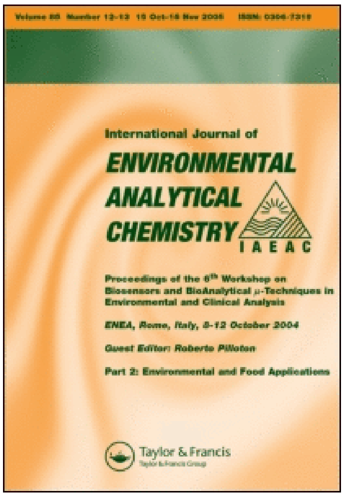

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The Determination of Sulfur Oxides in Flue Gases by the Barium Chloranilate-Controlled Condensation Method

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KEY WORDS Sulfur oxides, flue gases, condensation method.

An improved method for the determination of sulfur oxides is described which incorporates the optimization of collection and analysis methods and the design of a simple compact gas sampling train. SO_3 and SO_2 are collected by controlled condensation and by adsorption in aqueous peroxide, respectively. Sulfate analyses are performed by a modified barium chloranilate colorimetric procedure. The effect of parameters such as temperature, flow rate and concentration were investigated for SO_2 absorption in peroxide. The method was evaluated versus the Environmental Protection Agency sulfur oxides technique at a coal-fired power plant. The agreement between the SO_2 methods was good, with a correlation coefficient of 0.73, and the regression equation given by:

$$\text{ppm SO}_2\text{ (barium chloranilate)} = +0.90\text{ ppm SO}_2\text{ (barium ion)} +30.0.$$

INTRODUCTION

Wet chemical methods for the determination of sulfur oxides in stack gases provide standards for compliance testing and instrument calibration.

Analytical methods for the sulfur oxides which include barium ion[1-3] and sodium hydroxide titrations,[4] colorimetry,[5] turbidimetry,[6] and precipitation reactions[7,8] have all been reported. *The most widely used techniques* *for analysis of sulfur oxides are variants of the barium ion-thorin titration.* [1-3,9,10] This procedure has been adopted by the Environmental Protection Agency for the determination of SO_2 in flue gases.[11] The major disadvantage of this method is the indistinct color change associated with the endpoint.[12] In an effort to eliminate this problem, substituted naphthalene derivatives[13,14] have been employed in place of thorin. These indicators are, however, not completely satisfactory.[12,15]

The barium chloranilate method appears to be a reasonable substitute for the barium ion titration since the judgment error (of the titration) is eliminated by spectrophotometry. This colorimetric method has been used for sulfate in water,[16] sulfur in naphthas,[17] etc. The analysis is based upon the reaction of sulfate ion with barium chloranilate in a pH-controlled, 50% alcohol solution to yield the highly colored acid chloranilate. The concentration of the product species is determined spectrophotometrically at 530 nm. This method is applicable to the determination of SO_3 and SO_2 at concentrations up to 360 μg of sulfate per ml of final solution (higher concentrations can be determined by aliquot dilution). A solution containing 20 μg of sulfate ion per ml of solution will have an absorbance approximately twice that of the blank, using a 1-cm cell. To determine SO_3 at the 10-ppm level, a minimum gas sample of 25 l is required.

Collection techniques used for the sulfur oxides have been evaluated in detail in previous publications.[12,15] In general, the methods involve physical separation of the sulfur oxides in collectors during sampling. Statistical analysis of field test data[18] was used to select the best collection techniques for SO_2 and SO_3. The collection methods which provided the best "apparent" precision and accuracy were the controlled condensation and absorption in dilute aqueous peroxide for SO_3 and SO_2, respectively.[12,18]

Sulfur trioxide is condensed as sulfuric acid by controlled cooling of the flue gas. The resulting sulfuric acid aerosol is collected on a glass frit which is maintained at a temperature *above the water dewpoint.* This minimizes oxidation of dissolved sulfur dioxide (in aqueous solution), and provides improved precision and accuracy in SO_3 collection. Sulfur dioxide is collected in midget impingers (in series with the SO_3 collector) and oxidized to sulfuric acid by the aqueous 3% hydrogen peroxide absorbing solution.

