



Project Summary

A New Audit Method for EPA Reference Method 6

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A simple, inexpensive, and accurate method for evaluating and/or auditing sampling and analytical phases of EPA Source Reference Method 6 was developed. The method uses a known amount of a chemical compound in the form of a tablet or pill (or placed in a capsule) to generate sulfur dioxide (SO_2) quantitatively by reaction with an acid. The reaction takes place in a compact glass impinger system that can be taken to the field. The SO_2 generated in test runs was collected and analyzed using the Method 6 procedure. The SO_2 generation was quantitative and recoveries were found to be 94 ± 5 percent. The time to complete the reaction was less than 15 min at a flow rate of 1 L/min, but the recommended sampling time was 45 min. The tablets prepared gravimetrically were found to be stable over a 6-month period. The between-laboratory results obtained showed close agreement with the expected concentrations based on calculations from the stoichiometric reaction. The estimates of repeatability (or within-laboratory precision) were ± 5.0 mg 95 percent of the time for the two concentration levels tested. The reproducibility (or between-laboratory precision estimate) was within ± 5.9 mg at the low range and ± 23.8 mg at the high range about 95 percent of the time. The maximum bias observed for the method was 0.5 percent.

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

The U.S. Environmental Protection Agency (EPA) is interested in developing audit materials for all EPA source reference methods. These audit materials are used to conduct performance audits during stationary source measurements. EPA is currently providing liquid sulfate standards as audit materials for EPA Source Reference Method 6, which is used to determine SO_2 emissions from stationary sources. However, these liquid sulfate audit standards are useful only for evaluating the analytical phase of Method 6. Currently, sampling phase procedures are evaluated only by a systems audit; i.e., someone observing the sampling procedures in the field. Therefore, a method or device that can be used as an audit material for the evaluation of both the sampling and analytical phases of the source reference methods is needed.

Research Triangle Institute (RTI) was contracted by the Quality Assurance Division of EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, to develop a simple method or device for evaluating and/or auditing both the sampling and analytical phases of various source reference methods in the field. The main objectives of this study were to develop a device for auditing both the sampling and analytical phases of EPA Method 6 and to establish its accuracy, precision, and stability. The method uses a known amount of a chemical compound (sodium bisulfite or sodium sulfite) mixed with an inert binder (polyvinyl pyrrolidone) and formed into a tablet or pill to generate SO_2 quantitatively by reaction with sulfuric acid. The SO_2 generated in test runs was collected and analyzed using the Method 6 procedure as published in the *Federal*

Register (Vol. 42, No. 160, August 1977). The audit method developed was also evaluated at two concentration levels by six different laboratories to determine its repeatability, reproducibility, and accuracy. The various activities performed during the study and the results obtained are discussed in this report.

Experimental Procedures

The preliminary experiments to generate SO_2 from the chemical reaction of sodium bisulfite and sulfuric acid were conducted using the experimental system shown in Figure 1. Initially, a known amount of sodium bisulfite was placed in a three-way, stoppered, round-bottomed flask and dilute sulfuric acid (10 percent) was added slowly from a burette. Dry nitrogen or air was bubbled through the solution at a flow rate of 1 L/min to sweep the released SO_2 into a glass manifold. Glass wool was used to remove the aerosol vapors. The generated SO_2 was monitored continuously with a SO_2 source analyzer (TECO Model 40 fluorescent analyzer) to determine the time of completion of the reaction. Within 10 minutes the reaction was completed. In later experiments, the SO_2 gas generated from the chemical reaction was collected into an evacuated Tedlar bag. After 30 minutes of gas flow into the bag, the contents of the bag were further diluted with zero air and analyzed for SO_2 using the source analyzer. The analyzer was calibrated with a cylinder gas of SO_2 referenced to the National Bureau of Standards Standard Reference Materials. The experiments were repeated using various amounts of sodium bisulfite and different concentrations of sulfuric acid.

