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Simultaneous Determination of SO_{3(g)} and SO_{2(g)} in a Flowing Gas

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A method for assaying a flowing gas mixture for SO_{2(g)} and SO_{3(g)} is described. The proof-of-concept for this method presented here uses the quantitative reaction of SO_{3(g)} with CaC₂O_{4(s)} at 325 °C to produce CO_{2(g)}. The gas mixture is passed first through a plug of CaC₂O₄ and then through a series of two optical cells. SO_{2(g)} is measured directly at one cell by UV spectrometry, and SO_{3(g)} is measured indirectly as CO_{2(g)} at the second cell by IR spectrometry. Good correlation coefficients were found for both analytes. Potential interference by SO₂ on the IR response of CO₂ can be neglected within a 1% error margin—except when the ratio CO₂/SO₂ is very small. A summary of key analytical methods for the analysis of sulfur oxides is given.

1. Introduction

A combination of SO_{2(g)} and SO_{3(g)} can be produced in several processes, including combustion of hydrocarbons,^{1,2} thermal decomposition of sulfates,^{3,4} mineral and soil analyses,^{5,6} and industrial waste gases.⁷ When the gas matrix containing these sulfur oxides is a flowing one, a method for rapidly assaying them separately and simultaneously is often required. Many methods for the determination of SO_{2(g)} have been described in the literature, primarily because of the fact that SO_{2(g)} is a major air pollutant. Fewer methods have been published for the determination of SO_{3(g)}, in spite of the great need for analytical methods to monitor it in a continuous fashion (e.g., in flue gases).⁸ In addition, the analysis of SO_{3(g)} is typically difficult and challenging.⁹

Chemical methods have generally been used when only one of the analytes is present in the matrix or when one of the two has been selectively removed from it. These methods typically involve dissolving the analyte into a liquid and analyzing the resulting solution. (For historical completeness, some of the classical methods are also included below.)

Absorbing liquids used for SO_{2(g)} include the following: aqueous iodine/starch solutions analyzed by titration of excess iodine with thiosulfate;¹⁰ aqueous hydrogen peroxide solutions analyzed by measurement of electrical conductivity;¹¹ aqueous hydrogen peroxide solutions analyzed by measurement of the SO₄²⁻ formed, using titration with barium salts,^{12–15} lead salts,¹⁶ or an ion-selective electrode detector,¹⁷ or using precipitation with barium salts (turbidimetric detection),¹⁸ or by measurement of the H⁺ formed using titration with NaOH;^{19,20} aqueous formaldehyde and pararosaniline solution analyzed colorimetrically;²¹ and dimethyl sulfoxide solutions analyzed by pulse polarography.²²

In addition to aqueous NaOH solutions,^{23,24} other absorbing liquids used for SO_{3(g)} include the following: aqueous isopropanol solutions analyzed by measurement of the SO₄²⁻ formed using titration with lead salts,¹⁶ using titration with barium salts,^{13–15,25} or spectrophotometrically using barium salts,^{26–28} or by turbidimetry,²⁹ or by measurement of the H⁺ formed using titration with NaOH;²⁰ pure water, followed by contact with

pure isopropanol (this procedure prevents the formation of the mono- or diester);³⁰ and aqueous isopropanol/acetone solutions analyzed by measurement of electrical conductivity.³¹

In some cases, chemical methods have been combined to allow determination of both analytes in a common matrix. Most of them involve simultaneous absorption of the analytes in a liquid (e.g., in an alkali or a H₂O₂ solution) followed by chemical or instrumental analysis—typically acid/base or redox titrations,^{2,5–7,23} ion chromatography,¹ or gas chromatography.³² Alternatively, one of the gases is made to react with a dissolved reagent (typically iodine species)^{24,33–35} or with a solid substrate that retains it, and the other gas is then analyzed.^{2,36,37}

A more promising approach from the standpoint of flow analysis involves passing the gas matrix first through an isopropanol solution, which selectively dissolves SO_{3(g)} and inhibits oxidation of SO_{2(g)}, and then through a hydrogen peroxide solution, which dissolves the SO_{2(g)} and oxidizes it to SO₄²⁻.^{16,31} Each of the absorbing solutions is then analyzed separately by one of the methods stated above. A variation of this technique is to first condense the SO_{3(g)} and then absorb the SO_{2(g)} from the matrix into a hydrogen peroxide solution.^{20,38} The SO_{3(g)} condensate is dissolved in isopropanol and both solutions are analyzed. We evaluated both of these methods and found them unsatisfactory for the analysis of a flowing gas matrix. First, we were unable to absorb or condense efficiently a relatively large amount of flowing SO_{3(g)}. Second, isopropanol traps tended to retain SO_{2(g)}, which transferred to the H₂O₂ absorber only after extensive flushing. Finally, the methods of analysis were too slow to allow the acquisition of data for the rates at which SO_{3(g)} and SO_{2(g)} were being introduced into the carrier matrix.