In the following sections, we discuss the sampling train, collection efficiency studies, modifications of the analytical methods, and the test data obtained.

EXPERIMENTAL

Apparatus

After addition of solid barium chloranilate, the samples were shaken on a Burrell wrist-action shaker, centrifuged (2800–3000 ppm) with an Adams clinical centrifuge, and the absorbance was measured with a Beckman Model DU spectrophotometer.

To determine the collection efficiencies of SO_2 in aqueous hydrogen peroxide, a glass and Teflon dilution system was constructed. Reproducible concentrations of SO_2 could be prepared from 200 to 5000 ppm. A spirometer was used for the calibration of the air flow meters and critical orifices. The low flow rates of the SO_2 flow meter were determined with a 50-ml soap film buret.

Reagents

ACS-grade chemicals were used without further purification. Sulfate-free distilled water was prepared by passing distilled water through a column of Amberlite MB-3 resin. The cation exchange resin was prepared by washing sequentially with 1N HCl, 1N NaOH, methanol, and finally, once again with HCl. The barium chloranilate (solid) was purchased from Fisher Scientific Co.

Sampling train

A modular flue gas sampling apparatus for collection of SO_3 by the controlled condensation and collection of SO_2 by absorption in aqueous peroxide contained in midget impingers was employed.

The probe was constructed of a six-foot length of Pyrex tubing with a 12/5 socket joint on the downstream end. The stack end of the probe was fitted with a 3.8-cm diameter by 4-cm length of Pyrex tube and loosely packed with quartz wool for particulate filtration. The glass probe was encased in a 1″ stainless steel shell with stack adapter assembly which allowed various probe insertion depths. The glass probe was wrapped with 20-gauge asbestos-covered wire for heating of the glass insert above the acid dewpoint. For combustion flue gases (< 30 ppm SO_3) a probe heated to a temperature of $\sim$ 150°C is sufficient to prevent condensation of sulfuric acid mist. For stack temperatures higher than 800°F, vycor or quartz inserts should be used in place of Pyrex.

The condenser (Figure 1) was constructed of a pyrex glass coil with a medium porosity sintered glass frit at the downstream end. The upstream end of the condenser assembly terminates in a 12/5 ball joint which mates with the probe. The downstream ball joint mates with the socket joint in the SO_2 impinger (Figure 2). This design was somewhat different than that of Goksoyr and Ross.[4] The condenser temperature can be varied by adjustment of the temperature controller. The condenser was immersed in an electrically heated, thermostatted (Fenwal controller) copper water jacket. An operating temperature of $\sim$ 70°C was selected to provide operation at (water) dewpoints up to 60°C.

