



Project Summary

A Study to Evaluate and Improve EPA Reference Method 16

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A modification to EPA Reference Method 16 was developed to eliminate known deficiencies in the analysis of total reduced sulfur (TRS) from stationary sources at kraft pulp mills. The modifications include: (1) addition of a cold, citrate buffer gas scrubbing solution at the source; (2) elimination of the need for a heated sample system and a dilution system; (3) elimination of the need for two GC systems; (4) changing the GC separation columns and valving to eliminate interference from CO₂, COS, and SO₂; and (5) defining a method for checking the linearity of the calibration curve. The proposed method was field evaluated by testing a lime kiln, a recovery boiler, and a smelt dissolving tank vent at a kraft pulp mill. The proposed method produced accurate results from each source.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

On September 24, 1976 under Section 111 of the Clean Air Act, as amended, the U.S. Environmental Protection Agency (EPA) proposed a set of standards limiting emissions of reduced sulfur compounds from kraft pulp mills. The odorous quality of such emissions was considered a public nuisance and a

national total reduced sulfur (TRS) emission standard was promulgated in which a method for measuring TRS was included. This method, EPA Method 16, has undergone minor modifications since that date. The Quality Assurance Division of the Environmental Monitoring Systems Laboratory at Research Triangle Park, NC, has a program to evaluate and standardize EPA source test methods. While participating in this program, Harmon Engineering & Testing (HE&T) undertook a study of EPA Reference Method 16.

According to the published reference method, a sample of gas is extracted from the emission source and is diluted with clean, dry air. An aliquot of the diluted sample is then analyzed for hydrogen sulfide (H₂S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS), known collectively as TRS, by gas chromatographic (GC) separation and flame photometric detection (FPD). The method is applicable for analysis of reduced sulfur compounds from emission sources at kraft pulp mills.

After being used at mills for source tests by a number of researchers, the method was found to have several deficiencies that affected the accuracy and reproducibility of the results. These include:

1. The method requires the use of two gas chromatographs and two recorders to analyze the four reduced sulfur compounds simultaneously, thus presenting a

major logistical problem during most testing.

2. The specified dilution system does not always give accurate, reproducible dilutions in a field environment.
3. Carbon dioxide (CO₂) elutes at the same time as H₂S from the GC column and interferes with the determination of H₂S by a quenching effect on the flame, causing low results.
4. Carbonyl sulfide (COS) elutes from the GC column at the same time as H₂S. Since COS is not considered in TRS emission calculations, high results may be obtained.
5. Potential condensation of moisture within the sampling system requires a totally heated system prior to dilution of the sample gas with clean, dry air.

This project was undertaken to systematically evaluate Method 16 and to present recommendations for modifying the existing method to improve the accuracy, precision and reliability of collected data. Also, a goal of the project was to simplify the method as much as possible to reduce potential error during field sampling. Once deficiencies in the method were identified, corrective action was taken to solve and evaluate the problem in the laboratory. At the completion of the laboratory evaluation, two field evaluations of the modified method were conducted at a kraft pulp mill to determine the expected quality of the data that could be collected using the modified method.

The National Council of the Paper Industry for Air and Stream Improvement (NCASI) conducted a study to evaluate several scrubbing solutions used to remove SO₂ from a gas stream without affecting the TRS (A Study of Alternate SO₂ Scrubber Designs Used for TRS Monitoring. Special Report 77-05, New York, 1977). A citric acid/potassium citrate buffer at pH 5.6 was effective for removing the SO₂ from a gas stream, yet leaving the reduced sulfur compounds unaffected. This scrubbing solution was incorporated into Method 16 to remove SO₂ prior to analysis by GC, thus preventing potential SO₂ interference to the analysis.

Building on this information obtained by others and HE&T's field experience in using the method, it was determined that modifications were needed in the method to (1) improve the ability to conduct sample dilutions, (2) remove moisture from the gas stream at the

source to prevent the need for heated lines, (3) obtain better gas chromatographic separation of the reduced sulfur compounds and eliminate potential interference from COS and CO₂, and (4) eliminate the necessity of using two gas chromatographs during analysis.

Conclusions

The results of the project demonstrated that a modified analytical system could be used to obtain quality data on TRS emissions from the source using one gas chromatograph without a heated sample system. The need for dilution of the gas stream was also eliminated by using a smaller sample loop volume for analysis. It was also possible to select the gas chromatographic columns such that the eluting times of COS and CO₂ differed from that of H₂S, thus eliminating interferences. The following subsections discuss each component of the sampling and analysis systems.

