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EXPERIMENTAL EVALUATION OF VARIABLES AFFECTING THE LEAD DIOXIDE METHOD FOR MONITORING OF SULFUR DIOXIDE

BY

CHARANJIT SINGH

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "Experimental Evaluation of Variables Affecting the Lead Dioxide Method for Monitoring of Sulfur Dioxide", submitted by Charanjit Singh in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

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Date

ABSTRACT

Experimental evaluations of the effect of humidity, temperature, wind speed and sulfur dioxide concentrations on sulfation rate of lead dioxide cylinders were conducted with the use of environmental chambers and a closed loop wind tunnel. Sulfation candles with reactive coated area of 100 cm^2 were prepared using PbO_2 particles with specific surface areas ranging from 1.72 to 8.3 m^2/g. The effect of SO_2 concentrations were studied in the range of 0.08 to 0.32. The temperature effects were evaluated between -40 to 40°C. The relative [illegible] ities and wind speeds varied from 30 to 80% and 0 to 30 m/s, respectively. A continuous SO_2 monitor was used to control gas concentrations in these experiments.

The results of the study indicated that the effects of temperature and relative humidity were negligible as compared to the significant effects of gas concentrations and wind speeds.

The correlation factors agreed well with those obtained in the field by other investigators and those predicted by the gas phase resistance model proposed by Liang et al. The predicted sulfation rates by this model agreed with the experimentally obtained rates at various wind speeds. In the wind speed range of 0.3 to 8.4 m/s, the sulfation rate increased by 1.51 $mgSO_3/dm^2/d$ for an increase of 1 m/s in the wind speed. The average correlation factor for candles and plates was 0.0355 $ppm/mgSO_3/dm^2/d$ with $\pm 25\%$ deviation over the above wind speed range 0.7 to 2.0 m/s.

The adsorption coefficients obtained from the evaluation of SO_2 concentration effects provided the maximum allowable exposure periods for static monitoring devices. The sulfation rate remains linearly proportional to the ambient concentrations of sulfur dioxide during the maximum exposure periods. A conservative estimate of the

allowable exposure period using Matheson lead dioxide having a specific area of 5.5 m^2/g was approximately 3.5 months for Huey plates and a little over a year for sulfation candles. The sulfation rates were found to differ significantly when the static devices were made from different grades of lead dioxide having different specific surface areas. Provided that the various laboratories in Alberta employ reagents having similar specific area, preferably those having the area in excess of 5.5 m^2/g, consistent and reliable results can be obtained on long-term trends.

The evaluation of the turbidimetric method of sulfate analysis indicated that 15 mg/l sulfate in a solution was the minimum reproducible detection limit (MRDL) which corresponded to a sulfation rate of 0.1 $mgSO_3/dm^2/d$ averaged over a 30-day period. Since sulfation rates in Alberta have been generally lower than the MRDL, exposure periods of 3 months for the static monitoring devices are recommended. The sulfate analysis should be conducted at a pH of 1.5 to minimize the potential errors inherent in the analytical method. The method of preparation and analysis of sulfation candles and Huey plates as described in this report, should be adopted by various laboratories.

The field evaluations of the effect of shelter shape and shelter opening areas are based on limited data, but do reflect the need for standardization of shelter design. The practice of exposing Huey plates and sulfation candles in one shelter should be replaced with the Huey plates mounted in separate receptacles and sulfation candles in cubical shelters. The results of this study indicate Huey plates can be used for 3-month exposure periods and therefore provide an alternative to the use of candles. This fact needs to be evaluated further with additional field surveys conducted in a manner incorporating the above recommendations.

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CHAPTER I

INTRODUCTION

The lead peroxide method of estimating atmospheric sulfur dioxide was first developed in England in 1932. The object was to provide a useful index of general pollution in an area by measuring long term levels of sulfur dioxide in the atmosphere. It was expected that the index may reflect the overall air quality and assist in determining the effect of polluted atmospheres in causing damage to vegetation, paints, corrosion of structures, respiratory complications in humans, and aerosol formation. A solid material was sought which reacted with sulfur dioxide in a predictable and uniform manner. The material finally chosen was lead peroxide; also known as lead dioxide.

Although more precise, automated instrumental techniques for ambient monitoring of sulfur dioxide are available today, the use of the lead dioxide method has increased considerably since its introduction by Wilsdon and McConnell [3]. The wide-spread use of the lead dioxide cylinders evolved due to the low cost of preparation and the practicality of unattended operation lasting a month or more at a time. The cylinders therefore, provide a tool that can be used to establish an inexpensive network of monitoring stations and to determine the long-term levels of atmospheric sulphur dioxide in a region. Information so obtained provides an indication of the air pollution problems associated with industrialization and population density.

Except for slight modifications in the method of preparation, the cylinders used today are little different from those used originally, and little more is known of the factors that control their effectiveness. Further, lack of standardization of the technique has contributed to a low reliability of monitoring data. In 1974, a joint effort between the Alberta Department of the Environment and eleven other laboratories was initiated to determine the cause of inconsistencies in the reported data. Each agency prepared and analyzed its own cylinders which were exposed at a common-station site on a monthly basis throughout the year. Even though the cylinders from each laboratory were exposed at one site, the sulfation rates varied considerably and no reliable conclusions could be drawn to improve the accuracy of the technique. The data obtained at the common-station site is summarized in Appendix A.

In this work the common-station study was investigated further and significant differences were found in the method of cylinder preparation and analysis as practiced by various laboratories. The differences included using one calibration curve for the spectrophotometer to using a set of two curves, using different grades of lead dioxide with different specific surface areas, adjusting solutions to different pH levels before sulfate precipitation and the differences in analytical methods; turbidimetric versus gravimetric or different sulfate precipitating reagents. A bias analysis of the common-station data was conducted using the Sign test. Of the twelve laboratories participating in the common-station study, three laboratories had supplied insufficient data, and four laboratories exhibited significant biases as shown in Appendix A. The remaining data could be questioned as well due to the above mentioned differences and poorly kept records of the practices followed by various laboratories. A need to initiate a new study to determine the effects of various parameters on sulfation rates, especially under controlled environmental conditions was obvious at this stage. This was confirmed further when a literature review indicated few studies conducted under controlled environmental conditions.

This work was undertaken to study the effects of temperature, humidity, wind speed and sulfur dioxide concentrations on sulfation rates of cylinders or plates made from lead dioxide having different particle sizes. A closed loop wind tunnel and several environmental control chambers were used to obtain the desired atmospheric conditions. In each experiment a continuous sulfur dioxide monitor was used to control gas concentrations at all times. The sulfation rates and the correlation factors obtained from this work are compared to the predicted results of models proposed by Liang et al. [14].

Other aspects of this investigation include a field study of the effects of ambient exposure conditions on sulfation rates of cylinders and Huey plates exposed simultaneously. The work includes an evaluation of the turbidimetric method of analysis for sulfates.

CHAPTER II

HISTORICAL BACKGROUND

Historically, efforts have been made over 100 years to detect sulfur dioxide using solid reagents. In 1813, Brezelius and Marcet [1] first used lead dioxide as an adsorbent to separate sulfur dioxide and carbon dioxide. Russell and Smith [2] while studying the effects of metal oxides and hydroxides on the formation of sulfur trioxide, obtained some data on the adsorption of sulfur dioxide by the following substances:

- Lead Dioxide
- Barium Dioxide
- Manganese Dioxide
- Stannic Oxide
- Chromium Dioxide
- Barium Hydroxide
- Copper Oxide
- Aluminum Hydroxide
- Chromium Hydroxide
- Ferric Oxide
- Ferric Hydroxide

Of these, the only substances that were capable of adsorbing essentially all of sulfur dioxide without promoting the formation of sulfur trioxide were lead dioxide, barium dioxide and aluminum hydroxide. With the exception of the reaction product formed by aluminum hydroxide, the products of reaction obtained with the other two compounds were essentially insoluble in water. In 1934, Wilsdon and McConnell [3] found that the rate of adsorption of sulfur dioxide by lead dioxide was nearly three times as great as by barium dioxide. The experimental data indicated hardly any decrease in the rate of adsorption even when thirty percent of lead dioxide had been converted. This probably led to the selection of lead dioxide as the preferred adsorbent. However, due to the difficulties in maintaining constant concentrations of sulfur dioxide and introduction of other experimental errors, Wilson and McConnell estimated the upper limit of conversion of lead dioxide to fifteen percent and indicated that in this range of conversion the rate of adsorption was linearly proportional to the concentration of sulfur dioxide.

Wilsdon and McConnell were the first investigators to develop the "lead dioxide candle" technique which was subsequently adopted by the Pollution Research Committee of the Department of Scientific and Industrial Research (DSIR) in the United Kingdom. Wilsdon et al. worked on the lead candle method because the conventional methods employed at the time were not adaptable to wide-area monitoring of sulfur dioxide. The results of the monitoring were considered to provide an index for estimating overall pollution originating from burning of coal. The conventional methods involved aspiration of large volumes of ambient air through solutions of iodine or hydrogen peroxide followed by an analysis of absorbed sulfur dioxide.

Lead dioxide cylinders have been used extensively in England since their introduction. The use of cylinders in Canada was first recorded in air pollution investigations conducted between 1955 and 1957 at York, Redoubt, Halifax, Montreal, Ottawa, Saskatoon, Norman Wells and Trail [4]. The purpose of the investigations was to determine the suitability of the lead dioxide method for Canadian exposure conditions, to determine the factors affecting the variability of the method, and possibly, establish a correlation factor with volumetric measurements. The results showed that the method was well suited to Canadian exposure conditions.

In the United States, similar use of the "candle method" has been made in atmospheric air pollution surveys in the 1950's. A survey in Nashville, Tennessee in 1958 to 1959 [5] involved the collection of 1400 sulfation candles at 119 sampling stations in a 12-month period. The study was directed towards answering such questions as (1) how long, (2) how frequently, (3) how many, and (4) where the candles should be installed to determine long-term air pollution trends. The Tennessee Valley Authority has used the lead candles method since 1954 [6] for monitoring the atmosphere near power plants. In this study [6], the discussion relates principally to practical field experiences, correlation of sulfation with recorded sulfur dioxide concentration and usefulness of data in appraising air pollution from industrial sources.

2.1 Development of Lead Peroxide Method

The original lead peroxide method developed by Wilsdon and McConnell remains essentially unchanged today. A 10 by 10 cm piece of cotton gauze was wrapped around a porcelain cylinder and a thick paste, obtained by mixing lead dioxide, gum tragacanth and water, was applied to the gauze with a spatula. The lead candle so prepared was allowed to dry and then mounted on a post sheltered by a cowl to protect the candle from rain (Figure 1a). Later the DSIR replaced the

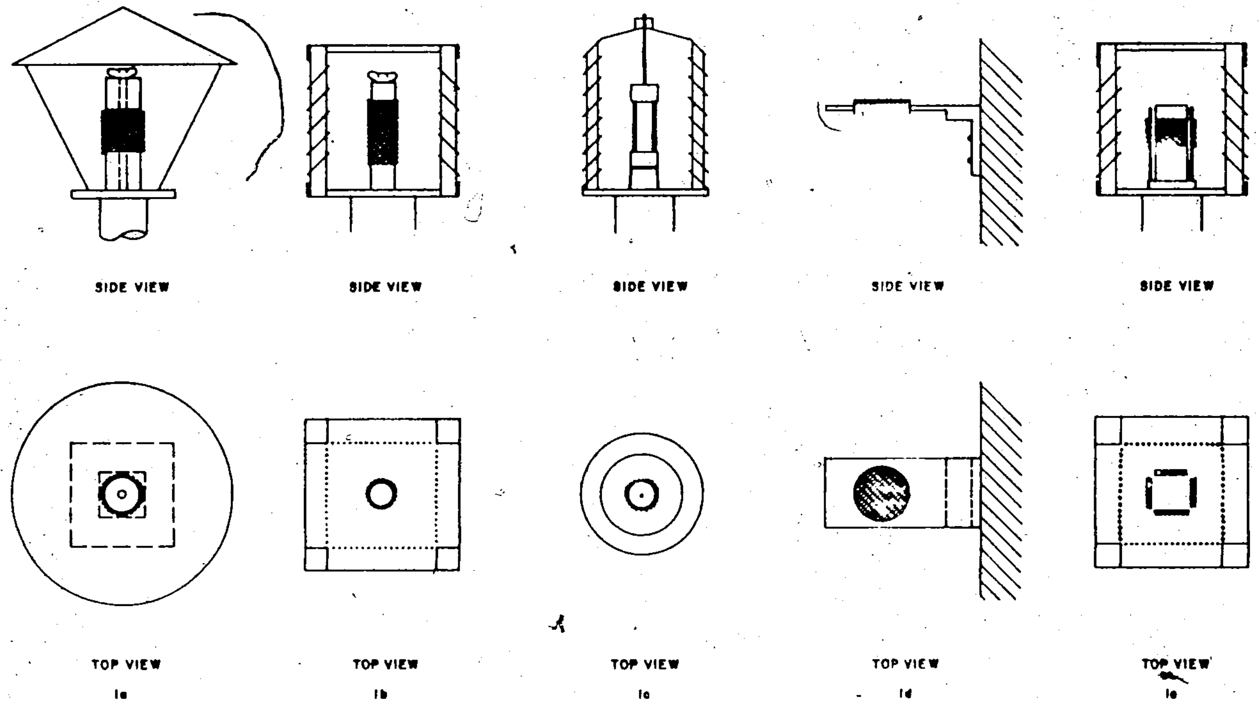


FIGURE I. EXPOSURE CONFIGURATIONS OF PbO_2 PASTES.

cowl with a cubical, louvered box which was considered a better shelter from rain (Figure 1b). Instead of sitting on the post, the candle is now capped into the ceiling of the louvered box.

