THE APPLICATION OF EPA METHOD 6 TO HIGH SULFUR DIOXIDE CONCENTRATIONS

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THE APPLICATION OF EPA METHOD 6 TO HIGH SULFUR DIOXIDE CONCENTRATIONS

by

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SECTION I

INTRODUCTION

The Quality Assurance Branch (QAB), Environmental Monitoring and Support Laboratory, Environmental Research Center,.of the Environmental Protection Agency, Research Triangle Park, North Carolina is engaged in a program to evaluate methods, recommended and promulgated, for the measurement of pollutant emissions from stationary sources. The present investigation deals with an evaluation of EPA Method 6 -- a procedure for the determination of sulfur dioxide emissions from stationary sources.[1] The study also attempts to answer certain questions regarding the collection efficiency of the method and its usefulness at SO_2 concentrations higher than those previously employed.

Method 6 is applicable to the measurement of SO_2 emissions from fossil fuel fired steam generating units. The standard of performance[2] is expressed in terms of an allowable SO_2 emission per thermal unit (1.4 g/10[6] cal when liquid fuel is burned and 2.2 g/10[6] cal when fossil fuel is burned). This standard, depending upon the proportion of excess air, is equivalent to an SO_2 concentration in the 1000-1800 mg/m^{3} range. Method 6 has been subjected to ruggedness[4] testing and to precision and accuracy[5] studies over the 200-2000 mg/m^{3} concentration range. Results of these investigations establish that the method is accurate below 500 mg/m^{3} but indicate that it acquires a 5-10 percent negative bias below the true concentration, when SO_2 concentrations exceed 800 mg/m^{3}. The present investigation is concerned with the validity of the latter contention and with examination of features of the method that may contribute to inaccuracy. Further, it is desirable to have a method

that is accurate at higher SO_2 concentrations, as for example, in the analysis of Claus Sulfur Recovery plant effluents in which SO_2 concentrations exceed 3000 mg/m^3. This report therefore presents information obtained on the response of Method 6 at SO_2 concentrations up to 80,000 mg/m^3.

SECTION II

EXPERIMENTAL

Method 6 analytical and sampling procedures (described in Appendix I) were used with only minor modifications. The essential features of Method 6 rely upon the following sequence: a measured volume of gas is collected and passed through a filter to remove particulate; through a midget bubbler containing 80% isopropyl alcohol solution and glass wool to remove acid mist; and, finally, through two midget impingers containing 3% H_2O_2, which absorbs SO_2 gas and oxidizes it to H_2SO_4. The latter solutions are combined and analyzed for sulfate by the barium-thorin method. Two modifications to the sampling trains were made: inclusion of additional sulfur dioxide-absorbing impingers and separate analysis of the impingers. In some instances, when quantities of SO_2 were sampled that were sufficiently large to exhaust the H_2O_2 in an absorbing solution, additional H_2O_2 was added to determine the presence of unreacted sulfite. An H_2O_2 solution containing copious quantities of absorbed SO_2 was tested for the presence of peroxysulfates. This test was accomplished by boiling for 2 hours and comparing the solutions with an unboiled aliquot that had been measured immediately after sample collection. A similar test was carried out using reagent grade potassium peroxydisulfate ($K_2S_2O_8$) in dilute perchloric acid solution. A solution of iodimetrically measured sodium metabisulfite ($Na_2S_2O_5$) was subjected to barium-thorin analysis after addition of H_2O_2.

A 5270 mg/m^3 sulfur dioxide/nitrogen standard gas mixture was obtained from a commercial gas supplier; SO_2/air mixtures of 13,000, 63,900 and 79,900 mg/m^3 were prepared by QAB. The tanks were connected to a laboratory gas manifold by means of stainless steel tubing. A

T-joint afforded symmetrical sampling ports to which the sampling trains could be connected and duplicate samples withdrawn. The gases were used undiluted and the system was operated slightly above atmospheric pressure.