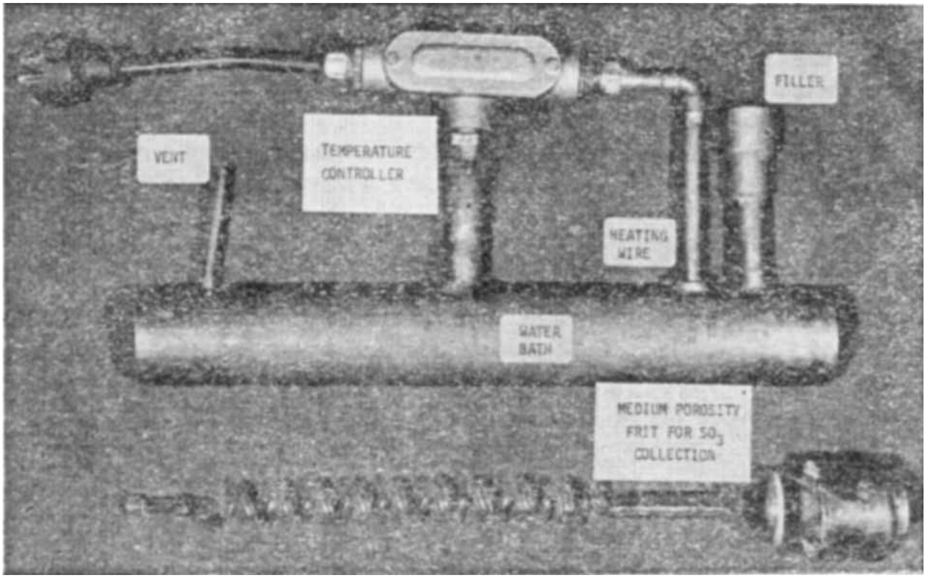

FIGURE 1 Walden prototype SO_3 condenser.

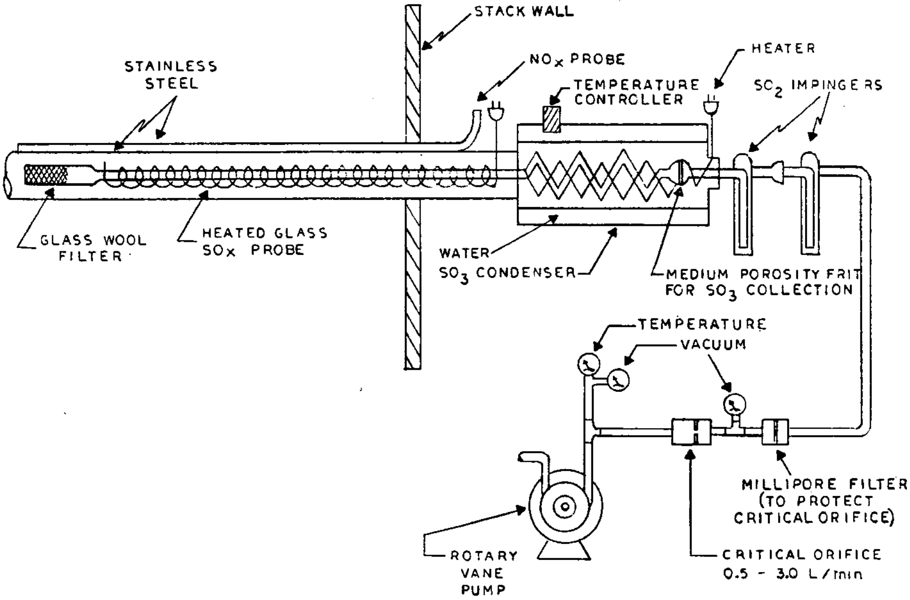

FIGURE 2 SO_x sampling train assembly.

A critical orifice (Millipore 0.5, 1.0, or 3.0 l/min) was used with vacuum gauges provided upstream *and* downstream to monitor the critical flow condition, $\Delta P > \sim 15$ in. Hg. The orifice was equipped with a Millipore filter upstream to prevent plugging and a dial thermometer for determining gas volume corrections. A Gast rotary carbon vane pump (Model 1531) was used as the suction source. Figure 3 is a photograph of the control module. Schematics of the sampling train are shown in detail in Figures 2 and 4.