Potentially more rapid instrumental methods have also been reported.

(a) For SO_{2(g)}, these include the following: fluorescence (emission between 2400 and 4200 Å°);^{39–41} UV absorption (normally between 3200 and 1800 Å°);^{8,42–44} IR absorption (bands at 518, 1151, and 1361 cm⁻¹);^{45,46} or with a quantum cascade laser,⁴⁷ or with superimposed polarized IR light;⁴⁸ mass spectrometry;^{49–51} Raman spectrometry (band at 1151 cm⁻¹);⁵² gas chromatography;^{32,53–56} or ion-exchange chromatography;^{1,57} solid-state potentiometric detection;^{58–65} changes in the resistance of metal oxide surfaces;^{66–68} changes in the capacitance of SO₂-sensitive films;^{69,70} and coulometry.⁷¹

(b) For SO_{3(g)}, these include the following: IR absorption (bands at 527 and 1391 cm⁻¹);⁷² UV absorption;^{8,73,74} mass spectrometry;^{50,51,75} Raman spectrometry (band at 1067 cm⁻¹);⁵²

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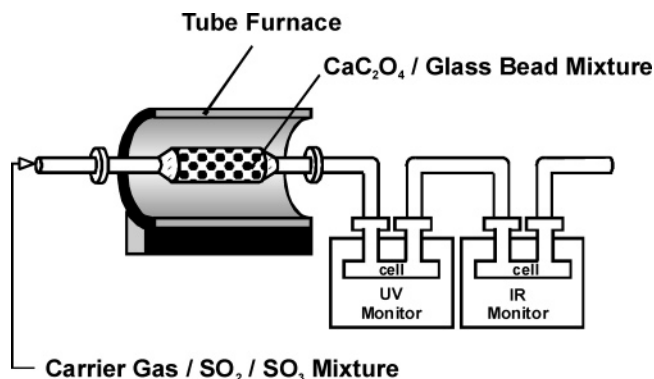


Figure 1. Experimental system.

gas chromatography;^{32,54} and solid-state potentiometric detection.^{58,65}

Although Raman spectrometry, gas and ion chromatography, mass spectrometry, and solid-state potentiometric detection have been used for simultaneous measurement of the two analytes,^{1,8,50–52,54,58} the extremely reactive nature of SO_{3(g)} makes it incompatible with the materials used in the construction of many commercial analytical sensors and instruments, and in the case of potentiometric detection, the SO₂–SO₃ equilibrium constant is required to estimate both simultaneously.⁶⁵ In virtually all the cases discussed here—with the exception of the ultrasensitive IR spectrometer⁴⁷ and the multivariate UV analysis⁸—the analytical techniques are unsuitable for the selective and continuous determination of SO_{2(g)} and SO_{3(g)}. In order to make use of the speed and convenience of instrumental analysis, we sought to find a reagent that would react quantitatively with SO_{3(g)} to produce a more stable and conveniently measured molecule.

As a result, we developed a method that uses the reaction between CaC₂O_{4(s)} and SO_{3(g)} (obtained from the thermal decomposition of zinc sulfate)^{3,4} to produce a mixture of CO_{2(g)} + CO_(g) (plus CaSO_{4(s)}) in order to assay a flowing gas matrix for SO_{2(g)} and SO_{3(g)} continuously and simultaneously. In this method, the gas mixture is passed first through a plug of CaC₂O₄ and then through a series of two optical cells. SO_{2(g)} is measured at one cell by UV absorption, and SO_{3(g)} is measured indirectly (as CO_{2(g)}) at the second cell by IR absorption. The method is described herein.