SECTION III

RESULTS AND DISCUSSION

The SO_2 concentrations of several bottled gas mixtures were analyzed and the results are compared with the values stated by the manufacturers. This comparison is illustrated in Table I. Both positive and negative deviations occurred. When a calibration gas was used (5,270 mg SO_2/m^3), the observed deviation was positive. Negative deviations were found when mixed gases prepared by QAB were employed. However, the latter tanks were not preconditioned nor analyzed by an independent means. The expected increase in negative bias with increasing SO_2 concentration based on a previous study[5], which described the method as accurate below 500 mg/m^3, but acquiring a negative bias above 800 mg/m^3, did not occur. See Table I.

Table II contains results of measurements which show the percent of the total SO_2 sampled which was collected in each impinger. The Table also includes values of the quantity of gas sampled as well as the SO_2 concentration. There is no evidence for a dependency of the measured SO_2 value on the quantity of gas sampled. Increasing the sampling flow rate from one to three 1/min did not produce an increase in the fraction of the SO_2 sample collected in the second H_2O_2 impinger. The 80% isopropyl alcohol bubbler retained only traces of SO_2. Nearly all of the sample was collected in the first H_2O_2 impinger. An exception occurred when large volumes of highly concentrated gas were sampled. In those instances, the use of additional impingers assured adequate sample collection efficiency.

Table 1. Comparison of Prepared Gas Mixtures with Values Obtained Using Method 6.

Prepared Conc. mg SO_2/m^3	Measured Conc. mg SO_2/m^3	Relative Deviation
5,270*	5,860	+11.2
13,300	12,300	-7.5
63,900	60,600	-5.2
79,900	75,900	-5.0

*Calibration gas mixture.

Table 2. Sulfur Dioxide Collection Efficiencies at Various Concentrations

Sample	Metered Volume liters	SO_2 Conc. mg/m^3	Measured Impinger Collection as Percent of Total Sample			
			IPA Bubbler	1st H_2O_2	2nd H_2O_2	3rd H_2O_2
1	8.2	5,740	NIL	100	NIL	NIL
2	11.1	6,050	NIL	100	NIL	NIL
3	20.3	5,800	NIL	99.4	0.6	NIL
4	61.4	5,810	NIL	97.3	2.6	0.04
5	20.7	12,300	0.05	99.4	0.5	NIL
6	21.2	60,050	0.02	67.9	31.9	0.17
7	20.8	61,150	0.06	72.3	27.5	0.18
8	5.6	76,500	0.06	99.3	0.6	NIL
9	8.3	77,400	NIL	98.9	1.1	0.01
10	11.1	74,700	0.05	99.1	0.9	NIL
11	20.5	76,000	0.001	57.5	42.3	0.2
12	35.4	74,800	0.001	33.1	33.0	32.2

[a]Gas samples were collected at a flow rate of one liter/min, except as noted.

[b]Gas sample collected at three liter/min.

[c]A fourth and fifth H_2O_2 impinger analyzed 1.6 and 0.1 percent, respectively.

A test was carried out to determine if unreacted SO_2 was present, after sample collection, in the absorbing solutions used in the Method 6 train. Particular attention was given to the 80% isopropyl alcohol bubbler that contained no added oxidant and in SO_2 absorbing solutions in which the H_2O_2 had been depleted. For this purpose, a quantity of H_2O_2 sufficient to raise the concentration by an additional 3% was added to aliquots of the absorbing solutions. The solutions were then analyzed for sulfate. Results were compared with measurements of identical aliquots that had received no additional quantity of H_2O_2. Table III shows the results of this comparison. Method 6 impingers contain approximately 14 millimoles of H_2O_2 which reacts with SO_2 on a mole-for-mole basis. Table III shows that the first impinger had its peroxide depleted, the second was partially depleted; relatively little of the peroxide in the third impinger was consumed. After readdition of peroxide, the quantity of sulfate detected in the first H_2O_2 impinger increased, but by less than 1%. Values corresponding to the other absorbing solutions actually decreased. However, those changes were also small and probably represent measurement variations. Thus, the results in Table III indicate that no unreacted SO_2 was detected by the experiment under consideration.