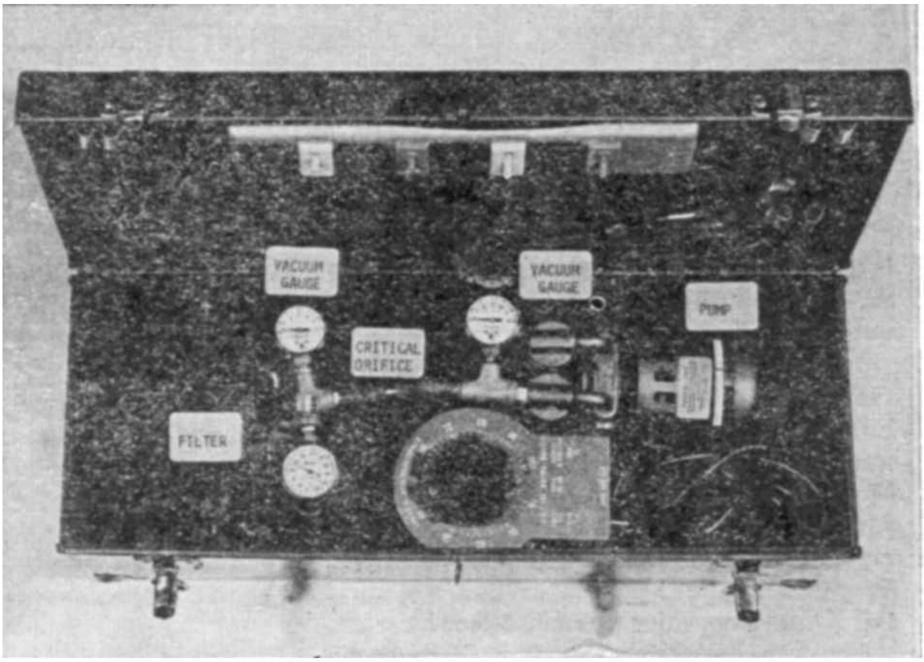

FIGURE 3 Walden prototype sampling system.

RESULTS AND DISCUSSION

Collection efficiencies

Collection efficiencies were determined by adding SO_2 to the glass and Teflon dilution system described previously. The SO_2 was collected in two midget impingers, in series, containing 15 ml of freshly prepared 3% hydrogen peroxide solution. Total sample volumes, which were metered by a calibrated critical orifice, ranged from 15 to 30 l. Sulfate analyses were performed by the barium chloranilate colorimetric method.

For high efficiency scrubbers (> 90%), the collection efficiency may be determined by analysis of both impingers to obtain the fraction collected

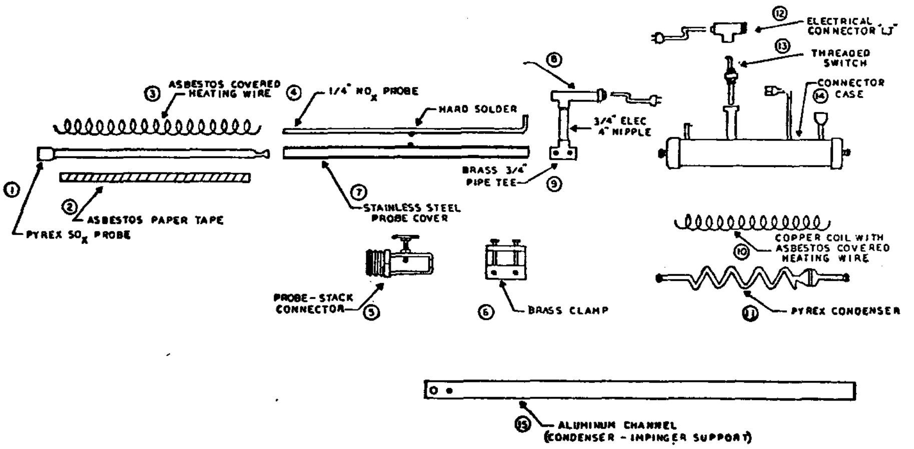

FIGURE 4 Detailed schematic of SO_x–NO_x sampling probe and condenser.

in the first, independent of source description. For a given collection medium, the collection efficiency may be assumed to be a function of SO_2 concentration, total flow rate, temperature and device geometry (pressure, except as influenced by flow pressure drop, constant).

