Analytical procedure for the determination of trace carbon impurity in elemental sulfur

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An analytical procedure has been developed for determining trace levels of carbon in elemental sulfur based on the standard combustion technique and incorporating gas chromatographic (GC) analysis of the products. Laboratory testing has shown a relative error of 5 ppmw or 5%, whichever is greater, in the results of the analysis for carbon contents of 50 ppmw and above and detection threshold of 15 ppmw carbon, along with good reproducibility.

Keywords: elemental sulfur; carbon; analysis

1. Introduction

Formed solid elemental sulfur produced from sour natural gas (or Claus recovered sulfur) is a highly pure commodity demanding a minimum product quality of 99.90% (dry basis) *(1,2)*. As produced and shipped within the Canadian Sulfur Industry this commodity must meet exacting standards in terms of export specifications, (see Table 1), which include allowable limits on ash, carbon, residual H_2S and the ASTs (arsenic, selenium and tellurium). The requirement for a low level of carbon is necessary to avoid formation of Carsul *(3)*, an insoluble polymer of carbon and sulfur, which may cause problems with plugging in liquid sulfur systems or off-color product appearance.

Although many of the methods used by the industry to analyze for impurities have been in place for a number of decades, those for carbon have been the least straightforward, prompting the development of a number of different analytical approaches. Historically, this has led to the development of a number of methods to measure carbon at these low levels in solid elemental sulfur, such as the Freeport combustion method and heat-treatment or Carsul test *(4)*. These methods, however, are either not simple to perform or lack the necessary precision and accuracy for a trace analysis. Some of the methods have aimed to develop ways to make the analysis of carbon as least demanding as possible for routine analysis of multiple samples, but at the expense of the fundamental basis of the analysis and accuracy.

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Table 1. Sulfur product quality (minimum 99.90% dry basis).

Impurity	Canadian Export Specifications Maximum
Ash	500 ppmw
Carbon	250 ppmw
Residual H_2S	0–30 ppmw
Arsenic	0.25 ppmw
Selenium	1.00 ppmw
Tellurium	1.00 ppmw
Water	1% as produced
	Common values
Acidity	<0.01 wt% (as H_2SO_4)
Chloride	<50 ppmw

In reality, combustion of all carbonaceous material to form CO_2 offers the only fundamental basis for the analytical determination of carbon in elemental sulfur. This approach, however, presents its own intrinsic difficulty to the analyst due to combustion of the sulfur itself to form SO_2, a source of much of the inherent unwieldiness associated with this method. Given the fundamental need for combustion as the basis of the analysis, a method was sought wherein quantifying the amount of CO_2 and handling the inevitable formation of SO_2 (and SO_3) could be achieved in as straightforward and analytically accurate a way as possible so as to simplify the overall procedure. The basis for such a method has been found in the use of gas chromatography (GC) to quantify the CO_2 by separation from both O_2 and SO_2 peaks. Unlike existing methods, the current method is less complicated and time-consuming to perform compared to other combustion methods, is universal (all forms of carbon are detected) and avoids questionable accuracy.

2.   Methods of analyzing for carbon in sulfur

The methods that have been developed for analyzing carbon in elemental sulfur can be divided into several groups, each offering their own advantages and disadvantages in terms of ease of performance and accuracy. Of the various methods, including combustion, wet oxidation and Carsul formation, only combustion offers a truly fundamental basis for carbon analysis. This is because all forms of carbon present in the sample are fully combusted to form CO_2, which is then determined by some analytical means. The various reported combustion methods including the Freeport and Texas Gulf Combustion methods have resorted to using gravimetric determination *(4)* or titrimetric *(5)* and turbidimetric *(6)* methods for quantifying the CO_2. The combustion method of carbon analysis is therefore a primary analytical method, as it depends on measuring directly the amount of CO_2 produced by combustion, which is related to the amount of carbon present in the sample.