Table 3. Effect of Readdition of H_2O_2 to Method 6 Impingers after Sample Collection

Impinger	SO₂ Collected Per Impinger[a] millimoles	
	With Addition	Without Addition
IPA Bubbler	0.0123	0.0124
1st H_2O_2	14.42	14.37
2nd H_2O_2	5.37	5.46
3rd H_2O_2	0.0282	0.0288

[a]After collecting 20.82 std. liters of gas containing 60,600 mg SO_2/m^3.

A test was also made to determine if peroxysulfates were produced during sample collection. Previous stoichiometric measurements have shown that the primary oxidation product in the SO_2/H_2O_2 reaction is sulfate and that infinitesimal amounts of other substances were formed.[8] However, peroxy-compounds have been postulated to be intermediates in the reaction between bisulfite ion and H_2O_2. Since these compounds are insensitive to barium-thorin analysis, the conversion of SO_2 to these species would result in erroneously low measurements. Above 90°C, aqueous solutions of peroxysulfates are rapidly decomposed to sulfates. Therefore, the following test was made to determine if peroxysulfates were formed under the conditions of the present study. Sulfur dioxide was collected in a 3% H_2O_2 solution. An aliquot of the freshly prepared solution was analyzed by the barium-thorin method; another aliquot was measured after boiling for three hours. A comparison was made with a quantity of $K_2S_2O_8$ in dilute $HClO_4$ solution that had received similar treatment. The result, listed in Table IV, was only a negligible change in the sulfate concentration after boiling. It must therefore be con-cluded that no significant quantity of peroxysulfates had been present.

A further test for the efficiency of conversion of sulfur(IV) to sulfur(VI) by 3% H_2O_2 solution was carried out as follows: A solution of $Na_2S_2O_5$ was made 3% in H_2O_2 and 0.015N in $HClO_4$ and analyzed by the barium-thorin method. The results were compared with an iodimetric analysis. The iodimetric and barium-thorin analyses yielded 441 and 454 micrograms of SO_2/ml, respectively.

Table 4. Test for the Presence of Peroxysulfates in 3% H_2O_2 Solution after Sulfur Dioxide Collection

Solution	$SO_4^=$ Detected Millimoles
SO_2 in 3% H_2O_2, freshly prepared	3.964
SO_2 in 3% H_2O_2, after boiling	3.993
$K_2S_2O_8$ in 3% H_2O_2, freshly prepared	--
$K_2S_2O_8$ in 3% H_2O_2, after boiling	0.214

[a]After collecting 20.82 std. liters of gas containing 12,300 mg SO_2/m^3 in air.

[b]In 15 ml of solution.

[c]25 ml of 3% H_2O_2 solution, containing 0.004619 M $K_2S_2O_8$ and 0.012 M $HClO_4$.

SECTION IV

CONCLUSIONS

A previous report[5] indicating that Method 6 suffers from a negative bias below the true value when measuring SO_2 concentrations greater than 2000 mg/m^3 was not confirmed by the present study. Measurements made using a calibration gas and other prepared gas mixtures in the 5000 to 80,000 mg SO_2/m^3 concentration range did not produce consistently low results. Analysis of individual impingers in multiple impinger trains showed that more than 99% of the SO_2 under analysis was collected in the first two impingers, except when sufficient sample was collected to deplete the H_2O_2 in the absorbing solutions, or when excessively high flow rates were used. Tests also showed the absence of SO_2 retention in the isopropyl alcohol bubbler, absence of unreacted SO_2 in the peroxide absorbing solutions and absence of peroxysulfates. Further, analysis of a standardized bisulfite solution yielded results consistent with an iodimetric analysis. From the above considerations and earlier studies,[5] it must be concluded that Method 6 is efficient for the measurement of gaseous SO_2 in the 200 to 80,000 mg/m^3 concentration range, provided that a sample flow rate of about 1 liter/min is maintained and a maximum volume of about 20 liters of gas is sampled at the higher concentration.