Design of the SO₂ Scrubber

Based on the work of the NCASI, it was determined that the best place to locate a scrubber to remove moisture and SO₂ was at the source rather than at the GC. By placing the SO₂ scrubbing solution in an ice bath, the moisture was removed from the sample stream, allowing the transport of the clean, dry sample. A Teflon container filled with glass wool was located as an in-stack filter to remove particulate matter immediately after the sample is introduced into the probe. The sample line is heated until just above the first impinger where rapid cooling and condensation of the water takes place as the gas stream enters the first impinger.

Due to extensive evaluation of the SO₂ removal efficiency of this scrubbing solution (potassium citrate-citric acid at pH 5.6) by the NCASI, additional evaluations were not performed by HE&T on the scrubbing solutions themselves. Locating the SO₂ scrubbers in an ice bath at the source eliminates the need for a long, heated sample line and also the requirement to dilute the gas sample with air to reduce the dew point. When the impingers are immersed in an ice bath, the gas temperature within the last impinger is less than 5°C. At this temperature, the sample gas contains less than 1 percent moisture.

Dilution System

Moisture condensation content at the source eliminates the need for diluting

the sample to prevent condensation. However, at times it is necessary to dilute the sample gas in order to obtain a signal in the linear range of the gas chromatograph. A simplified dilution system was developed to produce accurate reproducible dilutions without TRS losses to reactive surfaces. Since the incoming gas is dry, there is no requirement to heat the dilution system when the ambient temperature is above freezing. The system is maintained at ambient temperature and pressure and operates under a normal vacuum of 1.5 to 2.5 psi.

During analysis of gas streams from sources with TRS concentrations of less than 10 ppm, the dilution system only acts as a splitter and no dilution of the gas stream is provided. When acting as a splitter, the system simply maintains the constant pressure within the GC sample loop to give reproducible results. Also, a larger volume of gas is drawn through the system to reduce lag-time in sampling.

Gas Chromatographic System

A Tracor Model 250H Gas Chromatograph modified to incorporate a 4-port valve was used for the separation of the reduced sulfur compounds. The 10-port valve was used to inject the sample and backflush the precolumn. The 4-port valve was used to reverse the flow on the Separation Column 1, thus enabling the separation of all four reduced sulfur compounds at isothermal column conditions. Column 2 acted as a buffer to prevent flame blowout during valve switching.

Several sample loops of different lengths were used to provide a variety of sample sizes. Sample loop volumes ranged from 0.03 mL to 3.0 mL. A wide range of concentrations can be analyzed by varying the volume of sample injected into the GC.

Separation Column 1 was a 4.5-foot x 1/8-inch o.d. Teflon tube packed with Carbosorb B HT 100. Separation Column 2, used primarily to prevent flame blowout during valve switching, was a 3-foot x 1/8-inch o.d. Teflon tube packed with 3 percent polyphenyl ether plus 0.05 percent phosphoric acid on Teflon beads.

The multi-port valves were air actuated by means of solenoid valves. Since the time of valve switching is critical to the maintenance of accurate separation times, the timing sequence valve was

controlled by a digital valve interface which was timed from an electronic integrator. The electronic integrator served not only as a triggering device, but was also used to record the areas of the peaks obtained for each of the compounds.

Figure 1 shows a chromatogram obtained from the system for the analysis of all four reduced sulfur compounds designated as TRS. The instrument conditions and concentrations of the compounds are given on the chromatogram. All four compounds eluted in less than 5 minutes. The low carrier flow during the first 59 seconds of the run was necessary to obtain separation of CO₂ and air from the H₂S. The CO₂ elutes in approximately 50 seconds. A series of tests were performed to determine if CO₂ had a desensitizing effect on the H₂S. It was found that under normal operating conditions, CO₂ at 10 percent by volume did not affect the response of the detector to H₂S.