The two better-known combustion methods, namely the Freeport and Texas Gulf combustion methods, have been available for use within the industry since the 1950s *(7)*. Both of these methods are based on gravimetric determination of the amount of CO_2 produced after combusting the carbonaceous content of the sulfur and absorbing on Ascarite (Figure 1). The sulfur dioxide produced by combustion of the sulfur is removed from the gas stream by converting it to sulfuric acid in a chromic acid absorber. The main difference between the two methods appears to be the use of platinized asbestos in the Texas Gulf method for the purpose of converting SO_2 to SO_3, as well as carbonaceous compounds to CO_2. Both of these early combustion methods require an
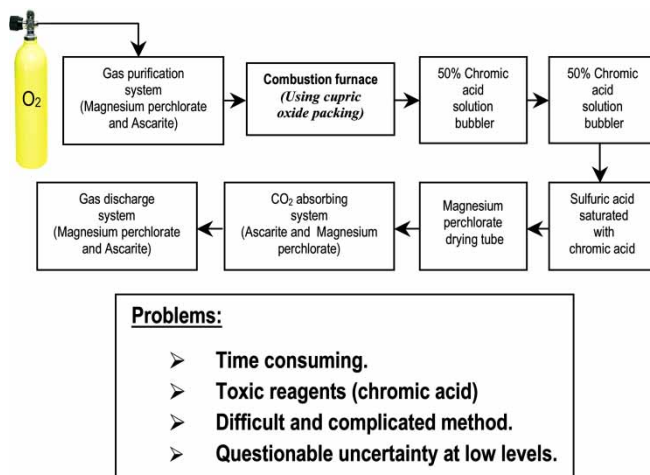
Figure 1. Diagram of Freeport combustion method.

elaborate analytical train and are demanding and cumbersome to perform. The uncertainty of the method also depends on achieving reproducible weights for the absorption tube, which is subject to the vagaries of handling and static charges. With careful performance the precision of these methods is said to be on the order of 0.005% (50 ppmw) carbon or 8% of the carbon present, whichever is greater, in the range of 0.05%–0.45% carbon, but to be subject to greater uncertainty at lower carbon contents.

Of the remaining methods that have been reported, none provide a proper basis for determining the actual amount of carbon in the sample or are empirical by design. These methods have been developed largely in response to the elaborate needs of the more fundamental combustion method or for easier and faster means of analysis. Two methods have been described, consisting of carbon analysis by wet oxidation *(4)* and analysis by infrared spectrophotometry *(8)*, which should more correctly be considered as hydrocarbon analyses. In particular, the use of both of these methods suffers from the fact that neither will include carbon present in the form of insoluble carbon–sulfur polymer or Carsul, which results from the interaction between sulfur and hydrocarbon materials at elevated temperatures *(3)*. This particular failing arises from the fact that these Carsul-type materials are not completely oxidized in the wet oxidation method or lack the C-H bonds necessary for detection of the carbon–hydrogen stretching vibrations in infrared spectrophotometry. The infrared method poses the additional problem that no reliable method exists for quantitative analysis of complex mixtures of unknown contaminants. This severely limits the usefulness of this technique except for perhaps qualitative identification of dissolved organic contaminants or quantitative analysis when the nature of the hydrocarbon is known.

Use has also been made of the property of sulfur to react with carbonaceous material to form Carsul, in developing an empirical method to analyze carbon in sulfur, referred to as the heat-treatment or Carsul test. This method, above all others, was designed to offer a rapid and easy method for routine analysis of sulfur samples. Two different versions of this method exists, which depend on achieving either a reasonably constant composition (in wt% C) for the Carsul formed by reacting under standardized conditions at the boiling point of sulfur *(4)*, or a colour-comparison to made-up standards *(7)*. The semi-quantitative basis of these methods stem from the fact that conditions of temperature, time and type of hydrocarbon are all important in terms of the extent and type of Carsul formed, both with respect to composition and colour.
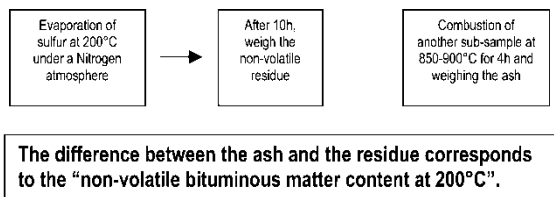
Figure 2.   ISO 3425-1975 (E) method.