SECTION V

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APPENDIX

METHOD 6 -- DETERMINATION OF SULFUR DIOXIDE

EMISSIONS FROM STATIONARY SOURCES

PLANT _____

DATE _____

RUN NO. _____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL	✕	✕	

	VOLUME OF LIQUID WATER COLLECTED	
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g
FINAL		
INITIAL		
LIQUID COLLECTED		
TOTAL VOLUME COLLECTED		g* ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER. (1 g. ml):

$$\frac{\text{INCREASE, g}}{(1 \text{ g/ml})} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

6.6.2 Concentration in lb./cu. ft.

$$c_s = \frac{\left(\frac{1}{453,600}\frac{\text{lb.}}{\text{mg}}\right) M_n}{V_{m\,std}} = 2.205 \times 10^{-3} \frac{M_n}{V_{m\,std}}$$ equation 5-5

where:
c_s = Concentration of particulate matter in stack gas, lb./s.c.f., dry basis.
453,600 = Mg. lb.

M_n = Total amount of particulate matter collected, mg.
$V_{m\,std}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

6.7 Isokinetic variation.

$$I = \frac{T_s\left[\frac{V_{lc}(\rho_{H_2O})R}{M_{H_2O}} + \frac{V_m}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n} \times 100$$

$$= \frac{\left(1.667\frac{\text{min.}}{\text{sec.}}\right)\left[\left(0.00267\frac{\text{in. Hg-cu. ft.}}{\text{ml.-R}}\right)V_{lc} + \frac{V_m}{T_m}\left(P_s + \frac{\Delta H}{13.6}\right)\right]T_s}{\theta V_s P_s A_n}$$

     Equation 5-6

where:
I = Percent of isokinetic sampling.
V_{lc} = Total volume of liquid collected in impingers and silica gel (See Fig. 5-3), ml.
ρ_{H_2O} = Density of water, 1 g. ml.
R = Ideal gas constant, 21.83 inches Hg-cu. ft. lb. mole °R.
M_{H_2O} = Molecular weight of water, 18 lb./lb.-mole.
V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.
T_m = Absolute average dry gas meter temperature (see Figure 5-2), °R.
P_{bar} = Barometric pressure at sampling site, inches Hg.
ΔH = Average pressure drop across the orifice (see Fig. 5-2), inches H$_2$O.
T_s = Absolute average stack gas temperature (see Fig. 5-2), °R.
θ = Total sampling time, min.
V_s = Stack gas velocity calculated by Method 2, Equation 2-2, ft./sec.
P_s = Absolute stack gas pressure, inches Hg.
A_n = Cross-sectional area of nozzle, sq. ft.

6.8 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:

If $90\% \leq I \leq 110\%$, the results are acceptable; otherwise, reject the results and repeat the test.

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Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, 1967.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and applicability.
1.1 Principle. A gas sample is extracted from the sampling point in the stack. The acid mist, including sulfur trioxide, is separated from the sulfur dioxide. The sulfur dioxide fraction is measured by the barium-thorin titration method.
1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. Apparatus.
2.1 Sampling. See Figure 6-1.
2.1.1 Probe—Pyrex[1] glass, approximately 5 to 6 mm. ID, with a heating system to prevent condensation and a filtering medium to remove particulate matter including sulfuric acid mist.
2.1.2 Midget bubbler—One, with glass wool packed in top to prevent sulfuric acid mist carryover.
2.1.3 Glass wool.
2.1.4 Midget impingers—Three.
2.1.5 Drying tube—Packed with 6 to 16 mesh indicating-type silica gel, or equivalent, to dry the sample.
2.1.6 Valve—Needle valve, or equivalent, to adjust flow rate.
2.1.7 Pump—Leak-free, vacuum type.
2.1.8 Rate meter—Rotameter or equivalent, to measure a 0–10 s.c.f.h. flow range.
2.1.9 Dry gas meter—Sufficiently accurate to measure the sample volume within 1%.
2.1.10 Pitot tube—Type S, or equivalent.