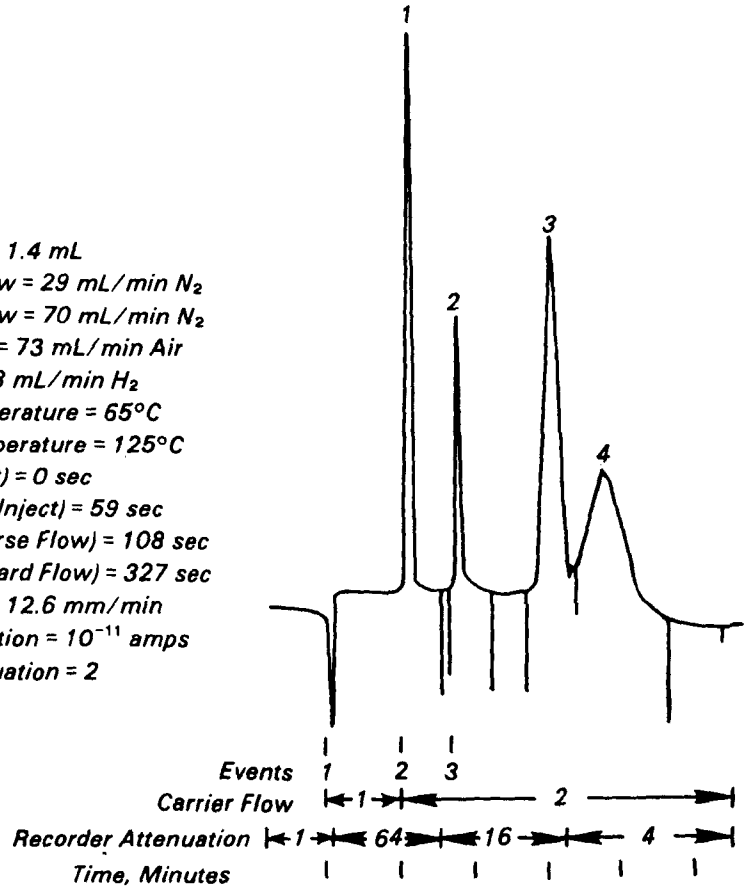
Carbonyl sulfide and sulfur dioxide coelute at a retention time of approximately 80 seconds. Baseline separation is achieved between the H₂S and the COS and SO₂ peak. Since COS and SO₂ are not of concern in TRS analysis, the coelution is of no consequence.

Field Evaluation

At the completion of the laboratory evaluation of all equipment within the system, a field evaluation was conducted at a kraft pulp mill to determine the applicability of the system for analyzing reduced sulfur compounds. A total of 16 days of field time was spent in the evaluation of a recovery boiler, a smelt dissolving tank vent and a lime kiln. The objective of the field evaluation was not to determine the emissions from the source, but rather to determine if the method could be used to conduct emission testing over a period of time and still obtain good recoveries of hydrogen sulfide through the system.

Due to construction activities at the mill, it was not possible to test all sources during a given field trip. Three different trips were required to test all sources and to complete the evaluation. During the first trip, a lime kiln was tested and it was discovered that some interference to the GC was present due to the high CO₂ concentration in the gas. At the completion of that field evaluation, the GC conditions were modified slightly to give a better separation between CO₂ and H₂S and

Sample Size = 1.4 mL
 Carrier (1) Flow = 29 mL/min N₂
 Carrier (2) Flow = 70 mL/min N₂
 Oxidant Flow = 73 mL/min Air
 Fuel Flow = 48 mL/min H₂
 Column Temperature = 65°C
 Detector Temperature = 125°C
 Event 1 (Inject) = 0 sec
 Event 2 (Stop Inject) = 59 sec
 Event 3 (Reverse Flow) = 108 sec
 Event 4 (Forward Flow) = 327 sec
 Chart Speed = 12.6 mm/min
 Input Attenuation = 10⁻¹¹ amps
 Output Attenuation = 2



Compounds	Retention Time (sec)	Concentration (ppm)	Area (μv-sec/16)	Retention Ratio
1 H ₂ S	66	3.4	5990	1.00
2 MeSH	106	4.3	4750	1.61
3 DMS	184	3.9	3509	2.79
4 DMDS	230	3.9	463	3.48

Figure 1. Chromatogram of H₂S, MeSH, DMS, and DMDS.

thus reduce the interference from CO₂. The lime kiln was tested again during a later field trip.

During the second field evaluation, the results obtained from the gas chromatograph were compared to those obtained simultaneously by a coulometric titrator (ITT Barton). Table 1 shows typical analyses of the emissions from the lime kiln during a day when the COS was present in the emissions. Throughout the day the mill operators were changing the concentrations of oxygen being introduced into the kiln and this change in oxygen concentra-

tion was found to correlate with the TRS concentration being emitted. The important thing to note from this table is that significant amounts of COS were being emitted.