3.   THE ISO 3425-1975(E) method

A method for determining the ash content of sulfur at 850–900 °C and residue at 200°C by evaporation under a N_2 atmosphere has been prepared by the International Organization for Standardization (ISO) and issued as International Standard ISO 3425-1975(E) by that body *(9)*. This standard makes reference to the difference between the ash at 850–900 °C and the residue at 200 °C as the 'non-volatile bituminous matter' content at 200 °C (Figure 2). Tuller *(4)* in 'The Analytical Chemistry of Sulfur and Its Compounds' states 'the carbon content of sulfur cannot be determined by burning off the sulfur and weighing the unburned residue as carbon, because any conditions that ensure that the carbon will not be burned will also ensure failure to remove all sulfur from the residue'. This is attributed to formation of Carsul, of variable composition, by reaction of the sulfur with some of the carbonaceous matter present and to the inability to decompose this material without loss of some of the carbon. Tuller's statement can also be interpreted to mean removal of the sulfur by non-combustion means such as evaporation, since this also requires application of temperatures where formation of Carsul would occur. This statement therefore suggests that the ISO 3425-1975(E) method and derivatives of this procedure, utilizing combustion of the sulfur in place of evaporation, cannot be reliably used to determine the carbon content of elemental sulfur.

4.   ASRL combustion method

A new analytical procedure developed by Alberta Sulphur Research Ltd for determination of carbon in elemental sulfur is based on combustion of the sample within a closed quartz tube, followed by analysis of the products using a gas chromatograph (see Figure 3). This method, although fundamentally similar to the earlier combustion methods, differs in that a direct instrumental analysis is used to quantify the CO_2, and a sealed combustion tube is used in place of the earlier flowing systems. This approach greatly simplifies the procedure compared to the elaborate combustion train used in earlier methods and takes advantage of the overall better sensitivity and detection limit available with a direct instrumental analysis compared to absorption and weighing of the CO_2.

The new procedure can be performed with a minimum of standard laboratory equipment including a tube furnace capable of heating to 800 °C (*e.g.* Thermolyne Model 21100) and suitable gas chromatograph. The analysis is carried out by fully combusting a 100-mg sample of sulfur in a quartz ampoule (volume = 70–80 mL), initially charged with 13–15 psig of pure O_2, at 800 °C using the tube furnace. An analytical blank, with O_2 alone, is performed before each analysis by
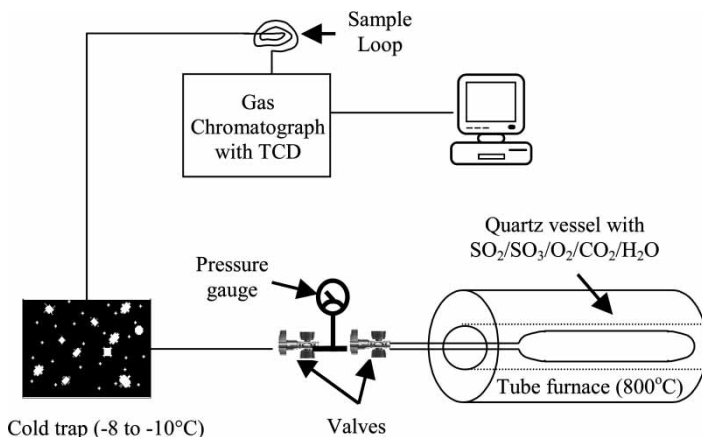
Figure 3. ASRL combustion method.

flushing the quartz vessel several times with pure O_2 supplied from a compressed gas cylinder, and then heating to 800 °C. This blank is performed to ensure both the absence of CO_2 contamination and to remove any trace organic residue from the glassware. Prudent analytical practice would require that this blank be repeated until a value is obtained that is in line with the detection limit of the method (see later). During analysis of the sample, the combustion tube is placed into the cold tube furnace and heated to 800 °C for a minimum of five minutes and then allowed to cool back to room temperature.

The quantification of the CO_2 produced by combustion of hydrocarbon materials in the sample is based on calculating the total number of moles present in the vessel after combustion of the sample using the ideal gas equation ($PV = nRT$) and the concentration of CO_2 determined by GC analysis. The value for the total number of moles within the tube is calculated from the temperature and pressure recorded after cooling, along with the internal volume of the assembled apparatus.