To investigate possible variability between impingers, five consecutive runs were conducted at constant flow rate, temperature, and SO_2 concentration with five different midget impingers of identical design. The results showed that the collection efficiency was not a strong function of impinger parameters. The standard deviation of the collection efficiency determined experimentally for the five different impingers was $\pm$ 2% which is the same as the precision of the analytical method. Any variation between impingers for this limited population was not detectable.

The collection efficiency has been determined as a function of flow rate at two levels of SO_2 concentration. The observed collection efficiencies (calculated from the fraction collected in the first of two series impingers) are given in Table I as a function of flow rate. At 875 ppm, the decrease in collection efficiency with increasing flow rate, although apparent, is sufficiently gradual so that essentially quantitative (99%) collection efficiency is maintained to flow rates of 5 l/min *for two impingers in series*. At the higher concentration, 1740 ppm, collection efficiency drops more rapidly (at rates above 1.5 l/min) so that the 99% collection efficiency limit for two series impingers occurs at about 3 l/min. Blowover of peroxide solution was observed at flow rates greater than 3 l/min, leading to possible loss of sample.

The collection efficiencies of single impingers were also determined at 39°C and found to be somewhat better at the higher temperature (98% for both 875 and 1740 ppm SO_2) than at 22°C.

TABLE I

Collection efficiency of midget impingers for SO_2 in peroxide[a]

Number of Replicate runs	Flow rate (l/min)	SO_2 (ppm)		Total SO_2 (ppm)	Efficiency $100\times\#1/(\#1+\#2)$
		1st impinger	2nd impinger		
5	0.5	853	37	890	96
3	1.5	831	40	871	95
3	3.0	794	65	859	92
3	5.0	774	80	854	91
3	1.5	1640	70	1710	96
2	3.0	1525	150	1675	90
3	5.0	1420	230	1650	86

[a] T = 22°C; 15 ml 3% H_2O_2.

It is concluded that the collection efficiency is not a very strong function of either sample flow rate or SO_2 concentration. The recommended flow rate for quantitative collection of SO_2 in two impingers containing aqueous hydrogen peroxide is 0.5 to 3.0 l/min.

Optimization of the analytical method

The barium chloranilate method for the determination of sulfate in aqueous solution has been studied by a number of investigators. The method has been run at pH 1.8,[19], 4.0,[16] 4.6,[17] and 5.2.[5] Kanno *et al.*[5] demonstrated the need for good pH control which results from a dependence of the absorbance on pH (up to pH 5.2). Our experiments confirm that absorbance independence of pH is achieved at pH 5.4 at a sacrifice of approx. 10% in sensitivity (Figure 5a). All further tests were run using pH 5.6 buffer.

The buffer capacity of the pH 5.6 sodium acetate-acetic acid buffer was determined by diluting known concentrations of sulfuric acid to a fixed volume of 20 ml, adding 5 ml of pH 5.6 buffer or distilled water and measuring the pH of the solutions. The data are given in Figure 5b. Even with the buffer added, strong sulfuric acid solutions are beyond the buffer capacity of the sodium acetate-acetic acid buffer. This points out the need for a good control of pH. Since stack gas samples involve collection of at least 15 or 20 l containing approx. 1000 ppm SO_2, the pH of the peroxide solution is about 1. Therefore, the pH must be adjusted to about pH 5 by the technique of Kanno *et al.*[5] prior to the addition of the buffer.