In 1964, Bowden [7] proposed further simplification of the candle method. The modifications dispensed with the glazed porcelain cylinder and the standard tapestry cloth. The porcelain cylinder was replaced with a 'perspex rod knurled' cylinder on the grounds that the porcelain cylinder dimensions were subject to variations due to firing shrinkage. Cylinders of nearly standard dimensions were machined in perspex, the central portion being knurled before the ends were fixed. The knurled ends were made smooth by flowing chloroform over them. Bowden further suggested coating the surface of perspex cylinders directly without the tapestory cloth which may shrink irregularly after the reactive paste is dried. The cloth was also considered difficult to detach from the porcelain cylinder without incurring the loss of the reacted paste. Tragacanth gum was found unsatisfactory for sticking the paste directly on the perspex surface and was replaced with sodium methyl-carbonycellulose ('Polycell'). These modifications were aimed at reducing the preparation time when a large number of cylinders are to be handled. The alterations were not expected to give improved results. Bowden also replaced the cubical shelter with a cylinderical louvered box to minimize effects of shelter orientation on sulfation rates (Figure 1c).

In 1968, Huey [8] simplified the exposure system further and dispensed with the elaborate type of shelter necessary for lead dioxide cylinders, also known as candles. The new sampler is a plastic petri dish of 4.8 cm I.D., commonly known as a Huey plate. The plate is placed in a bracket mounted on a post or powerline pole in an upside-down position (Figure 1d), completely exposed to the atmosphere. The petri dish serves as the shelter, shipping container and lead dioxide support. The plate is prepared for monitoring by coating its inside surface with lead dioxide paste and by drying it in the oven.

In 1969, Boulerice and Brabant [9] employed flat-glass plates for sulfation studies using a thin-layer chromatography applicator. This technique allowed the area and thickness of lead dioxide coatings to be controlled more accurately than the conventional method of preparing cylinders. Four plates, each with a 25 cm^2 coated area were attached to a wooden holder of a square-base prism shape. The system was then exposed in a regular shelter (Figure 1e). In some cases one or two of the four plates so mounted gave higher sulfation rates exhibiting the directional effects of prevailing winds. If the wind direction is not a consideration, the technique can be used to prepare only one glass plate 100 cm^2 coated with lead dioxide and set up vertically or horizontally in the regular candle shelter.

2.2 Development of Analytical Techniques

The usefulness of the lead dioxide candle as an economic device is hampered by the often tedious and time consuming gravimetric analysis of exposed candles as proposed originally [3]. In the original procedure [3], the exposed surface area is measured and the cotton fabric holding the paste stripped from the support and treated with sodium carbonate solution. The composite is allowed to stand for three hours while stiring it occasionally during this period.

The solution is then boiled for half an hour (30 minutes). Any loss of water during boiling is made up by the addition of distilled water. The hot solution is filtered with appropriate washings and the filtrate acidified with hydrochloric acid. The sulfate in the solution is precipitated by adding barium chloride. The precipitated barium sulfate is filtered, washed, ignited and weighed.

Efforts were made by various investigators to simplify the original method and to find more rapid alternate analytical techniques promising equal or better accuracy. In 1959, Kanno [10] used a colorimetric method instead of the gravimetric method and indicated that the colorimetric method was more accurate for concentrations as low as 1 $mgSO_3/dm^2/d$. The increased accuracy would permit shorter exposure periods for candles. Kanno, however, did not provide any comparative data between the two methods. Further, concentrations in Alberta are even lower and the suggested accuracies would need to be evaluated at these concentrations. Bowden [7] employed acidimetry for the analysis of sulfates. Lead sulfate was converted to sulfuric acid by a cation-exchange resin and the filtrate titrated against standardized sodium hydroxide. The method claimed good success at higher sulfation levels, but only satisfactory results at low sulfation rates. The range of sulfation measured varied between 2-6 $mgSO_3/dm^2/d$. The sulfation rates in Alberta are lower than this range. Rayner [11] converted the insoluble lead sulfate to soluble ammonium sulfate with ammonium carbonate and titrated the filtrate with barium perchlorate using thorin indicator. He indicated that the accuracy of this method is ±10% for 10 mg sulfate. For 2 mg sulfate, the results were 20% high. Once again the suggested accuracies do not provide an significant advantage over the turbidimetric method used in this study. Huey [8] employed a turbidimetric procedure while Vijan [12] proposed a high temperature combustion method in which liberated sulfur dioxide was titrated using potassium iodate as a titrant. The rapid combustion method proposed by Vijan at best produced results that were as accurate as the gravimetric technique, although some reduction in time spent in the analysis is claimed. Carlson and Black [13] proposed an atomic absorption method based on the premise that lead sulfate is significantly more soluble than lead dioxide in ammonium acetate solution. The exposed gauze is stirred with ammonium acetate solution, followed by separation of solid/liquid contents and analysis of lead in the centrifugate by conventional atomic absorption technique.

The above developments have not significantly altered the original lead dioxide method. Some improvements such as mechanized preparation of coated surfaces or a switch to a more rapid and easier analytical method or usage of low cost shelters have been adopted by some agencies; more so to cut the cost of monitoring than due to any expected improvement of results.

In Alberta, both the sulfation candles and the Huey plates are used to monitor ambient concentrations of sulfur dioxide. Except for a few modifications, the lead dioxide candles are prepared in a similar manner to that used by Wilsdon and McConnell [3]. Instead of the porcelain cylinder used by Wilsdon et al., an 8 ounce glass jar having a 20 cm circumference is used in Alberta. A surgical gauze 5 cm in width is wrapped around the jar and provides the required surface area of 100 cm^2. A lead dioxide paste, obtained by mixing the lead dioxide reagent with gum tragacanth and water, is applied to the gauze with a brush instead of a spatula. Application with the brush provides a smoother coated surface. The candle is dried at room temperature in a sulfur dioxide free atmosphere. The Huey plate is prepared as proposed originally by Huey [8] and the coated plates are dried at 50 to 55 degrees Celcius. The slow drying of candles at room temperature prevents development of cracks in dried paste. Huey plates being smaller in size, generally do not cause this problem. Currently, the lead dioxide reagents used in Alberta vary from one laboratory to another and a standardization of particle size or surface area is lacking. Different analytical procedures are used by various laboratories, some of which are less accurate than the others, thereby making a comparison of sulfation data difficult.

2.3 Effect of Variables

A review of the literature indicated that a large number of studies evaluating the effects of different variables on the lead dioxide method were conducted under actual field conditions and largely, during the summer months. While such evaluations are essential, the effects of individual parameters and their relative influence on total sulfation measurements can be studied only under controlled experimental conditions. Only few such studies were conducted in the laboratory and those reported in the literature were found to be inconsistent and inconclusive. A summary of these studies conducted either in a laboratory or under actual field conditions is presented below.

2.3.1 Effect of Humidity and Rainfall

In a field study conducted at the City of Leicester [25], the effects of relative humidity on reactivity were evaluated using data obtained at four stations over a period of 22 months. The humidity data was obtained from meteorological measurements. The reactivity was defined as the rate of production of sulfate divided by ambient concentration of sulfur dioxide, $(mgSO_3/dm^2/day)/ppm$, and is the reciprocal of the correlation factors commonly used in the literature to relate sulfation rate with ambient concentrations of sulfur dioxide. The Leicester study did not indicate any significant correlation between relative humidity and reactivity. The effects of rainfall on reactivity were, however, found to be significant. Observations over a 26-month period indicated a correlation of +0.64 with reactivity. The sulfation candles used in this study were partially protected from rain by a cowl open on its sides, as shown in Figure 1a, and the candles were found to become at least partially wet. The quantity of rainfall was measured in inches per month. In the same study laboratory tests were simulated to compare the reactivity of dry and wet lead dioxide cylinders. The cylinders were kept wet by a wick dipped in a beaker of distilled water. Although the wetness of the candles could not be maintained constant, the laboratory tests established that the wet candles adsorbed 10% to 90% more sulphur dioxide than the dry candles. However, since the rain would also reduce the concentration of sulfur dioxide in the ambient air, the study concluded that rain affected the ambient concentrations of sulfur dioxide and the reactivity of sulfation candles in opposite directions. The cowls were, therefore, replaced by a louvered box for better protection of candles from rain. Foran et al. [4], in their field study at the Trail site, did not find a correlation between rainfall and reactivity even though the sulfation candles in this study were also protected by cowls, similar to those used in the Leicester study. The Trail site study was conducted over a two year period to determine the suitability of the lead dioxide method to Canadian exposure conditions. The apparent anomaly in the effects of rainfall on reactivity at Leicester and Trail sites was explained with the supposition that the Trail site is not subject to driving rains as are the sites in the United Kingdom. Newall and Eaves [32] in a field study in London, also found lack of any correlation related to rainfall. Rider et al. [29] in their laboratory study evaluated the effects of 0%, 50%, and 100% humidity on Huey plates by adjusting relative humidity in a dessicator. They concluded that although the sulfation rates did not change with humidity, the capacity of the plate to adsorb sulfur dioxide appeared to increase with the effects of sulfation not occurring until a longer exposure period elapses. The amount of sulfation showed a marked increase at 50% and 100% humidity after long exposure periods. This was attributed to the possibility that humidity forms a water layer which slightly dissolves the lead sulfate at the surface, thereby exposing fresh lead dioxide for reaction. Although the suggested mechanism has not been confirmed, their findings confirm that wetness of the paste due to condensation of water vapour on the paste surface promotes the reactivity, but without condensation, the relative humidity has no effect on the sulfation rate of the lead dioxide candles.

2.3.2 Effect of the Sulfur Dioxide Concentration and the Lead Dioxide Particle Size

Wilsdon and McConnell [3] conducted experiments in a small wind tunnel to estimate the range of proportionality between the rate of adsorption and the concentration of sulfur dioxide. The porcelain base cylinders were placed in the tunnel and a stream of air containing known concentrations of sulfur dioxide was passed at a velocity of approximately 0.25 cm/s. The data was obtained at 40, 189 and 666 ppm of sulfur dioxide, with exposure times varying between 6 to 24 hours. The rate of formation of lead sulfate, W, mgSO_3 per 100 sq cm per day for a given concentration, C, was expressed as

$$C = KW \qquad \text{...Equation 2.1}$$

where C is in ppm and K, was shown to be independent of sulfur dioxide concentrations up to 1000 ppm.