As with earlier combustion methods, over-oxidation of SO_2 to SO_3 *(10)* and the formation of trace amounts of H_2O by the combustion of hydrocarbon materials are inevitable. This results in some formation of sulfuric acid within the combustion products, making the use of stainless steel valves and fittings unsuitable. The corrosion of these parts by H_2SO_4 can be avoided, however, by using Teflon (PFA) materials instead (Swagelok) and a Teflon gauge guard to protect the pressure gauge from attack (see Figure 4).

The presence of sulfuric acid within the combustion products means that necessary steps must also be taken to protect the GC injector system during analysis. This is conveniently done by removing SO_3 and H_2SO_4 from the stream by passing the sample, en route to the gas chromato-graph, through a cold trap held at -8 °C to -10 °C (IPA + dry ice). This loop is constructed out of narrow-bore (1/16" o.d. × 0.030" i.d.) coated stainless steel tubing (*e.g.* Restek Silcosteel or Alltech AT-Steel) to protect it from corrosion and is rinsed with acetone and H_2O to remove any trapped SO_3 or sulfuric acid. Other methods of conveniently cooling the stream to remove SO_3 and H_2SO_4 that avoids use of a liquid bath also exists, as for example a vortex-tube chilled cold trap. It is necessary, however, to avoid overcooling the stream much below -10 °C so as to avoid the possibility of condensation of SO_2. A variety of fixed-loop GC injection valves containing inert polytetrafluoroethylene (PTFE)-based rotor materials and corrosion-resistant valve bodies are also available (Valco Instruments).

The chromatographic analysis for CO_2 was carried out using an SRI 8610 gas chromatograph modified with a GOW-MAC Model 952 thermal conductivity detector. Most standard laboratory gas chromatographs would, however, also be suitable for this analysis. Separation of the CO_2
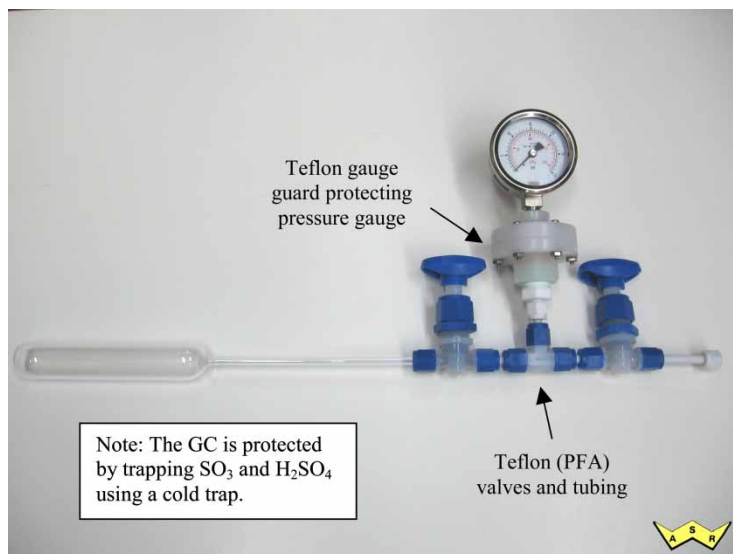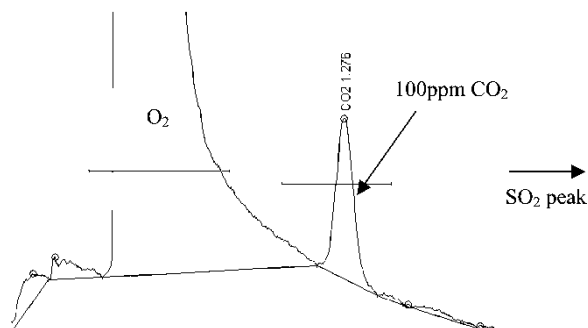
Figure 4.   Photograph of combustion apparatus.