2. Experimental Section

We tested a variety of reagents for reaction with SO_{3(g)}. Reactions with glycerin to form acrolein, and with 1,4-butanediol to form tetrahydrofuran, were not quantitative. In general, the reactions of SO_{3(g)} with organic compounds appeared to be indiscriminate and unsatisfactory. Reaction with metal carbonates (Li₂CO₃, Na₂CO₃, K₂CO₃, MgCO₃, and CaCO₃) to form CO_{2(g)}, though thermodynamically feasible, could not be made quantitative. Oxalic acid,⁵³ and barium and calcium oxalates,⁷⁶ have been reported to react with SO_{3(g)} to produce CO_{2(g)} and CO_(g). We tested calcium oxalate extensively and found that it will react selectively with SO_{3(g)} (but not with SO_{2(g)}) at temperatures between 300 and 375 °C and flow rates between 50 and 300 mL min^{−1} as follows:



2.1. Apparatus. The flow apparatus used is shown schematically in Figure 1. The tube containing a CaC₂O₄/glass bead mixture was fabricated from Pyrex glass. This tube was enclosed

inside a larger Pyrex tube (1.9 cm i.d.), which was wound on the outside with electrical heating tape and encased in an alumina insulating cylinder (Zircar Products, not shown in the figure). Temperature inside the heated tube was regulated with a controller (model ITC-K23–999, Valco Instruments) and monitored with a thermocouple (type K, model CAIN-Dual-116G-12) and a digital thermometer (model 199), both from Omega Engineering. The concentration of SO_{2(g)} in the carrier gas was measured at the first optical cell—which was part of a nondispersive ultraviolet monitor (model UA-5, band-pass = 254–280 nm, purchased from ISCO). The concentration of CO_{2(g)} in the carrier gas was measured at the second optical cell—which was part of a nondispersive infrared CO₂ monitor (model IR-703, Infrared Industries). UV and IR absorbances were recorded on a dual-pen integrating recorder (Servogor, model 321, Soltec Corp.). Carrier gas flow rate was regulated with a flow controller (model 1355CB1B7AAA, Brooks Instruments) and calibrated with a homemade soap bubble flow meter.

2.2. Reagents. CaC₂O₄·H₂O (Certified) was obtained from Fisher Scientific and dehydrated in situ. Glass beads (60–80 mesh) were obtained from Altech Associates and used as received. Pyrex wool was obtained from Corning Glass Works and used as received. CO_{2(g)} was obtained by sublimation from commercially prepared dry ice. CO_(g) (research grade) and SO_{2(g)} (anhydrous grade) were obtained from Union Carbide–Linde Division and used as received. ZnSO₄ was prepared by complete dehydration of ZnSO₄·7H₂O (certified ACS) which was obtained from Fisher Scientific. The hydrate as received was ground with a mortar and pestle before heating at 180 °C for 24 h. The resulting cake of ZnSO₄ was reground and stored at 175 °C in a laboratory oven. The carrier gas used was He (high-purity grade), used as received from Union Carbide–Linde Division.

2.3. Procedures. **2.3.1. Preparation of the CaC₂O₄ Plug.** CaC₂O₄·H₂O powder was mixed with glass beads, and a portion of the mixture was poured into the Pyrex tube to form a plug 2.5–5 cm long and ~1 cm in diameter. The plug was held in place by wads of Pyrex wool at each end. The ratio of CaC₂O₄·H₂O to glass beads was arbitrarily adjusted so that the resulting plug would allow passage of the carrier gas at flow rates from 50 to 300 mL min^{−1} by application of an upstream pressure only slightly above atmospheric. The loaded tube was connected to the carrier gas manifold and heated for 1 h at 325 °C with carrier gas flowing through it to dehydrate the reagent. When dehydration was complete, the tube was connected to the optical cells and the entire system purged with an inert carrier gas (He).

2.3.2. Conditioning of the CaC₂O₄ Plug. We repeatedly observed that, when SO_{2(g)} was passed through a freshly prepared CaC₂O₄ plug, a small but measurable absorbance was produced within the band-pass of both the UV and IR monitors. The IR absorbance decreased with increasing exposure of the CaC₂O₄ plug to SO_{2(g)} and eventually became negligible. Presumably, the SO_{2(g)} causes desorption of residual CO₂ in the CaC₂O₄. For this reason, all CaC₂O₄ plugs were conditioned by exposure to SO_{2(g)} prior to calibration of the system. Once conditioned, the plug did not retain CO_{2(g)} introduced into the carrier gas.

2.3.3. Calibration of Absorbance Monitors. CaC₂O₄ (at 325 °C) was found to convert SO_{3(g)} in the carrier to CO_{2(g)}. The SO_{3(g)} concentration was measured (as CO_{2(g)}) by the nondispersive IR monitor. The SO_{2(g)} concentration was measured directly by the nondispersive UV monitor.