Wilsdon et al. estimated that the rate of adsorption remained approximately linear even when as much as 15% of the lead dioxide had been converted. This corresponds to a mean daily rate of sulfation of 13 $mgSO_3/dm^2$/day [4] for a standard cylinder exposed for one month. This sulfation rate is much higher than the commonly encountered sulfation rate of less than 0.3 $mgSO_3/dm^2$/d in Alberta [28]. The concentrations of sulfur dioxide used in their experiments were hundreds of times greater than those prevalent generally in the atmosphere. Further, the studies did not consider the effects of particle size on sulfation rates or on percentage conversion of lead dioxide during which the adsorption rate would remain linear for a known gaseous concentration.

Foran et al. [4] in their field study attempted to determine the value of K by monitoring ambient sulfur dioxide concentrations with a Thomas Autometer, which was operated at the same site as the sulfation candles. The proportionality constant K is commonly referred to as the correlation factor. The autometer readings in ppm of sulfur dioxide were plotted against the sulfation rate in $mgSO_3/dm^2$/d and the slope of the line was determined to be 0.028, with 95% confidence limit of $\pm$0.002. Foran et al. assumed that climatic conditions at other exposure sites would not affect the correlation factor K any differently than at the Trail site and therefore concluded that ambient concentration of sulfur dioxide correlates very closely with the sulfation rate obtained by the lead dioxide method. However, the study conducted in the City of Leicester [25] indicated that the correlation factors are site specific and vary between 0.01 and 0.04. Thomas and Davidson [6] found considerable scatter and relatively low degree of correlation between the sulfation candles and six autometers operated in a region having low ambient sulfur dioxide concentrations. The lack of correlation was also attributed to inherent wide variations in estimating such concentrations from autometer charts. However, in another area, having moderate or average concentration of sulfur dioxide of approximately 0.02 ppm or greater, Thomas et al. found a high degree of correlation between the sulfation rate and gaseous concentrations. Stalker et al. [33] found that the correlation factor also varies with the type of chemical method used to determine the ambient sulfur dioxide concentrations. The sulfur dioxide concentrations were determined both by the tetrachloromercurate (TCM) procedure described by West and Gaeke [34] and the Thomas Autometer. The autometer measurements of sulfur dioxide were two to three times higher than the TCM measurements. The reason for the higher autometer readings was most likely the response of this instrument to other acidic pollutants such as hydrogen sulfide or nitrogen oxides in addition to sulfur dioxide present in the atmosphere. Stalker et al. expressed the opinion that, based upon their over-all experience, the candle method is a good procedure for estimating mean sulfur dioxide levels in communities which have mean gaseous concentration of at least 0.025 ppm. The reliability of these mean estimates would probably be in the order of ±25%.

The above mentioned studies [4, 6, 25, 34] at first appear to indicate contradictory conclusions reached by these authors. However, if the premise of correlation factors being site specific is accepted, then lack of correlation in a region with lower ambient gaseous concentrations may be simply due to the insensitivity of the analytical methods used in determining gaseous concentrations, especially if different analytical methods give different sulfation rates or gaseous concentrations as pointed out by Stalker et al. [33]. These studies did not consider the effect of lead dioxide particle size on the rate of sulfation. Since the particle size effects were found to be significant [24], Hickey and Hendrickson [24] attempted to provide a design basis for the lead dioxide cylinders. According to their design, the rate of sulfation would remain linear for ambient concentrations of sulfur dioxide provided the cylinders were made with lead dioxide of certain particle size or surface area. Conversely, if the surface area of the adsorbent is known, a maximum allowable exposure period for the cylinders could be calculated such that the sulfation rate would remain linear for the estimated ambient concentrations of sulfur dioxide. The term "critical loading percentage" (CLP), was used to determine the percentage conversion of lead dioxide of specific surface area for which the rate of sulfation remained linear corresponding to a known gaseous concentration. Such information could provide not only a consistent basis for sulfation candle preparation but may also provide consistency in the determination of correlation factors. Hickey et al. indicated that in many cases, Foran et al's. data [4] at the Halifax Federal Building had exceeded the critical loading percentage and the lower estimates of sulfur dioxide concentrations were due to the attenuation of sulfation rates at the saturated surfaces.

In deriving the design equation, Hickey et al. proposed that if each cylinder was to contain a conservative amount of seven grams (usually eight grams) of lead dioxide, then 100% adsorption would amount to

$$(7)\ (64060)/239.21 = 1873\ \text{mgSO}_2$$

where 239.21 = molecular weight of lead dioxide, and

64.06 = molecular weight of sulfur dioxide.

Then, the design equation that would maintain the rate of adsorption linear with sulfur dioxide concentration and show the effect of particle size, gaseous concentration and exposure time can be expressed as

$$MC = (1873)\ (P)/(Q)\ 100$$

...Equation 2.2

where M = time of exposure, days

C = concentration of sulfur dioxide, ppm

P = critical loading percentage, %

Q = adsorption coefficient, mgSO_2/ppm/day

The adsorption coefficient can be determined from experiments or previous surveys. This equation would also be applicable to Huey plates or other flat plates. Should the amount of lead dioxide used for cylinders or plates be different than the assumed 7 grams, the amount of sulfur dioxide adsorbed at 100% conversion can be recalculated and substituted in equation 2.2. The cylinders designed and exposed for periods permissible by equation 2.2 would continue to form the sulfation product with the rate of sulfation remaining linearly proportional to the ambient concentration of sulfur dioxide, unlike the data collected at the Halifax Federal Building [4] where some of the cylinders were saturated and the rate of sulfation had decreased.

2.3.3 Effect of Temperature

The effect of temperature on sulfation rate of candles has been, generally considered to be insignificant even though only one of the studies actually conducted an experimental evaluation of this parameter. Wilsdon and McConnell [3] expected a slight increase in reactivity with rise in temperature. This was based on a model describing the absorption of soluble gases in cylindrical liquid films with an expression of the form, for mass transfer coefficient,

$$Sh_{avg} = f(Re)^{0.8}$$

...Equation 2.3

The mass transfer coefficient in equation 2.3 has the same dimensions as 1/K in equation 2.1, $ML^{-2}T^{-1}$. Equation 2.3 was used to estimate any temperature effects on the sulfation reaction. The gas density and viscosity were expressed as functions of temperature of the form $\rho = \rho_0 (1 + \alpha_1 t')$ and $\mu = \mu_0 (1 + \alpha_2 t')$, respectively. α_1, α_2 are numerical constants and t is the temperature in degree Celcius. The density function is incorrect since the density of a gas decreases with an increase in temperature. Therefore, when the corrected density function, $\rho = \rho_0/(1 + \alpha_2 t)$, is substituted in equation 2.3, the increase in reactivity for an increase in temperature of 1°C was recalculated to be 0.02% instead of 0.4% deduced by Wilsdon et al. This increase in reactivity as a function of temperature is insignificant. Since many other investigators have cited Wilsdon et al's. work, the temperature dependence needs to be re-evaluated further.

Hickey and Hendrickson [24] conducted a few experiments at 25°C and at 45°C to determine the effect of temperature on sulfation rate. A 125 ml Erlenmeyer flask was used as the reaction vessel containing known amounts of lead dioxide, and sulfur dioxide was injected with a syringe. The exposure time was 5 minutes in all cases. Since the reaction is exothermic, it was difficult to maintain constant temperature. Tests were repeated three times at each of the two temperatures and no significant temperature effects were observed.

The literature survey did not reveal any similar evaluations at sub-zero temperatures under controlled laboratory conditions. There were, however, field surveys [5, 25, 33] which indicated that the sulfation rates in winter months were greater than those obtained in the summer. This was believed to be due more to the stabler atmospheric conditions in winter which would attenuate the rapid dispersion of sulfur dioxide and result in relatively higher ambient concentrations of the gas. The limited data of Hickey et al. combined with the lack of studies at colder temperatures indicates a need to evaluate the temperature effects over a broader temperature range.

2.3.4 Effect of Wind Speeds and Shelter Geometry

The effect of wind speeds on the candle reactivity was first determined by Wilsdon and McConnell [3] who exposed the lead dioxide candles in a wind tunnel at sulfur dioxide concentrations ranging between 34 to 666 ppm. The gas velocities varied between 0.3 to 30 cm/s. A logarithmic plot of the correlation factor K (equation 2.1) and wind speeds indicated that K varied inversely as the fourth root of wind velocity, that is,

$$\frac{W}{C} = \frac{1}{K} = \text{constant} \times U^{0.25}$$

...Equation 2.4

However, wind tunnel experiments conducted later by the Department of Scientific and Industrial Research (DSIR) [35] indicated that the reactivity was not significantly dependent on wind speed. In these tests, the sulfur dioxide concentrations in the wind tunnel were maintained between 1.0 to 6.0 ppm with the wind speeds ranging between 1.5 to 9 m/s. These findings of the DSIR were substantiated further by a field survey conducted in the City of Leicester [25]. The survey was conducted over a 26 month period at four central stations in the City of Leicester and did not show any significant effects of wind speeds on the reactivity of the candles. The candles in this survey were partially protected from rain by a cowl of standard dimensions as shown in Figure 1a. The atmospheric wind speeds ranged between 0.3 to 18 m/s.

However, contrary to the findings mentioned above, the field data obtained by Lawrence [36] indicated that reactivity was a function of wind speeds according to the following power law equation. The field data was obtained by exposing the sulfation candles in a louvered cubical shelter. The wind speeds in this survey varied between 0.3 to 0.9 m/s.

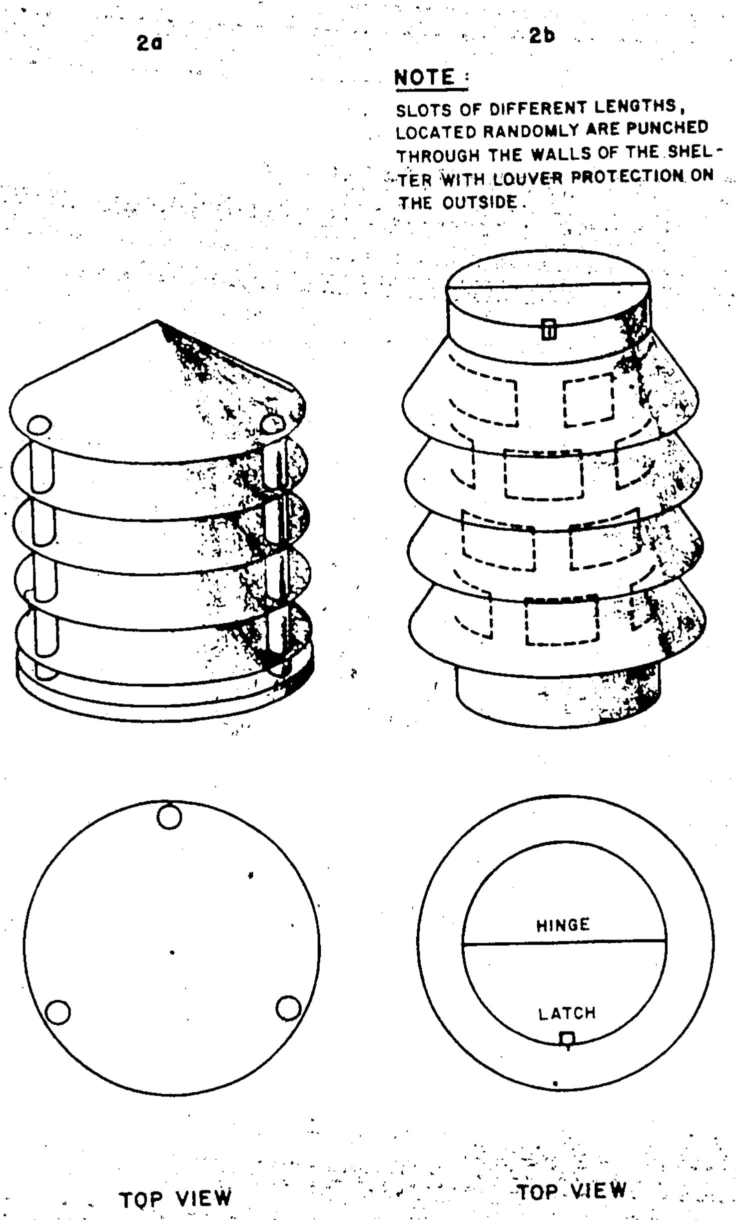
$$\frac{W}{C} = \text{Constant X } U0.55$$

...Equation 2.5

Lawrence [26] showed further that the shelter geometry also affected the sulfation rates of candles. A cubical and a cylindrical shelter were placed, in turn, in a wind tunnel and for a given external wind speed in the wind tunnel, the air flow inside the shelter was measured with an anemometer.