[1] Trade names.

necessary only if a sample traverse is required, or if stack gas velocity varies with time.
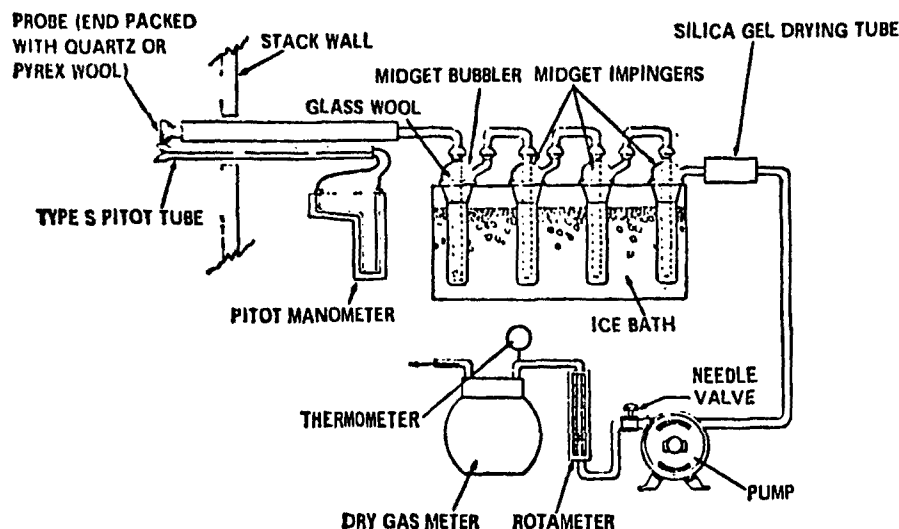
2.2 Sample recovery.

Figure 6-1. SO₂ sampling train.

2.2.1 Glass wash bottles—Two.
2.2.2 Polyethylene storage bottles—To store impinger samples.
2.3 Analysis.

2.3.1 Pipettes—Transfer type, 5 ml. and 10 ml. sizes (0.1 ml. divisions) and 25 ml. size (0.2 ml. divisions).
2.3.2 Volumetric flasks—50 ml., 100 ml., and 1,000 ml.
2.3.3 Burettes—5 ml. and 50 ml.
2.3.4 Erlenmeyer flask—125 ml.
3. Reagents.
3.1 Sampling.
3.1.1 Water—Deionized, distilled.
3.1.2 Isopropanol, 80%—Mix 80 ml. of isopropanol with 20 ml. of distilled water.
3.1.3 Hydrogen peroxide, 3%—dilute 100 ml. of 30% hydrogen peroxide to 1 liter with distilled water. Prepare fresh daily.
3.2 Sample recovery.
3.2.1 Water—Deionized, distilled.
3.2.2 Isopropanol, 80%.
3.3 Analysis.
3.3.1 Water—Deionized, distilled.
3.3.2 Isopropanol.
3.3.3 Thorin indicator—1-(o-arsonophen-ylazo)-2-naphthol-3,6-disulfonic acid, disodium salt (or equivalent). Dissolve 0.20 g. in 100 ml. distilled water.
3.3.4 Barium perchlorate (0.01 N)—Dissolve 1.95 g. of barium perchlorate [Ba(ClO₄)₂·3H₂O] in 200 ml. distilled water and dilute to 1 liter with isopropanol. Standardize with sulfuric acid. Barium chloride may be used.
3.3.5 Sulfuric acid standard (0.01 N)—Purchase or standardize to ±0.0002 N against 0.01N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).
4. Procedure.
4.1 Sampling.
4.1.1 Preparation of collection train. Pour 15 ml. of 80% isopropanol into the midget bubbler and 15 ml. of 3% hydrogen peroxide into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6-1. Leak check the sampling train at the sampling site by plugging the probe inlet and pulling a 10 inches Hg vacuum. A leakage rate not in excess of 1% of the sampling rate is acceptable. Carefully release the probe inlet plug and turn off the pump. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 70° F. or less.
4.1.2 Sample collection. Adjust the sample flow rate proportional to the stack gas

