (b) *Oxygen* — minimum 99.995% purity
- (c) *Tungsten (VI) oxide (WO<sub>3</sub>) granulate* — supplied by the instrument manufacturer
- (d) *Tungsten (VI) oxide (WO<sub>3</sub>) powder* — supplied by the instrument manufacturer
- (e) *Copper wires* — supplied by the instrument manufacturer
- (f) *Corundum balls (inert)* — supplied by the instrument manufacturer
- (g) *Quartz wool (inert)* — supplied by the instrument manufacturer
- (h) *Silver wool* — supplied by the instrument manufacturer
- (i) *Sicapent<sup>®</sup> with indicator* — supplied by the instrument manufacturer

## D. Calibration Curve and Daily Factor

Check calibration on the instrument **(B(a))**, **(B(b))**, daily and perform as needed according to the manufacturer's recommendation. For Apparatus A instruments **(B(a))**, it is recommended that a nonhygroscopic pure chemical standard be used for calibrating the instrument, such as sulfanilamide (≥99%) or phenylalanine (≥99%). Use a minimum of five calibration points to generate the calibration curve and cover the absolute sulfur range encompassing that of expected S concentration in unknowns. Any drift in the calibration curve can be observed and corrected for by daily use of an alternative nonhygroscopic pure chemical standard of known S concentration. Follow manufacturer's instructions for setting up and calculating drift corrections. If the drift correction or daily factor exceeds 0.9 or 1.1, perform necessary maintenance and ensure reagents in the combustion or reduction tubes are not depleted.

### *Special Consideration for Apparatus B Instruments —*

Apparatus B type instruments **(B(b))** pose several matrix and sensitivity analytical challenges, especially when S determination for a wide range of fertilizer products or an unknown source is required. Burn rates, scrubber types, and the need for accelerants is a function of the fertilizer type resulting in dramatically different scan shapes and peak areas for different products. Unknown and calibration materials must be matrix matched. For example, a pure ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] fertilizer source has a quick burn that requires no accelerant, whereas a blended fertilizer product containing potassium-magnesium sulfate (K<sub>2</sub>MgO<sub>8</sub>S<sub>2</sub>) and potassium chloride (KCl) is a slow burn that may require an accelerant and a halogen scrubber. Another requirement is the separation of unknowns into low and high S concentrations as low concentrations require a longer cell length that could be overwhelmed by high S concentrations. Failure to do so may result in excessive carryover. In cases where S concentrations and matrix types are known, they should be presorted and run to best match the calibration material and concentration range. In cases where the S source is unknown, it is necessary to make a test scan and compare to scans from various fertilizer sources to determine the best calibration material and concentration.

## E. Preparation of Test Samples (Analytical Samples)

*Liquid Fertilizers* — Collect liquid ammonium thiosulfate fertilizers using AOAC Method 969.01, or other recognized procedure. Accurately weigh test portions containing a sulfur amount within the calibration range (typically 20 – 100 mg) into a tared tin capsule or ceramic crucible **(B(d))**, already containing tungsten (IV) oxide powder **(C(d))** to be used as combustion aid. For tin capsules, cold weld with a capsule sealing press **(B(f))**, and accurately weigh the test portion to the nearest 0.01 mg. Do not include the WO<sub>3</sub> powder in the final weight. Insert weight into the operating software. Optionally, the test portion can be weighed into a tin foil containing WO<sub>3</sub> and dried at 60 °C for 2 hours. After which, the foil can be pelletized, **(B(e))**, to be run as a solid.

*Solid Fertilizers* — Solid elemental S fertilizers should be collected using AOAC Method 929.01, or other recognized procedure. Prepare an analytical sample of sufficiently small particle size to ensure sufficient representation at the expected test portion mass. Accurately weigh test portions containing a sulfur amount within the calibration range (typically 20 – 100 mg) into a tared tin foil cup or ceramic crucible **(B(d))**, to the nearest 0.01 mg. Additionally, add WO<sub>3</sub> powder **(C(d))**

creating an approximate 10:1 ratio of combustion aid to test portion. If using tin foil, pelletize the foil cup using an appropriate sealing device **(B(e))**.

#### F. Determination

- (a) Ensure that the instrument is powered on, leak free and the parameters are set according to the manufacturer's instructions. This includes furnace temperatures, flows and pressures.
- (b) Ensure that reagents **(C(a))**, **(C(b))**, **(C(d))**, **(C(e))**, **(C(f))**, **(C(g))**, **(C(h))**, **(C(i))** are not spent and still of functional use.
- (c) Run blanks and check the calibration according to Section D. Use the daily factor or recalibrate if necessary.
- (d) Prepare and weigh the test portion according to Section E.
- (e) Load the test portions onto the instrument and run the apparatus according to manufacturer's instructions.

#### G. Calculations

Element concentration (content, w/w %) is given by the instrument software. Absolute element content can be computed according to the following equation if needed:

$$A = \frac{W \times C}{100}$$

where: A = absolute element content in mg, W = sample weight in mg, and C = element concentration in percentage.

#### H. Appendix (Nonmandatory Information)

##### *Ruggedness trial* —

A ruggedness trial with eight determinations was used to explore the effects of the seven most important factors as described in the AOAC requirements for single laboratory validations: no blank measurement, improper addition of WO<sub>3</sub>, incorrect oxygen dosing, not wrapping test portion in tin, improper combustion temperature, high and low sample weights, and broken oxygen dosing device. (1) Each factor was assigned with reasonable high and low values. The effect of each factor was determined by the difference in S content when a factor was changed from high to low levels. Factors with extreme differences between high and low levels were noted. Magruder 2012-10 was the only matrix used in the trial. This material was selected as the most recent material available at the time of the trial. Source of S in Magruder 2012-10 is ammonium sulfate with an expected S value of 5.48%. The squared differences of each parameter were determined according to the Youden and Steiner Statistical Manual of the AOAC and listed based on their value (Table 2).

Ruggedness trial results showed no appreciable effect from the deviations of the method as noted, although caution should be taken to determine a blank measurement and use the proper 10:1 ratio of combustion aid to sample weight.

**Table 2.** Ruggedness trial method deviations and squared differences

Parameter	Squared difference
No blank measurement	0.08

WO <sub>3</sub> addition of 8:1 and 12:1	0.06
Wrong method oxygen dosing	0.03
Wrong test portion wrap, not tin	0.003
Combustion tube 1100°C or 1170°C	0.002
Test portion weight 20 or 60 mg	0.002
Broken oxygen dosing device	0.00001

*Quality Control* —

- (a) Perform blank determination before daily operation and any time a reagent or carrier gas tank is replaced.
- (b) Perform drift correction using a suitable standard before each day's analyses.
- (c) Include at least one reference material with each batch of 30 test portions. Results should be within limits specified for reference material. Reference materials can include a fine chemical of known S content such as sulfanilamide, a Magruder check sample, or a National Institute of Standards and Technology reference material.
- (d) Perform replicate analyses on at least 10% of the test portions, or every test portion if homogeneity is difficult to achieve. Replicate results should be within 10–15% of the mean value of the replicates.

**I. References**

- (1) Bernius et al., JAOAC, 97 (2014) p. 731-735. DOI: <http://dx.doi.org/10.5740/jaoacint.13-385>.