Table 2 shows a comparison of the TRS analysis by GC and by coulometric titrator. On this day, no TRS was observed being emitted from the lime kiln stack. During this 30-minute period, only COS was observed as being emitted; as would be expected, the coulometric titrator was measuring the COS as total reduced sulfur. Since a certified permeation device for COS was

not available in the field, the COS concentration was measured by the GC by plotting the COS peak areas on the H₂S calibration curve. This will not give the exact concentration of COS but should be within 10 percent of the actual concentration.

Upon completion of the field evaluation of the method, several important items were noted regarding total reduced sulfur emission testing. The most important of these are summarized below:

1. It was necessary to maintain the gas chromatograph, the dilution system and the calibration system in a relatively stable environment. Temperature changes caused fluctuation in the output of the calibration gases and drift would be noted within the gas chromatograph.
2. Significant losses of H₂S were not observed in the system after it had been used for sampling 8 to 10 hours while still obtaining greater than 80 percent recovery of H₂S. It is possible to use this system to perform three runs of 3 hours each on a given source without changing the scrubber solution or without cleaning the sample lines.
3. By reducing the gas temperature at the source with the cold scrubbing solution, it was unnecessary to use a heated sample system or to dilute the sample gas with air to reduce the dew point. This enabled a more sensitive analysis to take place without the added error of a dilution system.
4. The citrate buffer scrubbing solution proved to be effective in removing SO₂ without affecting the other reduced sulfur compounds of interest.

Recommendations

As a result of the laboratory and field evaluations of the procedures specified in Method 16, it is recommended that the reference method be modified to incorporate the improvements in the analytical techniques. The method should be rewritten to establish more flexibility in the way that the results are obtained. It would be more advantageous to establish performance specifications that an analytical system must meet rather than to present the actual details of how to configure the system. The modifications to the method should include a schematic of the modified system as an example, but each analyst

Table 1. Analysis of Lime Kiln Emissions

Time	H ₂ S concentration (ppm)	COS* concentration (ppm)
<i>Day 1</i>		
1507	2.3	3.7
1514	3.0	4.7
1528	3.8	4.4
1535	5.1	5.3
1542	8.7	6.4
1549	8.1	6.4
1556	7.8	6.8
1603	8.6	7.9
1610	18.9	10.0
1617	35.9	14.1
1624	24.3	13.3
1631	11.5	11.9
1638	7.9	9.9
1645	13.9	10.0
1652	25.3	15.0
1659	37.0	15.0
1706	26.9	13.8
1713	11.5	8.9
1720	5.8	6.6

* No calibration curve was available for COS and the apparent concentrations were determined using the H₂S calibration curve. The COS was identified by retention time.

Table 2. Comparison of TRS Analyses by GC and Coulometric Titrator on a Lime Kiln

Time	TRS concentration* (ppm)	COS** concentration (ppm)
<i>Day 2</i>		
1430	26.1	21.4
1435	29.3	25.8
1440	29.3	27.2
1445	29.3	28.4
1450	30.1	32.1
1455	32.5	32.1
1500	33.5	32.1
1505	32.5	28.4
Mean	30.3	28.4
RSD (%)	7.9	14.2

* The TRS concentration was measured with a Barton Coulometric Titrator. Instrument was operated in parallel with GC. The same SO₂ scrubber and sample line were used for both instruments.

** The COS concentration was determined by GC. The concentrations were calculated using a calibration curve for H₂S. H₂S concentration was less than 1 ppm during the comparison. The COS was identified by retention time.

should have the flexibility to establish his own system as long as it meets the performance criteria.

The modifications in the method should address potential interferences. The interferences that are known to be present are moisture, carbonyl sulfide, carbon dioxide, particulate matter and sulfur dioxide. Any method used for the

analysis of the TRS compounds from kraft pulp mill sources should not be subject to interference from any of these compounds.

Any system of analysis should produce a linear calibration curve from at least four concentrations that does not deviate more than 10 percent from the calculated curve and the calculated

concentrations. Repetitive injections of the same concentration gas should not have more than a 5 percent standard deviation in calculated concentrations.

The most important factor of the method is the calibration of the system to accurately determine the losses of TRS through the sampling system. A loss of more than 20 percent of a 5-ppm H₂S standard through the sample transport system should invalidate a run. The recovery of H₂S through the sample transport system should be checked before and after each run.

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The complete report, entitled "A Study to Evaluate and Improve EPA Reference Method 16," (Order No. PB 83-165 571; Cost: \$10.00, subject to change) will be available only from:

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