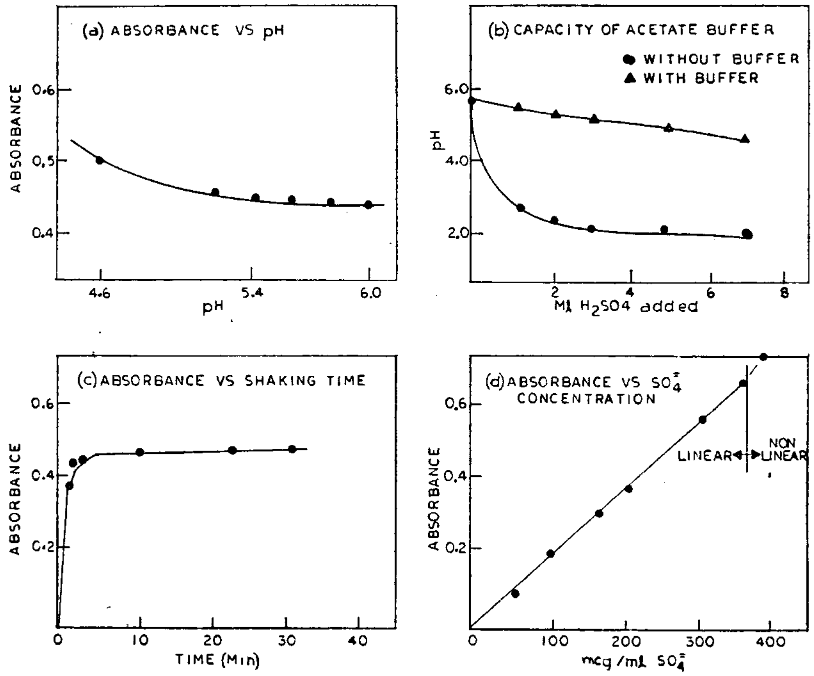

FIGURE 5 Effect of various parameters in the barium chloranilate method.

Centrifugation, rather than filtration, for removing unreacted barium chloranilate and precipitated barium sulfate appeared to improve the stability and lowered the absorbance of the blank to about 0.01 to 0.02 units. Another change in our method involved using a Burrell wrist-action shaker instead of hand-shaking. This did not improve the stability of the method but it did help (with the centrifuging) to reduce the analysis time of multiple samples to an average of 5 min per sample.

Experiments were performed to establish the minimum mixing time needed for color development to reach a plateau as a function of time with all experiments at room temperature. All solutions contained 5 ml of potassium sulfate solution (2500 mcg per ml), 5 ml of pH 5.6 buffer, 15 ml of sulfate-free water, 25 ml of ethanol, and 0.2 g of barium chloranilate. The solutions (except for the 0 and the 1-min samples) were shaken on a Burrell wrist-action shaker at the maximum rate obtainable. The 0-min solution was simply swirled several times, then centrifuged. The 1-min solution was hand-shaken for 1 min at approximately the same rate as the solutions on the shaker. The results are shown in Figure 5c. A 20-min mixing time was selected; however, the data indicate no apparent change after 10 minutes.

Several experiments established that hand-shaking a solution for 20 min using a pattern of shaking vigorously 10 times and then letting the solution stand for 2 min before repeating was sufficient to reproduce the absorbance observed by use of the wrist-action shaker. This allowed the freedom to shake solutions by hand in constant-temperature baths to determine the effect of temperature on color development. Solutions were prepared as given previously and were hand-shaken for 20 min. Six samples were hand-shaken in constant-temperature baths, three each at 20°C and at 30°C. Measured absorbances were 0.449, 0.450, 0.452 at 20°C and 0.460, 0.460, and 0.459 at 30°C. The change on reaching room temperature was 0.002–0.003 for those initially at 20°C and 0.003 for those initially at 30°C. Thus, no temperature correction appears necessary if the samples and calibration curve solutions are mixed at a temperature differential of 5°C or less.

Three samples were measured initially, and at 1 hr after centrifugation. The data showed no detectable change in the absorbance. Thus, color stability seems reasonably constant for at least a 1-hr period after centrifuging.

Solutions containing 25 to 500 μg/ml of sulfate ion were prepared from a stock solution of K_2SO_4. The absorbance of the solutions is plotted as a function of concentration in Figure 5d. This plot indicates, as found previously,[16] that the absorbance is linear up to about 350 μg/ml of sulfate ion.