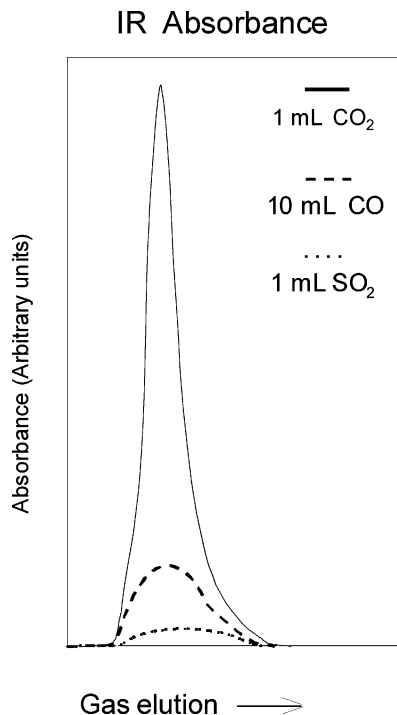


Figure 2. Typical IR absorbance curves.

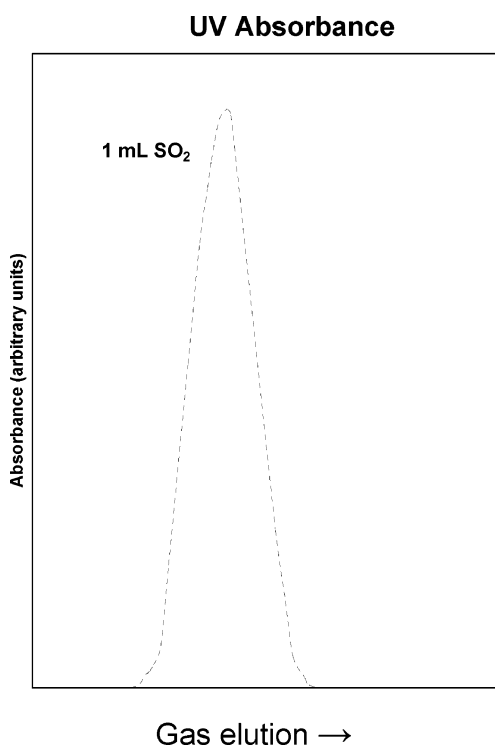


Figure 3. Typical UV absorbance curve.

Figures 2 and 3 show typical IR and UV absorbance curves, respectively, produced when calibration samples of the possible analytes $\text{CO}_{(\text{g})}$, $\text{CO}_{2(\text{g})}$, and $\text{SO}_{2(\text{g})}$ were separately injected into the carrier gas upstream from the CaC_2O_4 plug with a gas syringe. Only $\text{SO}_{2(\text{g})}$ produced an observable absorbance within the band-pass of the UV monitor. Injection of a series of $\text{SO}_{2(\text{g})}$ samples of various volumes (STP) showed that the area under its absorbance curve is directly proportional to the amount of $\text{SO}_{2(\text{g})}$ injected (see Figure 4). This linear relationship between volume of $\text{SO}_{2(\text{g})}$ injected and area held at flow rates ranging from 50 to 300 mL min^{-1} and at CaC_2O_4