The tests showed that for a given external wind speed, the percent transmission of air through the cylindrical shelter was greater than for the cubical shelter, resulting in approximately 10% to 20% greater sulfation rate for the cylindrical shelter. This finding was confirmed by Bowden [7] in a field survey which indicated that sulfation rates were 20% greater in the cylindrical shelter.

Lawrence's results also showed that the percent transmission of air through the cubical shelter was a function of the shelter orientation with respect to the external wind direction. With unsymmetrical wind distribution such as may occur in a valley, the sulfation measurement in a cubical shelter could be affected by the shelter orientation. Orientation errors may even occur at many urban sites, although to a lesser degree. In the present study, the comparison of the two shelters was made in a field survey as discussed in Chapter 5. There was, however, a difference in the design of the cylindrical shelter used in this study and that used by Lawrence [26]. The cylindrical shelter used by Lawrence was made by placing three posts symmetrically (Figure 2a) with the screen louvres wrapped around these posts at different heights. The space between successive layers of the louvres was completely open except where the louvres were connected to the post. In contrast, the cylindrical shelter used in the present study was a cylindrical sheet metal box with randomly punched slits for passage of air (Figure 2b). For experimental purposes, the number and size of the slits was such that the total opening area of the cylindrical shelter was approximately equal to the opening area of the cubical cylinder. A schematic of the cubical shelter is shown in Figure 1b.



NOTE :

SLOTS OF DIFFERENT LENGTHS, LOCATED RANDOMLY ARE PUNCHED THROUGH THE WALLS OF THE SHELTER WITH LOUVER PROTECTION ON THE OUTSIDE.

FIG. 2 CYLINDRICAL SHELTERS

Although any effect of wind speed variations was expected to be reflected in the sulfation rate, whether these variations affected the ambient concentrations of sulfur dioxide was first evaluated by Newall and Eaves [32]. They reviewed the ambient monitored concentrations of sulfur dioxide for the months of November to February during the years 1956 to 1960. The data was obtained during various atmospheric pollution surveys in England. The wind data, obtained at a meteorological station, was divided into four ranges and for each range of wind speed, the corresponding average concentration of sulfur dioxide was obtained. The data plots indicated that the average daily concentration of sulfur dioxide was an inverse function of wind speed but the effect was far less marked at wind speeds above than below 2.5 m/s.

The works cited in the previous sections indicate inconsistencies in the conclusions drawn by various investigators independent of whether the tests were conducted in the laboratory or in the field. The problem is complicated further since most of the data cited in the literature were obtained with methods of varying accuracy in measuring sulfation rates or gaseous concentrations or variations in the locations of wind speed monitors. Further, the effect of individual parameters on sulfation rates appears to be different under laboratory conditions than in the field. In the field, the sulfation rate of candles is under a multiple effect of various parameters as compared to singular parameter evaluations conducted in the laboratory. However, due to the conflicting conclusions reached in the literature, insufficient data in somes cases, and failure to obtain comparable data in the common station study done in Alberta, it was decided to re-study these singular effects in the laboratory so that their relative significance under the field conditions could be estimated. The present study was extended to include an evaluation of the turbidimetric method and its limitations.

CHAPTER III

THEORETICAL CONSIDERATIONS AND MASS TRANSFER MODELS

3.1 Theoretical Considerations:

Measurement of sulfur dioxide in air is based on the facility with which the gas combines with solid lead dioxide to form lead sulfate, the exothermic reaction being

$$PbO_2 + SO_2 = PbSO_4 \qquad \text{...Equation 3.1}$$

The free energies of formation [15] of PbO_2, SO_2 and $PbSO_4$ are -52.34, -71.79 and -193.89 kilocalories per mole respectively. Thus, from

$$\Delta G = \Sigma\Delta G \text{ products} - \Sigma\Delta G \text{ reactants} \qquad \text{...Equation 3.2}$$

we have

$$\Delta G = (-193.89) - [(-52.34) + (-71.79)] = -69.76$$

indicating that the reaction could proceed spontaneously.

The Arrhenius equation,

$$k = B\, e^{-E/RT} \qquad \text{...Equation 3.3}$$

where

k = reaction velocity constant

T = absolute temperature

E = energy of activation

R = gas constant

B = frequency factor

indicates that reaction velocity should be a function of temperature.

If k can be determined at a minimum of two temperatures, the activation energy can be estimated [15] from the slope of the straight line obtained by plotting log k versus 1/T since the frequency factor B is related to the specific surface area. Its value increases with increase in area and in simple cases is proportional to the specific surface area [18].

In gas-solid heterogeneous reactions, since one reactant is in the solid phase and is consumed, the rate of reaction varies with time. In many types a solid product builds up around the reacting core. For some cases the rate of reaction at the interface may be rate controlling whereas in others, the rate of diffusion of one or the other of the reactants through the product layer may become rate controlling. Pilling and Bedsworth [16] illustrate the different rate controlling steps in their work on the classification of metals into two groups with respect to formation of oxides. Bikerman [17] summarized part of their findings as follows:

> If a unit volume of metal is transformed into oxide, the number of gram-atoms consumed is ρ_1/M_1, if ρ_1, is the density of the metal and M_1 is its atomic weight. If the oxide molecule contains n atoms of the metal, ρ_1/nM_1 moles of oxide are formed. If the density of the oxide is ρ_2 and its molecular weight is M_2, the the volume of oxide formed is $\rho_1 M_2/n\rho_2 M_1$. If $\rho_1 M_2/n\rho_2 M_1$ is greater than unity, the oxide occupies a larger volume than the metal from which it originated; otherwise oxidation involves contraction.

For potassium, sodium, calcium, barium and magnesium the ratio $\rho_1 M_2 / n\rho_2 M_1$, ranged from 0.41 to 0.79, indicating that a porous or discontinuous coating is formed [16]. The rate of corrosion for these metals was found to be constant. However, for metals such as cadmium, aluminum, zinc, tin, lead, and tungsten the volume ratio of oxide to metal ranged from 1.21 to 3.59. This partly explains the protective nature of oxide films such as the oxide on aluminum.

In the formation of lead sulfate from lead dioxide and sulfur dioxide, the volume ratio of solid product to solid reactant is

$$\frac{(9.375)\ (303.27)}{(1)\ (6.2)\ (239.21)} = 1.92 \qquad \text{...Equation 3.4}$$

where, 303.27, 239.21 are the molecular weights of the solid product and the reactant, and 6.2 and 9.375 are their respective densities. Therefore, it might be expected that the sulfation reaction could be categorized with the metals forming protective films. This may, in a general way, account for the finding [3] that adsorption of sulfur dioxide by lead dioxide was proportional to the gas concentration until some certain percentage of the lead dioxide had reacted. This could mean that the mechanism of adsorption or rate controlling step changes as adsorption proceeds.

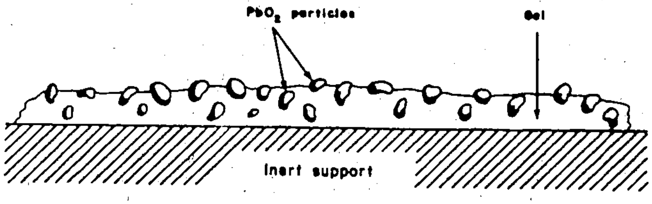
Although experiments conducted in this study were not designed to evaluate the kinetics of the lead dioxide reaction with sulfur dioxide, the experimental data obtained in this study was used to determine the predominant rate controlling step. The experimentally determined rate of sulfation is compared with that determined from two different models [14]. In the first model, the mass transfer rate is calculated from the gas phase resistance alone whereas in the second case, the diffusion resistance in the gel phase is assumed to be rate controlling. The experimental data was also used to evaluate the effects of temperature using the Arrhenius expression.

3.2 Mass Transfer Models:

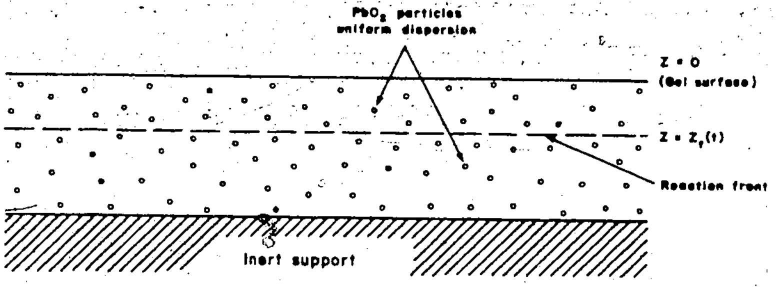
Model 1 - Gas Phase Resistance Controlling

A pictorial representation of this model is shown in Figure 3.1. The model assumes that

(i) the gas phase resistance is the only controlling resistance,
(ii) the lead dioxide particles are dispersed uniformly in the gel phase,
(iii) the gel phase is very thin such that all the lead dioxide particles are exposed at the gel surface,
(iv) the gel surface has an infinite capacity to adsorb sulfur dioxide over the test period since, in actual sampling, only a small fraction of the lead dioxide is converted,
(v) the reaction rate is very fast such that the concentration of sulfur dioxide at the gel surface is zero over the test period, and
(vi) the rate of mass transfer for the Huey plate is equivalent to that of mass transfer in a flat plate of similar dimensions.



Model 1. GAS PHASE RESISTANCE CONTROLLING FAST SURFACE REACTION



Model 2. GEL PHASE DIFFUSION CONTROLLING GAS PHASE RESISTANCE NEGLECTED

All PbO$_2$ particles are converted to PbSO$_4$ between $Z = 0$, $Z = Z_f(t)$.

FIGURE 3.1 DESCRIPTION OF THE TWO MODELS.

Based on the above assumptions, a steady state mass transfer correlation for forced convection can be applied to determine the rate of sulfation in a Huey plate. For a fluid flowing past a surface, the flux at steady state is given by,

$$N_A = k_c \Delta C_A = -D\frac{dC_A}{dy}\bigg|_{y=0}$$

...Equation 3.5

where N_A = mass flux, moles/cm^2/s

k_c = convective mass transfer coefficient, cm/s

and ΔC_A = concentration gradient, mole/cm^3

By solving the concentration variation term of equation 3.5 [37], a dimensionless expression of the following form is obtained

$$\frac{k_c x}{D} = Sh_x = 0.332\ Re_x^{1/2}\ Sc^{1/3}$$

...Equation 3.6

The average mass transfer coefficient over a plate of width b and length ℓ, is obtained by integration. For a plate of these dimensions, the total mass transfer rate W_A, may be evaluated by

$$W_A = \bar{k}_c A(C_A - C_{A,0}) = \int_A k_c(C_A - C_{A,0})\,dA \quad .$$

and from equation 3.6,

$$= k_c\, b\, \ell\ (C_A - C_{A,0})$$

$$W_A = b\int_0^{\ell} \frac{D\ (C_A - C_{A,0})\ Sh_x}{x}\, dx$$

$$\text{Therefore, } \bar{k}_c\, \ell\ \ (C_A - C_{A,0}) = \int_0^{\ell} \frac{D(C_A - C_{A,0})\ Sh_x}{x}\, dx$$

...Equation 3.7

Comparing equations 3.5 and 3.7, the rate of mass transfer in a Huey plate is given by:

$$N_A = W_1 = \frac{1}{\ell}\int_0^{\ell} \frac{D(C_A - C_{A,0})\ Sh_x}{x}\, dx$$

...Equation 3.8

where

W_1 = amount of sulfation, mole/cm^2/s

D = diffusivity of SO_2 in air, cm^2/s

ℓ = length of Huey Plate (diameter of disc), cm

C_A, $C_{A,0}$ = SO_2 concentration in air and at gel surface, respectively, mole/cm

In the above equation, Sh_x is the dimensionless Sherwood number for flow past a flat plate and is approximated by,

$$Sh_x = 0.332\ Re_x^{1/2}\ Sc^{1/3} \quad \text{for } Re_x < 2 \times 10^5$$

$$= 0.296 Re_x^{0.8}\ Sc^{1/3} \quad \text{for } Re_x > 2 \times 10^5$$

...Equation 3.9

where

$Re_x = U\,x/\nu$, $Sc = \nu/D$

U = average wind velocity, cm/sec

ν = kinematic viscosity of air, cm^2/sec

In the case of the reactive candle, the rate of mass transfer is given by:

$$W_1 = (C_A - C_{A,0})\,D\,Sh_d/d$$

...Equation 3.10

where

d = diameter of candle, cm.