The sampling train component parts, except for the SO_2 gas generator, were the same as those in the EPA Method 6 train. The sampling probe was not required and hence not included in the train. A modified midget impinger (Ace Glass, Inc., Model #7544-35) was used as an SO_2 generator in place of a test-site stack sample to generate a gas sample (SO_2) from the chemical reaction.

The sample collection procedure was followed as described in EPA Method 6 except for the following modifications. The gas sample was drawn through the SO_2 generator for 45 minutes. The tablet generally took 15 minutes to dissolve completely; however, the sample collection was continued for an additional 30 minutes. Since ambient air was used to draw the sample from the generator, a blank run (without a tablet) was performed for 45 minutes and impinger solutions were analyzed.

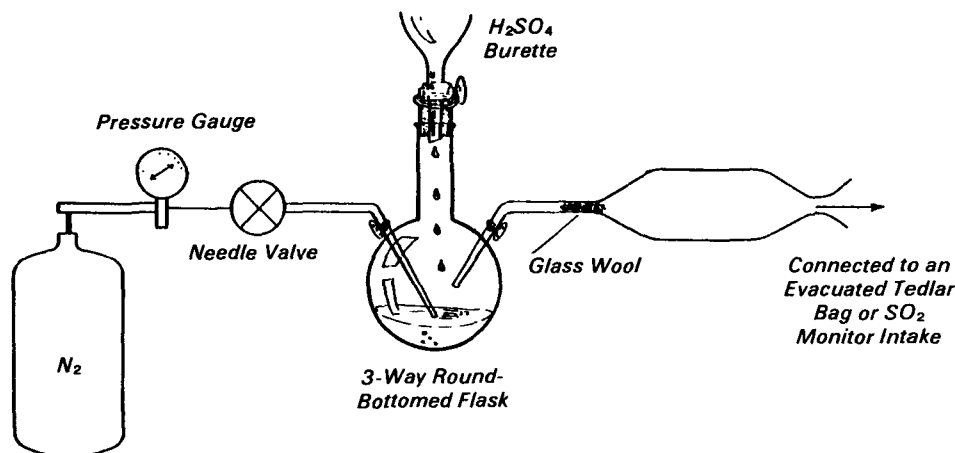


Figure 1. Preliminary SO_2 generation system.

The impinger solutions were analyzed after each run for sulfate (converted form of SO_2 collected) by ion chromatography instead of barium perchlorate-thorin colorimetric titration as described in EPA Method 6. However, it was established initially that both analytical procedures gave identical results.

Because the amount of sodium bisulfite or sodium sulfite required to generate source concentrations of SO_2 (~400- to 1,000-ppm levels) is so small, an inert binder (polyvinyl pyrrolidone, PVP) was used for mixing. The mixture was made in the form of a tablet or pill. The tablets or pills were made using either a KBr die (commonly used to make KBr pellets for infrared spectrophotometric studies) or a tablet press. The tablets or pills were made by adding to the die a layer of binder, a weighed amount of sodium bisulfite, and another layer of binder. Several hundred pounds of pressure was applied using a hydraulic press to form the tablet. The PVP binder was found to be inert and water-soluble and, because the chemical compound was contained between the two layers of binder, the tablets could be handled safely. The binder also helped reduce the rate of reaction of SO_2 generation. Tablets were made with varying amounts of sodium bisulfite to generate different concentrations of SO_2 .

Collaborative Testing Procedures

From those laboratories having contracts with EPA, six were selected for the collaborative study based on their past experience in source testing. They were Engineering-Science, Inc., Entropy Envi-

ronmentalists, Inc., PEDCo Environmental, Inc., Radian Corporation, TRC-Environmental Consultants, Inc., and TRW-Environmental Engineering Division. Seven tablets representing two concentration levels were shipped to each of the six laboratories for analyses. Of the seven tablets, three were low concentration (60 mg SO_2) and four were high concentration (120 mg SO_2). The true concentrations of the tablets were based on theoretical concentrations calculated from gravimetric preparations and stoichiometric chemical reaction. A SO_2 generator (modified midget impinger), general instructions to perform the experiments, and a data sheet for reporting the results were also sent to each laboratory. Each laboratory was provided with the true concentration for one tablet and was asked to analyze the true concentration tablet first; if the measured value were within ± 10 percent, they were to analyze the remaining six tablets. The trial run was thought necessary because most laboratories had not used this method before. The laboratories were informed that these samples were not for an audit but were for an evaluation of the developed method. The types of compounds in the tablets were not disclosed.