Solutions of potential anionic interferences (NO_3^-, Cl^-, HCO_3^- and $PO_4^{\equiv}$) were prepared at 0.2M, 0.1M (1% in case of H_2O_2) and added to 250 μg/ml $SO_4^=$. The data showed that only phosphate had a greater than 5% interference. Phosphate ions, however, are not present to any large extent in combustion effluent. Cationic species such as Na^+, K^+ or Mg^{++} do not interfere, but Cu^{++}, Zn^{++} and Ca^{++} present a major problem.[16] Cationic species can usually be removed by ion exchange; however, the peroxide which is used as the SO_2 collection medium presents a considerable problem.

PROCEDURE

Sample collection

The probe is fitted to the stack flue. Power cords are connected between the SO_x probe heater and the variable transformer. The probe is then heated to the operating temperature of 160°C. The SO_3 condenser is electrically connected to the power control panel. The condenser heater is switched on and allowed to come to operating temperature (~ 70°C). The SO_2 impingers are charged with 15 ml of a 3% peroxide solution. After the probe and SO_3 condenser have reached their respective operating temperatures, the collector module is assembled as shown in Figure 4. The pump is connected to the second peroxide impinger with a vacuum hose and started from the switch on the control module. The time is recorded. The operator checks the ΔP

across the critical orifice selected (0.5, 1.0, 3.0 l/min) and records the pressure and temperature values (at 5-min intervals) during sampling. The stack gas temperature and moisture content as well as CO_2 and O_2 can also be determined at this time. At the end of the 20 to 30-min sampling period, the pump is switched off and the time is recorded. The sample module is disassembled, the SO_3 collector is rinsed† with several portions of isopropanol and the sample) is collected in a polyethylene bottle. Clean air (or ambient air passed through a column of 10–12 mesh activated charcoal) is drawn through the collector for a short period of time. Now the system is ready to be recycled. Transfer the contents of the two midget impingers (which contain the SO_2 sample) into a polyethylene bottle. Rinse the impingers several times with sulfate-free distilled water and add these washings to the contents of the polyethylene bottle. After the impingers are charged with 15 ml of 3% hydrogen peroxide, the system is ready for collection of additional samples.

LABORATORY PROCEDURE

Standardization

0.025*M* H_2SO_4 Heat approx. 3 g of analytical-reagent-grade anhydrous sodium carbonate for 4 hr at 250°C to decompose any residual bicarbonate and to remove water. Cool in a dessicator. Accurately weigh 0.115±0.005 g of the dried sodium carbonate into each of three 250-ml Erlenmeyer flasks and dissolve the samples in 50 ml of deionized water. Add two drops of 0.1% methyl orange and titrate with the 0.025M H_2SO_4 in a 50-ml buret to a color change from yellow to red-orange. A blank of 50 ml deionized water plus indicator should be determined with each set of titrations.

The normality of the 0.025M H_2SO_4 solution is calculated as follows:

$$N = \frac{\text{Wt. of } Na_2CO_3(g)}{(A-B)(0.0530)}$$

where

A = ml of titrant needed to reach the endpoint

B = ml of titrant needed for the blank.

Absorbance A standard curve is prepared by pipetting 0.5, 1, 2, 5, and 10 ml of 0.025M H_2SO_4 into 50-ml volumetric flasks. Add water to the first four to bring all volumes up to about 10 ml. Add one drop of phenolphthalein solution, then add 1N NaOH dropwise until a pink color appears. Add 1N HCl dropwise until the pink color disappears. (This will usually require

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† The isopropanol can be forced through the frit by applying a slight pressure from a squeeze bulb attached to a 12/5 ball joint.

just one drop.) Pipet 5 ml of pH 5.6 buffer into each flask. Pipet 25 ml of isopropanol into each flask. Mix well, then bring to the mark with water, stopper, and again mix well. Pour the contents of each flask into a corresponding 125-ml screw-top shaker flask containing 0.2–0.3 g of barium chloranilate. Shake for 20 min on a wrist-action shaker, then centrifuge 10–15 ml of this suspension for 5 min at 2800–3000 rpm. Decant the centrifugate into 1-cm cells and read the absorbance versus water at 530 nm. The blank (no sulfate) versus water should read no more than 0.01 to 0.03 absorbance units. Plot the absorbance versus sulfate concentration in μg/ml final solution.