The dimensionless Sherwood number, Sh_d, for flow past a short cylinder can be estimated by the following equation [20].

$$Sh_d = \frac{2}{\left(\frac{d}{2H} + 1\right) \ln \left(1 + \frac{2H}{d}\right)} + 0.6 Sc^{1/3} Re_d^{1/2}$$

...Equation 3.11

where

$Re_d = U\,d/\nu$

H = height of the reactive candle, cm

The correlation factor, C/W, can be obtained by substituting equations 3.9 and 3.11 into equations 3.8 and 3.10 respectively.

Integration of equation 3.5 for laminar flow is given by,

$$W_1 = \frac{0.332\ D\ C_A\ Sc^{1/3}}{\ell} \int_0^{\ell} \frac{Re_x{}^{1/2}}{x}\ dx$$

$$= \frac{0.664\ D\ C_A\ Sc^{1/3}\ Re_\ell{}^{1/2}}{\ell}$$

Conversion of units of W_1 and C_A to those of W and C, results in the following equations:

Huey Plate

$$W = C\ \frac{55.94 \times 10^2\ D\ Sc^{1/3}\ Re_\ell{}^{1/2}}{T_A\ \ell} \qquad \text{for } Re_\ell < 2 \times 10^5$$

$$= C\ \frac{311.69\ D\ Sc^{1/3}\ Re_\ell{}^{0.8}}{T_A\ \ell} \qquad \text{for } Re_\ell > 2 \times 10^5$$

...Equation 3.12

Reactive Candle

$$W = C\ \frac{84.24 \times 10^2\ D\ Sh_d}{T_A\ d}$$

...Equation 3.13

where

W = amount of sulfation, $mgSO_3/\ dm^2/d$

C = average ambient SO_2 concentration, ppm

T_A = absolute ambient temperature, °K

$Re_\ell = U\ell/\nu$

Model 2: Gel Phase Diffusion Resistance Controlling

This model is also described in Figure 3.1. The lead dioxide particles are again assumed to be uniformly distributed in the gel phase and the gel phase is assumed to have a finite thickness. The sulfation reaction is assumed to occur in the gel phase during the test period. In addition, the model assumes that

(i) there is no fluid motion in the gel phase,

(ii) the gas phase resistance is negligible since the effective sulfur dioxide diffusivity inside the gel phase is much smaller than the gas phase diffusivity.

(iii) during the test period, all the lead dioxide particles between the gel surface, Z=0, and the moving reaction front inside the gel phase at $Z = Z_{f(t)}$, are converted to lead sulfate and sulfur dioxide would be required to diffuse through this layer to react with the fresh particles at the reaction front.

Therefore, Fick's second law of diffusion can be used to describe the mass transfer of sulfur dioxide inside the gel phase and the applicable boundary conditions are given below:

$$\frac{\partial C_A}{\partial t} = D_{eff} \frac{\partial^2 C_A}{\partial Z^2}$$

...Equation 3.14

I.C. at $t < 0$, $C_A = 0$ for all $Z > 0$

...Equation 3.15

B.C. at $t \geq 0$, $C_A = \overline{C}_A$ at $Z = 0$

...Equation 3.16

$$C_A = 0 \text{ at } Z = Z_f(t)$$

...Equation 3.17

$$-D_{eff}\frac{\partial C_A}{\partial Z} = C_B\frac{dZ_f(t)}{dt} \quad \text{at } Z = Z_f(t)$$

...Equation 3.18

In the above equation D_{eff} is the effective diffusivity of sulfur dioxide in the porous gel and C_B is the initial lead peroxide concentration in the gel, mole/L. In addition, $\overline{C}_A$ is the average sulfur dioxide concentration at the gel phase (Z = 0), which is the same as the bulk sulfur dioxide concentration in air since the gas phase resistance is neglected.

Equation 3.14 was solved as described in [30], and has the following solution:

$$C_A = \overline{C}_A\left\{1 - \frac{1}{\mathrm{erf}\sqrt{\alpha/D_{eff}}}\quad \mathrm{erf}\left[\frac{Z}{\sqrt{4D_{eff}\,t}}\right]\right\}$$

...Equation 3.19

where the parameter α is determined by

$$C_B\sqrt{\pi\alpha/D_{eff}}\cdot\mathrm{erf}\sqrt{\alpha/D_{eff}} = \overline{C}_A\exp(-\alpha/D_{eff})$$

...Equation 3.20

From the concentration profiles of equation 3.19 [30], the average rate of sulfation can be calculated over the test period τ.

$$W = 4.7 \times 10^6 C_B \sqrt{\alpha / \tau}$$

...Equation 3.21

where the right hand side of equation 3.20 is multiplied by the conversion factor 4.7 X 10^6 to get the units of W, the rate of sulfation. The conversion factor includes a multiple of 2 to indicate that average rate up to time τ (days), is twice the instantaneous rate. In equation 3.20, the value of C_A/C_B is generally less than 10^{-6}, hence, the value of α/D_{eff} is less than 0.01, and then equation 3.20 can be simplified by employing series expansion of the exponential terms and integration of the error function, to a first term approximation as given by,

$$\alpha = \frac{D_{eff} \overline{C}_A}{1.13 C_B \sqrt{\pi}}$$

...Equation 3.22

Hence,

$$W = 4.7 \times 10^6 \sqrt{D_{eff} \overline{C}_A C_B / 1.13 \sqrt{\pi} \tau}$$

...Equation 3.23

CHAPTER IV

EXPERIMENTAL TECHNIQUES

4.1 Apparatus

The apparatus used in this study consisted of four major pieces of equipment: exposure tunnel, exposure box, sulfur dioxide monitoring console and environmental control chambers. The details of each piece of equipment and its purpose in this study is described below.

4.1.1 Exposure Tunnel

A closed-loop exposure tunnel was designed and constructed to study the effect of wind speed on the sulfation rate of lead dioxide cylinders and flat-plates. A photograph and a schematic of the tunnel is shown in Figure 4.1.

The tunnel was constructed from sheet metal except for the test section which was made of plexiglass. The tunnel cross section was about 0.09 m^2 (1 ft^2) with the straight sections being 2.9 m long. Air and gas mixture was recirculated with an aluminum fan. Flow straighteners of egg-crate shape 23 cm (9 in.) deep and 7.6 cm X 7.6 cm (3 in. X 3 in.) in cross-section, were installed before the test section. The tunnel was installed in an ordinary room and all experiments conducted with it were at room temperature.

Wind speed was varied by changing the fan speed and by adjusting the damper to a predetermined setting. The fan speed was controlled

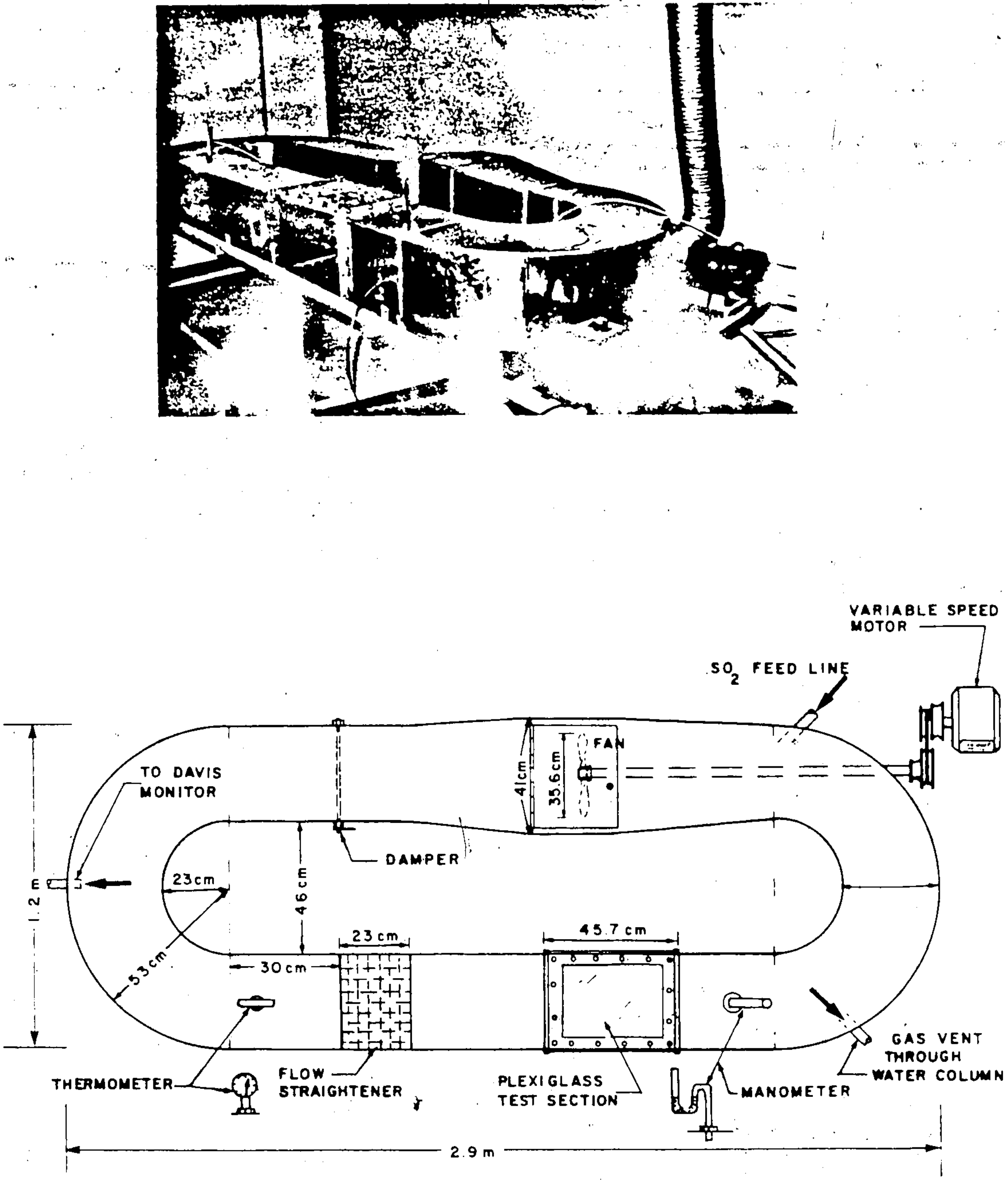


FIGURE 4.1 PHOTOGRAPH & TOP VIEW OF WIND TUNNEL

by a 3/4 HP Impact V * S Drive coupled with a 1/3 HP, 1725 RPM electric motor, both manufactured by Reliance Electric Company. Wind speeds up to 30 km/h could be generated in the exposure tunnel. The tunnel was calibrated for wind speeds corresponding to various "drive settings" before conducting any experimental runs and the calibration was not repeated during testing. During the calibration the top plate of the test section was replaced with a perforated plate having a set of openings across the width of the tunnel. Only one opening at a time was used to insert the probe of a hot wire anemometer for measurement of wind velocity at a predetermined setting, while the remainder of the openings were covered with a masking tape. The velocities were measured at the mid-point depth of the tunnel to correspond to the mid-point of the lead dioxide gauze on the test cylinders. When using the flat plates, the base height was raised to the mid-point levels in the test section. Wind velocities were measured across the cross section and a region with small velocity variations was selected to place the test plates and cylinders. The velocities in this region did not vary by more than ten percent.