Results and Discussion

The measured SO_2 concentrations from the preliminary Tedlar bag experiments and the corresponding expected concentrations from the stoichiometric chemical reaction are shown in Table 1. The results show that the percent difference obtained ranged from 20 to 25 percent low between the concentration of SO_2 measured and the expected SO_2 .

concentration from the stoichiometric reaction for various amounts of sodium bisulfite. The SO₂ generation was also found to be independent of flow rate (varied 0.1 to 1.4 L/min) and the amount of sulfuric acid. The sulfuric acid must be slightly in excess of the amount of sulfuric acid. The sulfuric acid must be slightly in excess of the amount actually required for completion of the reaction. The lower measured SO₂ concentrations were probably a result of the combination of loss of SO₂ in the bag plus loss of wet SO₂ on the glass system, but the actual reasons are not known nor were they determined. However, the percent difference was constant within experimental error for various amounts of sodium bisulfite.

The results obtained for different amounts of sodium bisulfite (ranging from 10 to 800 mg) using the described method are shown in Table 2. As the results indicate, the percent difference between the measured concentration and the expected concentration ranged from 2 to 7 percent; i.e., SO₂ recoveries obtained were between 93 and 98 percent. Lower SO₂ recoveries were obtained for small amounts of sodium bisulfite (10- to 40-mg range). Similar results were obtained for sodium sulfite. However, the SO₂ recoveries were found to be poor for sodium metabisulfite. Since ambient air was used to draw the sample from the generator, a blank run (without a tablet) was performed to test the ambient air. Analysis results showed a negligible amount of SO₂. The SO₂ generated from the material was found to be independent of flow rate and total volume of sample collection.

A study was also performed to determine the storage stability of the prepared tablets over a 6-month period at room temperature. The prepared tablets were analyzed periodically. The results of this study are shown in Table 3. These results demonstrate that the tablets are stable within experimental error over the 6-month period. The stability study is still in progress.

The results of the analyses of the samples by the different laboratories and the expected concentrations are shown in Table 4. The analysis results, in general, showed close agreement between the expected values. For example, results of analyses of the low concentration tablets ranged from -4 to +7 percent different from the expected value. Likewise, the results of analyses of the high concentration tablets ranged from -5 to +8 percent different from the expected

Table 1. Bag Results

Amount of NaHSO ₃ (mg)	Amount of SO ₂ expected ^a (ppm)	Amount of SO ₂ measured (ppm)	Percent difference ^b
102.6	650	507	-21.9
199.9	804	646	-19.7
200.5	863	660	-23.5
200.6	801	604	-24.5
202.9	869	676	-22.2
201.4	799	652	-18.4
207.5	1003	794	-20.8
202.3	842	712	-15.4
202.5	739	593	-19.8
401.9	944	721	-23.6

^aCalculated from stoichiometric chemical reaction.

^bPercent difference = $100 \times \frac{\text{Measured SO}_2 \text{ concentration} - \text{Expected SO}_2 \text{ concentration}}{\text{Expected SO}_2 \text{ concentration}}$

Table 2. Results of SO₂ Generated from the Prepared Tablets^{a, b}

Weight of NaHSO ₃ (mg)	Amount of SO ₂ expected (mg) ^c	Amount of SO ₂ measured (mg)	Percent difference ^d
12.9	7.9	5.2	-34.2
40.1	24.6	21.9	-11.0
50.6	31.1	31.3	+0.6
100.4	61.8	57.6	-6.8
101.6	62.5	61.5	-2.0
102.9	63.3	59.6	-5.8
202.9	124.9	120.3	-3.7
401.9	247.3	235.1	-2.0
802.3	493.7	464.4	-5.9
114.4 ^e	38.5	23.9	-37.9
204.3 ^f	103.8	105.1	+1.3

^aFlow rate 1 L/min for 45 minutes.