Analysis for sulfur oxides

Quantitatively transfer the samples collected to a 50-ml volumetric flask (25-ml volumetric flask for SO_3). Pipet a suitable sized aliquot into a 50-ml volumetric flask (25-ml volumetric flask for SO_3). Add one drop of phenolphthalein solution to the flask, then add NaOH dropwise until the solution just turns pink. Add one drop of 1N HCl to return the solution to colorless. Pipet in 5 ml of pH 5.6 buffer (2.5 ml for SO_3 analysis), then add 25 ml isopropanol (12.5 ml for SO_3 analysis) and mix well. Dilute to the mark with deionized water. Pour contents into a 125-ml screw-top shaker flask containing 0.2–0.3 g of barium chloranilate. Shake for 20 min on a wrist-action shaker. Centrifuge 15 ml of the solution at 2800–3000 rpm for 6 min, decant the solution into 1-cm cells, then read the solution absorbance versus a water blank at 530 nm.

CALCULATIONS

The concentration of SO_x by volume is calculated as follows:

$$\text{ppm } SO_2(SO_3) = \frac{(A)\,(S)\,(50)^{\ddagger}(24.1)(50/X)^{\ddagger}}{96\,V_s}$$

where

X = volume of sample analyzed

A = absorbance of sample less absorbance of blank

S = slope of calibration curve (μg/ml/Abs unit)

V_s = sample gas volume (STP) = (Sampling rate of orifice converted to STP × time)

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‡ For SO_3 analysis use 25 and 25/X, respectively.

TEST RESULTS

In order to validate this method, samples of sulfur oxides were collected from the effluent of a coal-fired power plant. The SO_2 (peroxide) samples were split into two portions. One was analyzed in duplicate by the barium ion titration[11] and the other portion was analyzed in duplicate by the barium chloranilate procedure described in the previous section. The results are given in Table II. The agreement between the two methods for SO_2 is quite good. The correlation coefficient between the two methods is 0.73. The regression equation is ppm SO_2 (Ba Chlor) = $+30.0+0.90$ ppm $SO_2(Ba^{++})$. The important feature to note is that the regression equation which has a slope close to unity and a small intercept is an indication that the two methods are

TABLE II

SO_2 test results from an uncontrolled coal-fired power plant

	Train a		Train b	
No.	Sample (Ba Chlor)	SO_3 (ppm) (Ba Chlor)	SO_2 (ppm) (Ba^{++})	SO_3 (ppm) (Ba^{++})
38A	—	443	—	470
38B		445		473
39A	0.7	443	8.8	484
39B		453		485
40A	1.6	—	9.6	461
40B		424		450
41A	3.2	410	3.4	465
41B		423		511
43A	1.6	380	5.0	408
43B		395		414
44A	0.5	443	2.4	423
44B		453		424
45A	2.6	464	3.2	465
45B		476		474
46A		431		443
46B		417		446
47A	6.6	418	5.9	422
47B		405		427
48A	5.0	475	4.8	502
48B		431		503
49A	2.1	538	8.8	517
49B		530		536
50A	3.8	530	8.1	505
50B		530		497

in good agreement with each other. From the replicate analysis of the above samples, the coefficient of variation (S.D. × 100/mean) for the barium ion titration and barium chloranilate methods was 1.0 and 2.6%, respectively.

CONCLUSIONS

On the basis of preliminary and limited test data, we have shown that good agreement is obtained between the barium ion and barium chloranilate methods for fossil fuel sources.

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