A mixture of sulfur dioxide and air was fed in the cavity of the fan as shown in Figure 4.1. Excess mixture of the gases was vented through a two inch column of water, which was also the pressure maintained in the tunnel during all experiments. The gaseous mixture was made in the sulfur dioxide monitoring console and pumped into the tunnel. A water manometer was installed on the tunnel to indicate gas pressures in the tunnel. A large pressure build-up, more than approximately four inches of water was avoided so as to prevent leakage of gases through the fan-axle bearings. An elephant hose was placed on top of the bearing to vent any leaked gases to the building vent system.

A teflon sample line from the tunnel to the analyser provided a continuous check on sulfur dioxide concentrations. These measures provided a closed-loop, dynamically controlled, well-mixed gaseous mixture that could be made to flow past the cylinders at the desired wind speeds.

4.1.2 Exposure Box

The exposure box was a modified version of a "Fisher Isolator Lab" as shown in Figure 4.2. The box is mounted on a stand with rollers and could be wheeled into or out of environmental chambers. The exposure box was used to study the effects of humidity, temperature and concentration of sulfur dioxide on the sulfation rate of candles, which were made of lead dioxide particles of two sizes.

The exposure box was equipped with a 1/200 HP blower motor installed on its inside wall. The blower fan had a baffle plate mounted at its immediate outlet to prevent direct blowing of gases on the cylinders placed inside the box. During the experimental runs, the cylinders were located approximately two feet away from the blower outlet towards the opposite end of the box. A flow profile inside the box was made using a hot wire anemometer and the cylinders were placed at locations where the measured velocities varied from 10.1 to 25.4 cm/s.

A mixture of sulfur dioxide and air was pumped into the box near the blower fan location as shown in Figure 4.2. Excess mixture of the gases was vented through a column of water. Sulfur dioxide concentrations were continuously monitored by withdrawing a sample of gases through a 0.6 cm (1/4 in.) 90° elbow made of stainless steel tubing.

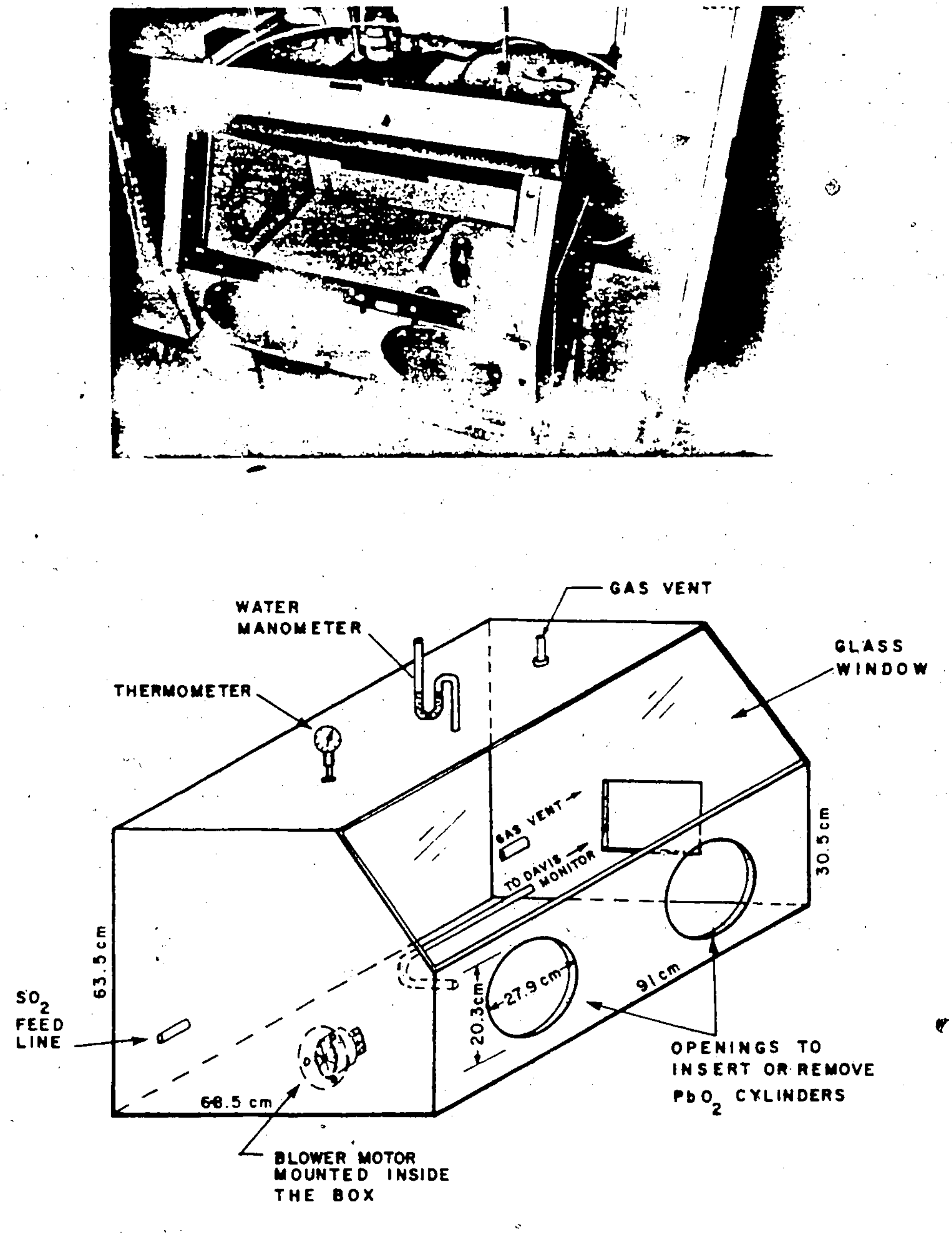


FIGURE 4.2 PHOTOGRAPH AND SCHEMATIC OF CONTROL BOX

4.1.3 Sulfur Dioxide Monitoring Console

The console was used to generate, control and monitor the various concentrations of sulfur dioxide required in different experiments. It may be connected to either the exposure tunnel or the exposure box. The console consists of three main components: a source to supply sulfur dioxide, a gas mixing system and a gas monitor capable of analysing continuously concentrations of sulfur dioxide in a test enclosure. Figure 4.3 illustrates a photograph and schematic of the console.

In this study, Teflon permeation tubes were used to supply sulfur dioxide gas in all experiments. The permeation tubes were placed in "AID's constant temperature calibration system, model 303", which was capable of ±0.25 degrees centigrade temperature control. The permeation rate is extremely temperature-sensitive and can vary up to 8 to 10 percent per degree centigrade change [21]. The tubes were calibrated over a period of several days as explained in the calibration section.

The gas mixing system consisted of an oil-less pump, two rotameters with needle valves and a timer activated-solenoid valve. The arrangement of the components is shown in Figure 4.3. The components enclosed in the dotted rectangle were not a part of the mixing system. Air was pumped through the mixing system to make required concentrations of sulfur dioxide. Needle valve #1 was used to control the total supply of dilution air. The air stream was proportioned along two routes; a small volume passing through rotameter #1 and oven to sweep the permeated sulfur dioxide and the remaining volume of air passing straight through needle valve #3. The mixed stream is metered through rotameter #2.

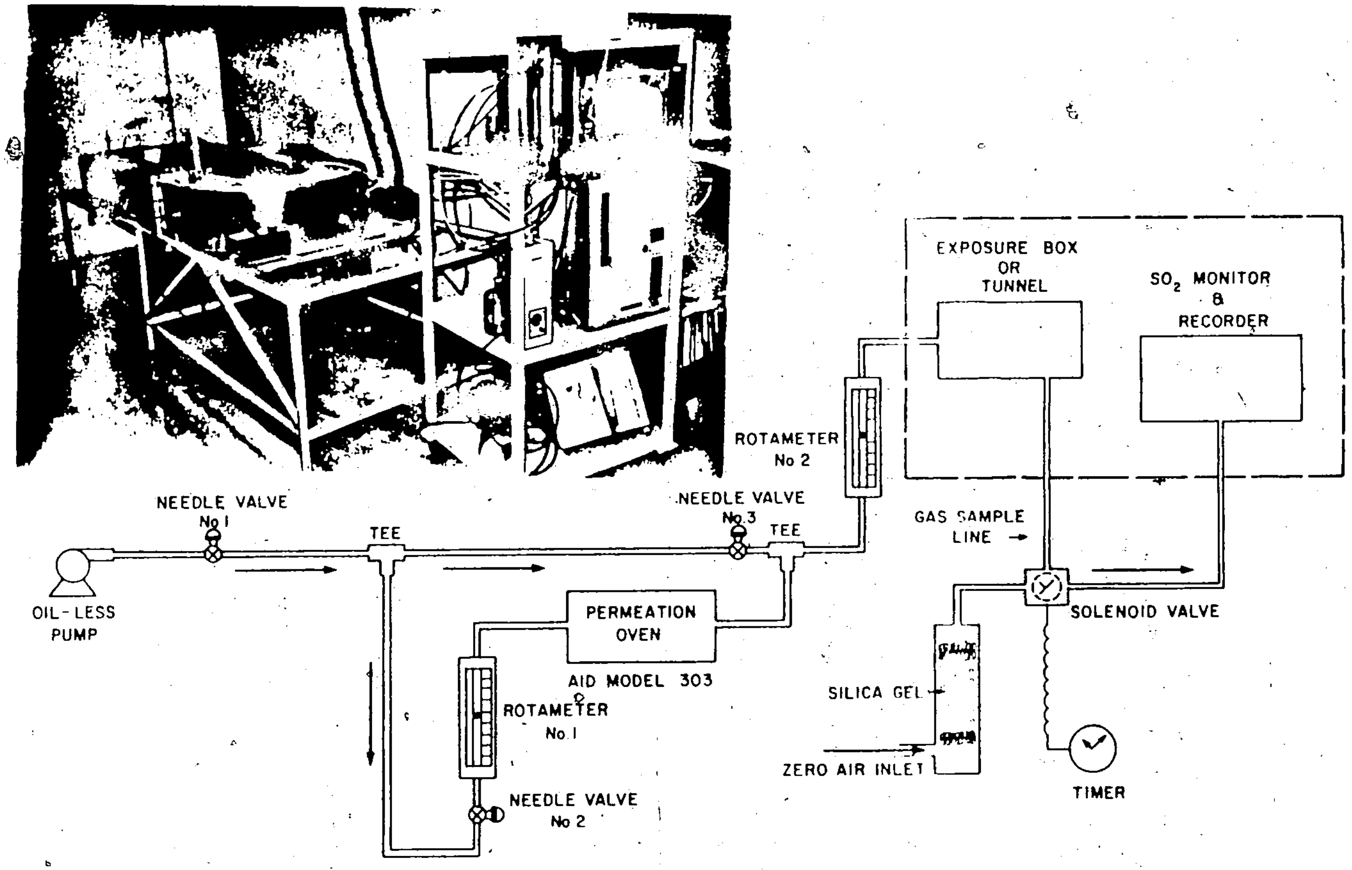


FIGURE 4.3 PHOTOGRAPH AND SCHEMATIC OF SULFUR DIOXIDE MONITORING CONSOLE CONNECTED TO EXPOSURE SYSTEM.

Needle valves #2 and #3 were adjusted to ensure that a small volume of air was continually sweeping the permeated sulfur dioxide in the oven. The mixture was allowed to fill the exposure system-under-experimentation continually and the excess gases were vented through a column of water. A sample of the gaseous mixture was continually withdrawn, analysed and recorded by the continuous sulfur dioxide monitor. The timer activated-solenoid valve allowed an automatic zero check two times every 24 hours by alternatively switching to zero air once every 12 hours. The zero air consisted of room air which was passed through a silica gel column before being sampled by the monitor.