Figure 5.   Chromatographic analysis for CO_2.

from the O_2 and SO_2 peaks (Figure 5) was achieved on a porous polymer column (Chromosorb 108; $1.8\,m \times 2\,mm$ i.d.) using helium as the carrier gas and a suitable temperature program. Calibration of the thermal conductivity detector was performed with purchased calibration gas mixtures (Matheson Tri-Gas) of 100, 500 and 1000 ppmv CO_2 in N_2. The proper use of calibration mixtures was ensured by directly flushing the injection loop on the GC by means of a Teflon line, before introducing the sample to the column. This method of purging the injection valve ensures delivery of a proper sample and conditions the surface of the transfer line for any adsorption *(11)*. Multiple samples of the calibration gas were also injected as part of the procedure as a further precaution against adsorption. The grade of calibration mixture used had a stated accuracy of less than 5% and was otherwise used as received from the supplier. This method of chromatographic analysis generally affords a relative error of better than 5% in the measured value.

   Detection limit, precision and accuracy. Statistical analysis of the results of a large number of blank analyses performed with O_2 alone showed the detection limit for the method to be on the order of 15 ppmw carbon, whereas the limit of quantitation based on 10 times the standard deviation of the blank was 50 ppmw *(12)*. These values could likely be improved by a factor of two by going to a higher-end GC system, thus making the method even more sensitive. The

Table 2. Reproducibility and accuracy of the method for 50, 100 and 250 ppmw carbon standards.

	Sample 1 (ppmw)	Sample 2 (ppmw)	Sample 3 (ppmw)	Average (ppmw)
249 ppmw				
Injection 1	278	273	240	
Injection 2	272	275	232	
Injection 3	271	281	227	
Mean	274	276	233	261
Standard deviation	3.8	4.2	6.6	21.5
Relative standard deviation (%)	1.4	1.5	2.8	8.2
100 ppmw				
Injection 1	96	111	94	
Injection 2	98	120	109	
Injection 3	99	112	104	
Mean	98	114	102	105
Standard deviation	1.5	4.9	7.6	8.8
Relative standard deviation (%)	1.6	4.3	7.5	8.4
49 ppmw				
Injection 1	59	55	55	
Injection 2	53	55	52	
Injection 3	57	52	53	
Mean	56	54	53	54
Standard deviation	3.1	1.7	1.5	2.4
Relative standard deviation (%)	5.4	3.2	2.9	4.3

reproducibility or precision of the method was examined by making up standards of 50, 100 and 250 ppmw carbon in elemental sulfur, using quinoline, and analyzing each of these standards in triplicate. The result of each analysis itself was based on triplicate GC analyses of the combustion product, which further afford a value for the reproducibility of just the GC measurement. These standards were made up from a single-stock 2092 ppmw carbon sample using the same liquid sulfur to perform the dilution in all cases. The choice of 50, 100 and 250 ppmw carbon for the three standards was based on the maximum allowable export specification of 250 ppmw, thus corresponding to a low, medium, and high level of carbon contamination for a commercial sulfur product.

The results of the reproducibility tests are shown in Table 2 along with the mean, standard deviation, and relative standard deviation for both the GC measurement and the method as a whole. These values show that the GC measurement has an average reproducibility on the order of 5% or less, also confirmed by replicate measurements with the calibration mixtures, whereas the method as a whole displays a precision closer to 8%. The uncertainty of the method can also be gaged by comparing the average for the three separate analyses with the expected value for each standard. This comparison shows that the measured and calculated values are within 5 ppmw or 5% of each other, whichever is greater, for carbon levels of 50 ppmw and above.

Replicate analyses of the sulfur blank and the 2092 ppmw carbon sample were also performed as shown in Table 3. These results provide a value of 27 ppmw carbon for the sulfur blank and also serve to verify the accuracy of the method over a wider range, up to 2100 ppmw carbon, as shown by the correlation plot in Figure 6. The level of carbon determined for the sulfur blank is likely, however, less than 27 ppmw, since part of this measurement can be attributed to noise. Based on the limit of quantitation, accurate results to the specified precision and accuracy should be reported only for values of 50 ppmw and greater.

Sample size and tube volume. The choice of a 100-mg sample size for a combustion tube volume of 70–80 mL is based on the calculated amount of O_2 required to fully combust this amount of sulfur to SO_2. Thus, roughly 1 atm of pure O_2 contained in this volume is required

Table 3.   Results of analyses of the sulfur blank and 2092 ppmw carbon standard.