velocity. Take readings at least every five minutes and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the tip of the probe at the first sampling point and start the pump. Sample proportionally throughout the run. At the conclusion of each run, turn off the pump and record the final readings. Remove the probe from the stack and disconnect it from the train. Drain the ice bath and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes.
4.2 Sample recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a polyethylene shipment bottle. Rinse the three midget impingers and the connecting tubes with distilled water and add these washings to the same storage container.
4.3 Sample analysis. Transfer the contents of the storage container to a 50 ml. volumetric flask. Dilute to the mark with deionized, distilled water. Pipette a 10 ml. aliquot of this solution into a 125 ml. Erlenmeyer flask. Add 40 ml. of isopropanol and two to four drops of thorin indicator. Titrate to a pink endpoint using 0.01 N barium perchlorate. Run a blank with each series of samples.
5. Calibration.
5.1 Use standard methods and equipment

which have been approved by the Administrator to calibrate the rotameter, pitot tube, dry gas meter, and probe heater.
5.2 Standardize the barium perchlorate against 25 ml. of standard sulfuric acid containing 100 ml. of isopropanol.
6. Calculations.
6.1 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F. and 29.92 inches Hg) by using equation 6-1.

$$V_{m_{std}} = V_m \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right) =$$

$$17.71 \frac{°R}{in.\ Hg}\left(\frac{V_m P_{bar}}{T_m}\right) \qquad \text{equation 6-1}$$

where:

$V_{m_{std}}$ — Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m — Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} — Absolute temperature at standard conditions, 530° R.

T_m — Average dry gas meter temperature, °R.

P_{bar} — Barometric pressure at the orifice meter, inches Hg.

P_{std} — Absolute pressure at standard conditions, 29.92 inches Hg.

6.2 Sulfur dioxide concentration.

$$C_{SO_2} = \left(7.05 \times 10^{-5} \frac{lb.-l.}{g.-ml.}\right) \frac{(V_t - V_{tb})N\left(\frac{V_{soln}}{V_a}\right)}{V_{m_{std}}} \qquad \text{equation 6-2}$$

where:

C_{SO_2} — Concentration of sulfur dioxide at standard conditions, dry basis, lb./cu. ft.

7.05×10^{-5} — Conversion factor, including the number of grams per gram equivalent of sulfur dioxide (32 g./g.-eq.), 453.6 g./lb., and 1,000 ml./l., lb.-l./g.-ml.

V_t — Volume of barium perchlorate titrant used for the sample, ml.

V_{tb} — Volume of barium perchlorate titrant used for the blank, ml.

N — Normality of barium perchlorate titrant, g.-eq./l.

V_{soln} — Total solution volume of sulfur dioxide, 50 ml.

V_a — Volume of sample aliquot titrated, ml.

$V_{m_{std}}$ — Volume of gas sample through the dry gas meter (standard conditions), cu. ft., see Equation 6-1.

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METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and applicability.
1.1 Principle. A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION•NO.

4. TITLE AND SUBTITLE	5. REPORT DATE
THE APPLICATION OF EPA METHOD 6 TO HIGH SULFUR DIOXIDE CONCENTRATIONS	
	6. PERFORMING ORGANIZATION CODE

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Environmental Monitoring and Support Laboratory	Final
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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The application of EPA test method (M-6) to the analysis of higher sulfur dioxide concentrations than had previously been employed has been studied. The use of prepared gas mixtures showed that the method is efficient for the measurement of gaseous sulfur dioxide in concentrations of up to 80,000 mg/m . The investigation also showed no evidence of retention of significant quantities of sulfur dioxide in the isopropyl alcohol bubbler or of the production of sulfur compounds that are in-sensitive to barium-thorin analysis. When multiple impinger trains were employed, analysis of individual impinger contents showed that more than 99% of the sampled sulfur dioxide was collected in the first two impingers, even at the higher concentration, except when sufficient sample was collected to deplete the hydrogen peroxide in the absorbing solutions or when excessively high flow rates were used. These results contradict earlier reports that Method 6 suffers from a negative bias at high sulfur dioxide concentrations.

17.	KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sampling Sulfur dioxide Air pollution Stack gases			13B

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