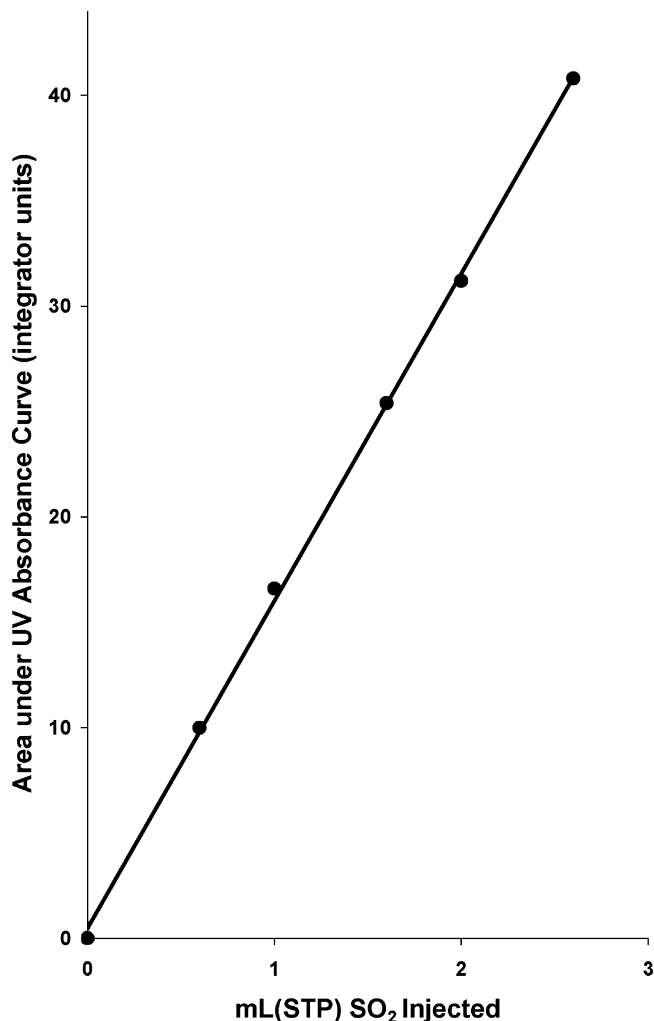


Figure 4. Calibration curve for $\text{SO}_{2(\text{g})}$.

temperatures ranging from 20 to 375 $^{\circ}\text{C}$. At temperatures above 375 $^{\circ}\text{C}$, $\text{SO}_{2(\text{g})}$ reacted with the solid to produce CO_2 . A calibration factor in $(\text{mmol of SO}_2)/(\text{unit area})$ was determined prior to each experiment. The area under an experimentally measured absorbance curve was multiplied by this factor without further correction to obtain the amount of $\text{SO}_{2(\text{g})}$ introduced into the carrier by the experiment. $\text{CO}_{2(\text{g})}$ produced a strong IR absorbance. Again, injection of a series of gas samples showed that the area under this absorbance curve is directly proportional to the amount of $\text{CO}_{2(\text{g})}$ injected (see Figure 5), and a calibration factor in $(\text{mmol of CO}_2)/(\text{unit area})$ was determined prior to each experiment. However, both $\text{CO}_{(\text{g})}$ and $\text{SO}_{2(\text{g})}$ also produced a measurable absorbance within the band-pass of the IR monitor. In fact, a 1.0 mL sample of $\text{SO}_{2(\text{g})}$ engenders $<1\%$ of the IR response produced by a 1.0 mL sample of $\text{CO}_{2(\text{g})}$. Thus, this potential interference can be neglected within this error margin except when the ratio CO_2/SO_2 is very small. Equal amounts of $\text{CO}_{2(\text{g})}$ and $\text{CO}_{(\text{g})}$ give IR absorbance curves with an area ratio $\text{CO}_2/\text{CO} = 51.6$. On the basis of eq 1, the reaction of $\text{SO}_{3(\text{g})}$ with CaC_2O_4 should produce an equimolar mixture of CO and CO_2 in the carrier gas. For this reason, all experimental IR absorbance curves areas were multiplied by a factor of 0.981 to remove the $\text{CO}_{(\text{g})}$ contribution before conversion to an equivalent amount of $\text{SO}_{3(\text{g})}$ by application of the $\text{CO}_{2(\text{g})}$ conversion factor.

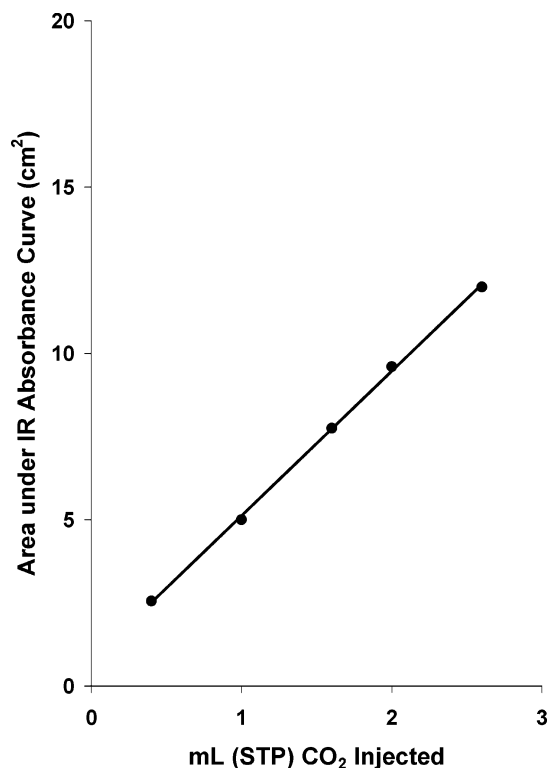


Figure 5. Calibration curve for CO_{2(g)}.