The gas monitor utilized in this study was a Davis, model 70 A1, sulfur dioxide continuous analyser (Figure 4.3). The analyser operates on the principle of electrical conductance caused by ionization of dissolved material. This is accomplished by measuring resistance of a sample and water mixture passing over a pair of electrodes. The primary element of the measuring system is the conductivity cell shown in Figure 4.4. The cell is fabricated from clear, resistant plastic which minimizes solubility of the plastic. The active and water check electrodes are both housed in the cell.

The air sample enters the cell at point " and the ion free water enters the cell at point "B" (Figure 4.4). The water passes over the water check electrodes which are positioned upstream from the mixing of the sample and water. Both sample and water mix together in the cell chamber. From the chamber, the solution passes between the active electrodes where its electrical resistance is measured. After being analysed, the solution leaves the cell at point "C" where it is sent through a suction device back to the ion exchange reservoir, wherein deionization takes place.

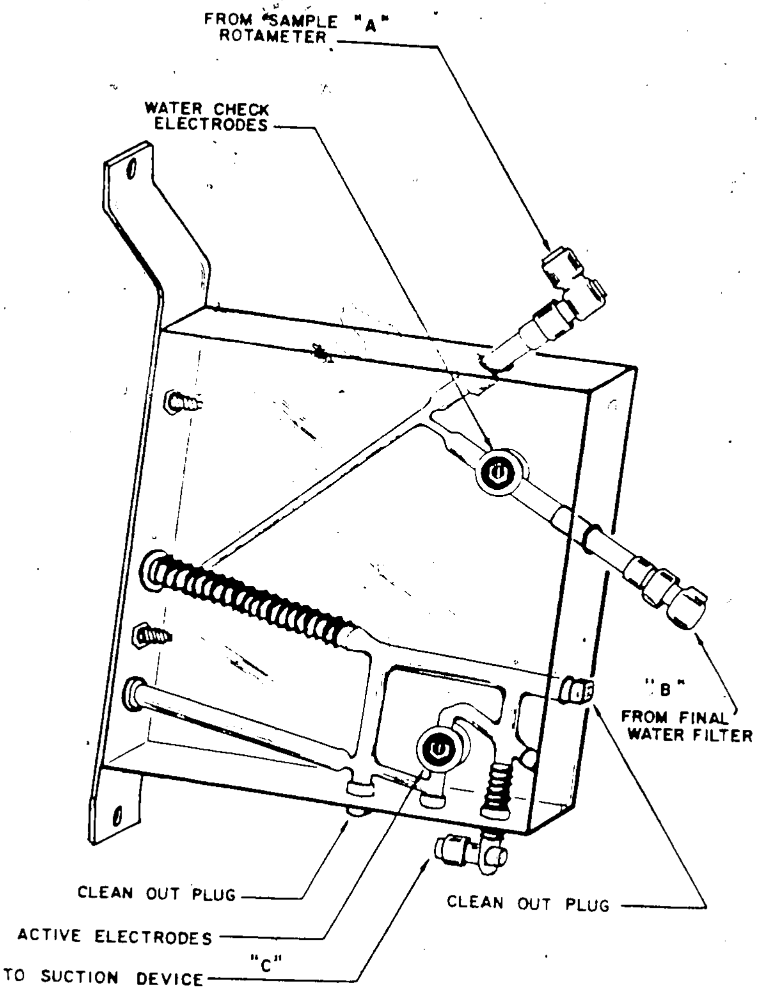


FIG. 4.4 CONDUCTIVITY CELL OF SO_2 MONITOR

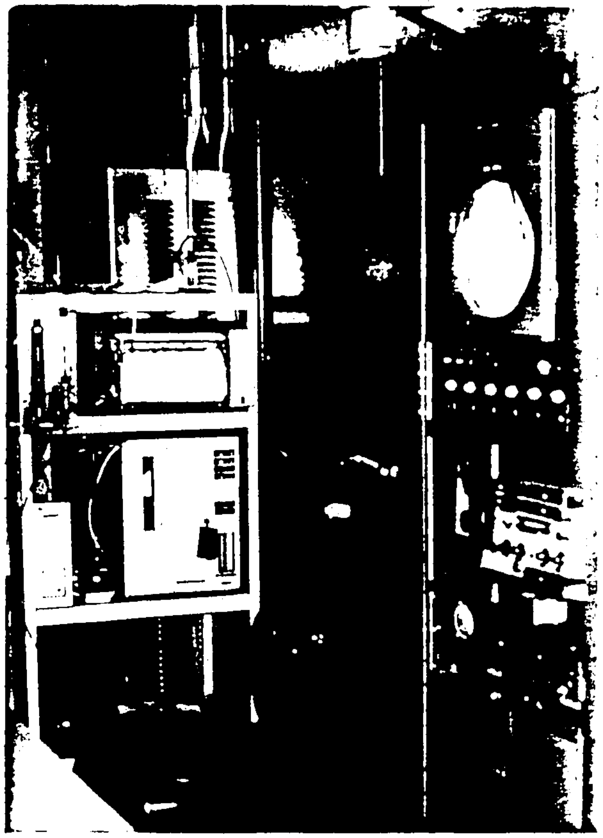
The sensitivity of the monitor is dependent upon the total number of ions formed. The sensitivity is affected by the rates of flow of the sample with respect to the rate of flow of water since these determine the concentrations of the sample in water.

The measuring circuit is A.C. operated while the indicating portion is D.C. operated. Errors due to polarization, that is, the change in the composition of the solution adjacent to the electrodes, are eliminated by employing alternating current. The output from the cell is rectified and sent through the measuring circuit. Additional operating instruction can be obtained from the Davis instruction book [22].

4.1.4 Environmental Control Chambers

Two types of chambers were used in this study to determine effects of humidity and temperature. The first kind had the capability of generating relative humidities between 20 to 80 percent over a temperature range of 5 to 50 degrees Celsius. These chambers measured approximately 31 cubic metres and were lined with shining aluminum panels on the walls and ceiling. A photograph of the sulfur dioxide console connected to the exposure box inside the chamber is shown in Figure 4.5. The control panels of the chambers were capable of maintaining humidity levels within 5% and temperature control within 1°C of the nominal settings, respectively. These chambers are located in the Biological Sciences Building at the University of Alberta.

To study low temperature effects, smaller chambers of approximately 7 cubic metre size were utilized. The temperature could be varied from 0 to -60 degrees Celsius. Humidity control was obviously not possible once the temperature was set at 10 degrees Celsius or lower in either of the two types of environmental



SO_2 MONITORING CONSOLE ON THE LEFT, AND CONSOLE FOR CHAMBER HUMIDITY AND TEMPERATURE CONTROL, ON THE RIGHT.

EXPOSURE BOX INSIDE THE ENVIRONMENTAL CHAMBER.

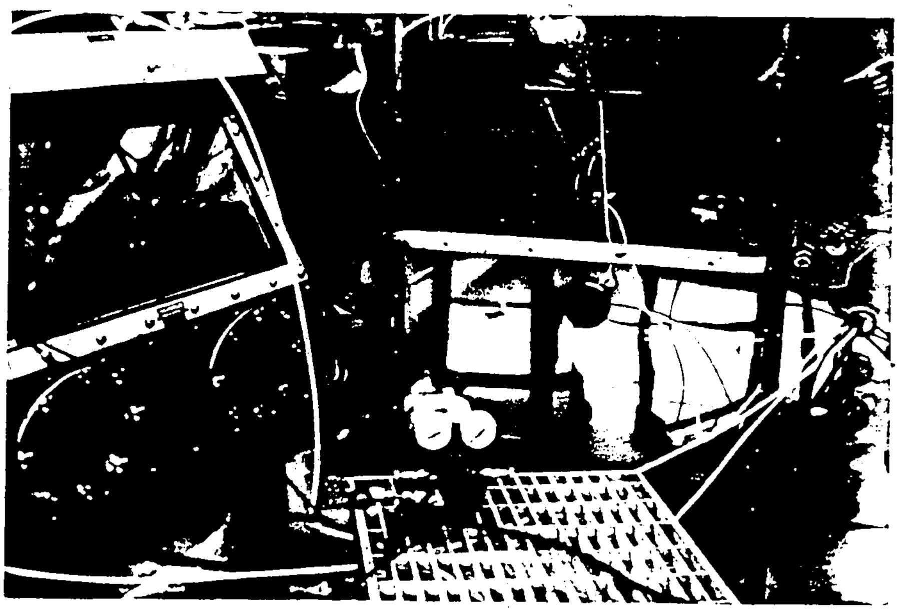


FIGURE 4·5 SO_2 CONSOLE CONNECTED TO EXPOSURE BOX chambers. These chambers were located in the Mechanical Engineering Building at the same university.

4.1.5 Preparation of Lead Dioxide Cylinders and Plates

Before preparing the candles, each grade of lead dioxide used in this study was characterized using the Brunauer, Emmett and Teller (BET) adsorption apparatus at the Alberta Research Council to determine specific surface areas. The apparatus is rather complicated as are the calibrations and corrections involved in its operation. A good description of the equipment and procedures with reference to the determination of specific surface areas is given in reference [23]. The surface areas of Matheson and Baber lead dioxides were obtained by the above method and the data is discussed in Chapter VI during the evaluation of the critical loading percentage. Calculations in this study were based on specific surface areas since no assumptions of particle shape are required when the BET adsorption technique is used.

To prepare the candles, a tape of surgical gauze, 60 cm long and 5 cm wide was wrapped around 8 ounce jars of 20 cm circumference. The gauze was secured to the jar with cotton thread and painted with a lead dioxide mixture. The mixture was prepared by adding 300 ml of 2% gum tragacanth solution slowly to approximately 300 g of lead dioxide, in portions, with continuous stirring until a smooth paste entirely free from lumps was obtained. A mortar and pestle could be used for this purpose. The gum solution is prepared by dissolving 20 g gum in 100 ml methanol and diluting it to 1 litre with distilled water. The lead dioxide paste is evenly spread on the surgical gauze around the jar with a small brush. A set of 25 cylinders could be prepared, each containing approximately 8 g of lead dioxide. After drying, the amount of lead dioxide coated averaged 8 ± 0.75 g and the pasted area measurements were within 5% of the required 100 square centimetres. Flat-glass plates with 100 cm^2 surface area were coated with the same lead dioxide mixture. However, since no gauze was used for the plates, it was necessary to dry each previous coat before applying another to retain a smooth surface. The weight of lead dioxide on the plates ranged between 6 to 7 g.

Huey plates used in the field study were prepared by grinding 4 g of Gelman paper in a grinding mill and transferring it to a blender containing 400 ml of water. After blending the contents for a minute, 64 g of lead dioxide and approximately 20 ml of 2% gum tragacanth solution were added and the mixture blended for a few more minutes. A circular gauze was attached to the Huey plate with acetone. Approximately 1 ml acetone was poured into the plate and allowed to dry in a fume hood. A 10 ml portion of the blended suspension was then placed into each Huey plate and the plates were then dried in an oven at 50 to 55 degrees Celsius. The amount of lead dioxide in the plates averaged 1.60 ± 0.04 g with an average pasted area of 19.65 ± 0.01 cm^2.

4.2 Procedures

4.2.1 Operating Procedure

A schematic of the complete experimental system used in this study is shown in Figure 4.3. The oil-less pump and the exposure box were placed inside environmental chambers during study of the humidity, concentration and the temperature effects. The sulfur dioxide monitoring console was positioned outside the chamber at room temperature and the sulfur dioxide feed and sample lines were connected to the equipment inside the chambers through receptacles in the chamber walls. The complete arrangement of Figure 4.3 operated at room temperature only when the wind tunnel was used as the exposure system. In any event the monitoring console was to be operated at room temperature at all times to avoid changes in solution conductivities and to prevent freezing of water lines in the monitor at colder temperatures.