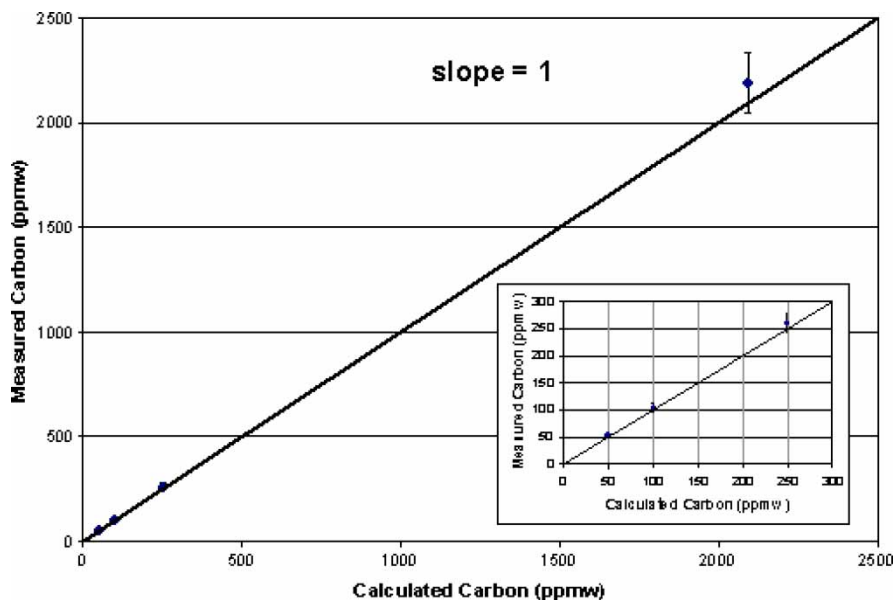| Sample	Number of replicates	Mean (ppmw)	Standard deviation (ppmw)	Relative standard deviation (%)
Sulfur blank	6	27	5.0	18.5
2092 ppmw carbon sample	6	2190	124	5.7

Figure 6.   Correlation plot for measured and calculated values.

to convert 100 mg of sulfur entirely into SO_2. This leaves the amount of over-pressure (or gauge pressure) initially within the vessel as the driving force for sample delivery to the GC, since the O_2 consumption:SO_2 production ratio is 1:1. The amount of this over-pressure must also be limited, for safety reasons, to remain within the safe working pressure of the tube during heating to 800 °C. These two requirements can be satisfied by using an initial charge pressure of 13–15 psig for the O_2 (~1 atmg), while also allowing the GC analysis to be performed in triplicate. This combination of sample size, initial O_2 pressure and combustion tube volume also provides a CO_2 concentration on the order of 130 ppmv within the combustion products for an initial 100 ppmw carbon in the sample. This level of CO_2 is easily quantified by modern gas chromatographs using a high-sensitivity thermal conductivity detector, which are capable of measuring to even lower concentrations depending on the exact analytical GC system.

   The previous discussion suggests that it may be possible to improve the analytical detection by using an even larger sample size, up to approximately two-fold. This improvement would come from having a higher CO_2 concentration for the same parts per million by weight of carbon in the sample, due to doubling of the sample size, and minimizing the size of the residual O_2 peak in the chromatography. In the absence of any SO_3 formation (O_2 consumption:SO_3 production ratio of 1.5:1), the final pressure within the tube, after combustion and cooling to room temperature, should remain the same as the initial charge pressure since the O_2:SO_2 ratio is 1:1. This final pressure is normally observed, however, to be lower than the initial pressure, even accounting for expansion into the gauge section, confirming a loss of moles during combustion and hence formation of SO_3. This suggests that the potential gain from increasing the sample size may be

offset by the extent to which SO_3 is formed and the need to ensure complete combustion of the sample. The optimum sample size of 100 mg is therefore recommended for a combustion tube volume of 70–80 mL.

5. Conclusion

The new analytical technique for measuring carbon in elemental sulfur offers an easier and more convenient approach than previous combustion methods, along with better accuracy. This improvement is achieved by going to a sealed combustion tube and direct instrumental analysis to measure the CO_2. Overall, the results provide an uncertainty to within 5 ppmw or 5%, whichever is greater, for carbon levels of 50 ppmw and above, along with a detection threshold of 15 ppmw and good reproducibility.

Acknowledgements

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