^b3 to 5 mL of 10 percent H₂SO₄ added.

^cCalculated from stoichiometric chemical reaction.

^dPercent difference = $100 \times \frac{\text{Amount of SO}_2 \text{ measured} - \text{Amount of SO}_2 \text{ expected}}{\text{Amount of SO}_2 \text{ expected}}$

^eSodium metabisulfite was used.

^fSodium sulfite was used.

Table 3. Stability Study Results

No. of days	Amount of SO ₂ expected (mg)	Amount of SO ₂ measured (mg)	Percent difference ^a
0	122.7	121.9	-0.65
15	123.1	125.5	+1.95
29	123.0	124.9	+1.54
48	123.2	126.8	+2.90
68	121.7	124.4	+2.20
94	122.1	126.5	+3.55
180	121.5	125.3	+3.13

^aPercent difference = $100 \times \frac{\text{Amount of SO}_2 \text{ measured} - \text{Amount of SO}_2 \text{ expected}}{\text{Amount of SO}_2 \text{ expected}}$

value. Two values reported from two laboratories were discarded during the statistical analysis because the laboratories identified problems during the SO₂ generation. Blank values reported by the laboratories were also negligible.

Conclusions

A new audit method that is simple and inexpensive was developed for evaluating both the sampling and analytical phases of EPA Method 6 in the field. The SO₂

generation was found to be quantitative and the recoveries were found to be 94 ± 5 percent over the 40- to 800-mg range of sodium bisulfite. The method was also evaluated at two concentration levels with six different laboratories to determine its repeatability, reproducibility, and bias. The interlaboratory results obtained showed close agreement with the expected concentrations based on calculation from the stoichiometric reaction. The repeatability within a laboratory was found to be within ± 5.0 mg 95 percent of the time for the two concentration levels tested. The reproducibility between laboratories was within ± 5.9 mg at the low range and ± 23.8 mg at the high range about 95 percent of the time. The maximum bias observed was 0.5 percent by comparison with the expected concentrations. The SO_2 generation from the material was found to be independent of flow rate and total volume, and the prepared tablets were stable at room temperature over a 6-month period. It is recommended that a performance audit using this new audit method for EPA Method 6 be used during future source SO_2 emissions analyses as a routine quality assurance procedure.

Table 4. Interlaboratory Results (mg)

	Known	Low			High		
		1	2	3	1	2	3
Lab 1							
RV	119.7	59.9	59.1	60.4	119.0	119.9	122.6
EV	121.8	60.3	60.4	60.3	122.2	122.3	122.1
Lab 2							
RV	126.5	64.5	61.5	57.9	129.4	128.0	131.7
EV	122.2	60.3	60.2	60.4	122.0	121.8	121.9
Lab 3							
RV	114.2	^a	58.2	58.1	118.7	115.8	115.6
EV	122.2	-	60.7	60.7	121.9	122.1	122.0
Lab 4							
RV	123.2	63.0	62.3	61.9	128.4	124.9	125.6
EV	122.7	60.5	60.4	60.5	122.4	122.6	122.5
Lab 5							
RV	116.1	60.1	60.7	62.0	116.7	119.6	120.5
EV	121.8	59.9	60.0	60.3	122.1	122.1	122.2
Lab 6							
RV	116	58.3	^a	60.2	117.0	118.0	118.0
EV	122.4	60.9	-	60.8	122.4	122.3	122.3

RV = Report value.

EV = Expected value.

^aValues discarded.

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The complete report, entitled "A New Audit Method for EPA Reference Method 6," (Order No. PB 84-172 097; Cost: \$8.50, subject to change) will be available only from:

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