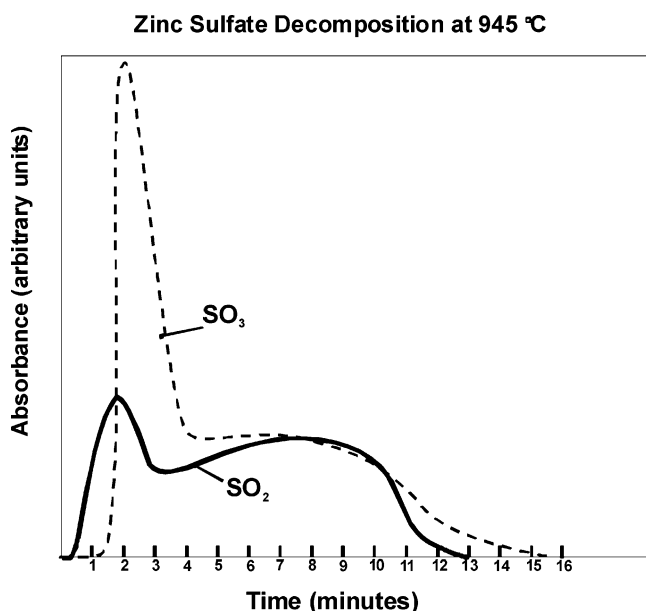


Figure 6. Typical absorbance curves of the products of the thermal decomposition of 1 mmol samples of ZnSO₄.

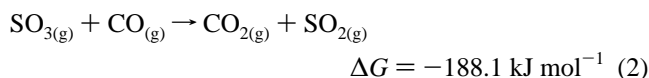
3. Results and Discussion

When the product gases evolved during the thermal decomposition of 1 mmol samples of ZnSO₄ were entrained in the carrier gas and swept through the CaC₂O₄ plug, absorbance curves such as those shown in Figure 6 were observed. The areas under each of the two curves were converted to the respective yields of SO_{2(g)} and SO_{3(g)}, and these yields were converted to percentages of the amount of SO₄²⁻ present in the ZnSO₄ sample. Experiments were repeated as a function of carrier gas flow rate and CaC₂O₄ temperature. A typical set of results is given in Table 1 for a CaC₂O₄ temperature of 325 °C. We consistently obtained mole yields of SO_{2(g)} and SO_{3(g)} (as CO_{2(g)}) that were equal in sum to the theoretical mole yield

Table 1. Yields of SO_{3(g)} and SO_{2(g)} from the Thermal Decomposition of ZnSO₄ at 945 °C (CaC₂O₄ Temperature = 325 °C)

carrier gas flow rate (mL min ⁻¹)	% of available sulfur converted to		
	SO ₃	SO ₂	SO ₂ + SO ₃
50	43.7	56.1	99.8
150	52.7	47.5	100.2
200	52.9	49.5	102.4
300	55.0	43.5	98.5

(±3%) expected for complete conversion of the available SO₄²⁻, as long as the carrier gas flow rate was between 50 and 300 mL min⁻¹ and the CaC₂O₄ temperature was between 325 and 350 °C. The reaction



which would result in anomalously high yields of SO_{2(g)} + CO_{2(g)}, did not appear to interfere. The thermal decomposition of SO_{3(g)}, although thermodynamically feasible, did not show significant interference either.

At higher temperatures, the reaction of SO_{2(g)} with CaC₂O₄ became significant as noted above. When the CaC₂O₄ temperature was <300 °C, the measured yields of SO_{2(g)} and SO_{3(g)} were less in sum than the theoretical yield. This deficiency was obviously due to a low CO₂ yield, indicating incomplete reaction of SO_{3(g)} with CaC₂O_{4(s)}.

The CaC₂O_{4(s)} plug described earlier has the capacity to react with ~3 mmol of SO_{3(g)} before breakthrough becomes obvious. Larger plugs would have a greater capacity but would require a higher system pressure to produce rapid gas flow. Better methods for providing gas/CaC₂O_{4(s)} contact would be required to produce a high reaction efficiency and capacity at low pressures.

4. Conclusions

Our results demonstrate as a proof-of-concept that SO_{3(g)} reacts quantitatively with CaC₂O_{4(s)} to give CO_{2(g)} and that an experimental method based on a series of two optical cells (UV and IR) can be used effectively to assay a gas mixture for SO_{2(g)} and SO_{3(g)} simultaneously and continuously.

Acknowledgment

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