Calibrated rotameters were used to determine the range of sulfur dioxide concentrations that could be obtained by adjusting needle valve No. 2 and 3 in Figure 4.3. The needle valves control the rate of flow of air and the permeated sulfur dioxide at a fixed permeation tube temperature. This procedure provided an estimate of the system's capabilities. Additional details on rotameter calibration are given in Appendix B. Before conducting experimental runs,a preliminary set of candles or plates was inserted in the system and the system was allowed to reach a steady concentration of sulfur dioxide. Initially there was considerable adsorption of sulfur dioxide on the system walls and lines but continuous operation of the system for half a day was found to be sufficient to reach a state of dynamic equilibrium. Steady state concentrations of sulfur dioxide could be maintained easily after this period. After reaching the equilibrium, the system responded quickly to any stimulus; flow rate adjustments or adjustment of permeation tube temperatures. The 90% response time of the monitor to changes in the input was less than a minute. Repeated calibrations of the permeation tube at fixed temperatures indicated a ± 5% variation in the gas permeation rate.

During experiments with the exposure box in the circuit, the box contained two sets of duplicate candles of two types. With the tunnel in circuit, only one candle or plate was inserted at a time. The steady velocity profile and good mixing of gases in the exposure box permitted placement of a set of four candles at a time. This was substantiated further by identical sulfation rates of duplicate candles in most runs. Preliminary candles or plates were exposed in the system to maintain steady conditions when no experiments were being conducted. This ensured minimum adjustment time of less than 10 minutes for gas concentrations to rise to steady levels upon change of candles or plates at the end of a test run.

Occasionally leaks had developed in the monitor circuit affecting the rates of flow of sample with respect to the rate of flow of water in the conductivity cell. This would cause a rise or fall of gas concentrations on the chart recorder. Elimination of leaks and proper adjustment of sample and water flows was sufficient to normalize operation of the monitor. A zero check was made twice daily and the zero drift was estimated to be one-half division per 24 hours.

4.2.2 Analytical Procedure

The analytical procedure to determine the sulfate content of the reacted lead dioxide surface was very similar to the ASTM's turbidimetric method. Despite the availability of more sophisticated and accurate analytical techniques, this simple technique was followed to determine its limitations and whether, with some modifications while maintaining the simplicity of the method, acceptable results with known precision and accuracy limits could be obtained. To retain the simplicity, measurement of the coated area of each candle or plate after exposure was considered undesirable provided an estimate of inherent statistical deviation had been obtained. Such estimate is described in section 4.1.5.

In the analysis of sulfation candles, the impregnated cloth surface was cut with a razor blade and separated from the glass support either by a spatula or knife point. The contents were transferred to a 400 ml beaker containing approximately 5 g of sodium carbonate (anhydrous powder) dissolved in 150 ml of distilled water. Extreme care is necessary to prevent loss of reacted lead dioxide during the transfer process. In case of flat plates, the reacted lead dioxide was scrapped off the glass surface. With Huey plates, the whole plate without the lid was placed in the beaker. The contents of the beaker were stirred occasionally and the mixture was allowed to soak overnight. Reacted lead dioxide in the Huey plate was lightly brushed into the beaker and the plate rinsed and removed. The solution was then heated for 30 to 45 minutes keeping the volume close to 100 ml for the candle or the flat plate and 50 ml for Huey plates. Distilled water was used to make up any loss of water. The hot contents were filtered through Whatman No. 2V, 18.5 cm folded filter paper and the filter contents were washed several times with distilled water. The filtrate was allowed to cool to room temperature and neutralized with 50% HCl. The pH of the filtrate was adjusted to 1.5 using a pH meter. The filtrate volume was exactly adjusted to 250 ml for candles or 125 ml for Huey plates, and the contents were shaken to mix the solution well. A 50 ml aliquot was pipetted into a spectrophotometer cell and a spoonful (approximately 0.5 g) of Sulfaver IV was added to precipitate sulfate. The spectrophotometer was set at 100% transmission with reagent blank. In this case the reagent blank consisted of distilled water mixed with a spoonful of Sulfaver IV. The cell was allowed to stand for 5 minutes and the precipitates were shaken vigorously. Percent transmittance was read at 420 nm. A few sample blanks consisting of unexposed candles were analyzed but the spectrophotometer adjustment was found to be equal to those reflected by the reagent blanks. Therefore, only reagent blanks were used for the remaining tests. The calibration of the spectrophotometer was checked periodically with at least a set of two standards. Complete details of spectrophotometer calibration are given in Appendix B.

CHAPTER V

RESULTS

The results of experiments conducted to study the effects of various parameters on the sulfation rates of full size candles or plates are described in this chapter. Except for Huey plates which were used in field tests, the pasted area of the candles or flat plates was 100 cm^2 within 5%. The sulfur dioxide concentrations were maintained constant at the selected levels within ±0.01 ppm. Larger deviations in gas concentrations occurred invariably due to the introduction of leaks in the monitoring system. The leaks caused a variation in the rate of flow of sample with respect to the rate of flow of water in the conductivity cell. Once the leaks were eliminated, the monitor operated normally. Experiments for which large deviations in gas concentrations occurred, were repeated. Before conducting any experiments the linearity between rotameter flow rates and indicated concentrations on the chart recorder was checked as explained in Appendix B.

Visual observation of the flat glass plates indicated that sulfation is mostly a surface phenomenon. The lead dioxide immediately in contact with the glass remains the same shade as at the beginning of the exposure period, while the outer area assumes a somewhat lighter color after the completion of chemical reaction.

5.1 Effect of Humidity

The relative humidity of the exposure box was controlled by pumping humid air of pre-set relative humidity from the environmental chamber. Cylinders were exposed to nominal relative humidity settings of 30, 45, 60 and 80 percent, respectively. Humidity variations were limited to ± 2% deviation between runs conducted at the same humidity level. The sulfur dioxide concentration and the dry bulb temperature of the environmental chamber were kept constant at 0.2 ppm and 21°C, respectively. Experiments conducted at 80 percent relative humidity were rejected due to the occurrence of condensation in the sampling lines. The experimental results are listed in Table 5.1 and plotted in Figure 5.1.

The straight vertical lines on Figure 5.1 indicate that the sulfation rates are independent of the effect of relative humidity for both types of lead dioxide cylinders. The two types of cylinders refer to candles pasted with two batches of lead dioxide of different surface areas per gram of the reagent. The surface area of the lead dioxide particles influences the sulfation rate more significantly.

During the 80 percent relative humidity run, the gaseous mixture in the teflon sampling lines started to condense on the inside walls of the tubing and even though attempts were made to prevent such condensation, these were unsuccessful. Consequently, the sulfur dioxide in the gaseous mixture dissolved on the wet walls of the sampling lines, thereby causing a significant drop in the concentration of sulfur dioxide. The monitor indicated almost 100% loss of sulfur dioxide concentrations with concentration readings approximating zero ppm. This experience indicated that should high ambient humidities

TABLE 5.1
EXPERIMENTAL DATA OF HUMIDITY EFFECTS ON SULFATION RATES OF TWO TYPES* OF CANDLES

Temperature = 21°C Sulfur Dioxide Concentration = 0.2 ppm

R.H./Exposure % Hour	Cylinders	Sulfation Readings			Sulfation Rate**
		% T	Avg % T	mg/l SO_4	$mgSO_3/dm^2/d$
32/48	M - 55	40.5	41.25	36.5	4.368
	- 56	42.0			
	B - 57	64.0	64.75	22.0	2.634
	- 58	65.5			
31.6/48	M - 59	40.5	41.25	36.5	4.368
	- 60	42.0			
	B - 61	67.0	66.50	21.2	2.538
	B - 62	66.0			
43.0/48	M - 65	44.0	43.50	34.8	4.167
	- 66	43.0			
	B - 63	64.5	61.25	24.0	2.873
	- 64	58.0			
41.5/49	M - 67	45.5	44.50	34.0	3.987
	- 68	43.5			
	B - 69	64.0	64.00	22.5	2.639
	- 70	64.0			
62.05/48	M - 73	44.0	44.12	34.4	4.118
	- 74	44.3			
	B - 71	61.0	62.25	23.4	2.802
	- 72	63.5			
60/47.5	M - 77	50.3	47.40	32.0	3.871
	- 78	44.5			
	B - 75	64.0	63.87	22.5	2.72
	- 76	63.8			

* The two types of cylinders are denoted in Table 5.1 by prefixes 'M' and 'B' and refer to Matheson and Baker lead dioxides having different surface areas per gram of reagent.

** The sulfation rate has been adjusted to account for a 13% loss of sulfate in digestion and filtration steps of the analytical method (see Section 5.7).

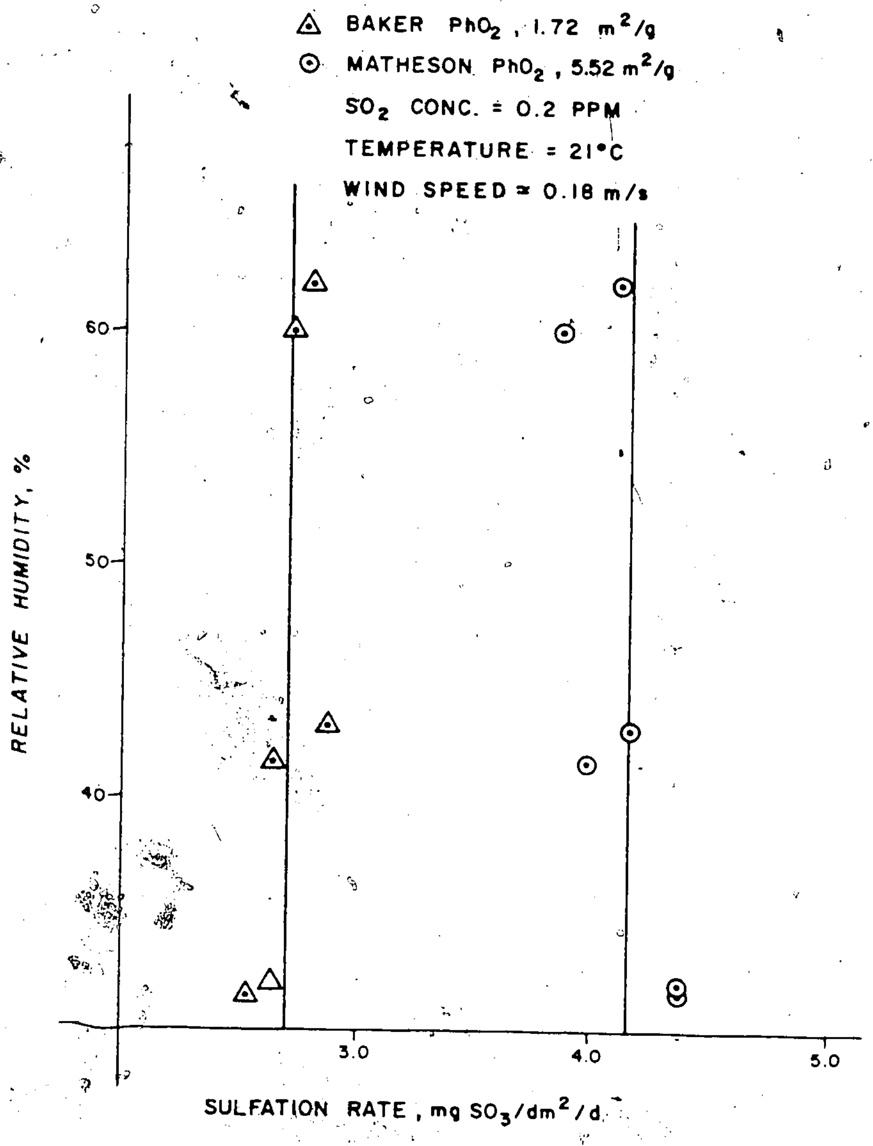


FIG. 5.1 EFFECT OF HUMIDITY ON SULFATION RATE OF CANDLES

persist, surface condensation on the exposed candles could occur and a film of water on the wet paste would promote the dissolution of sulfur dioxide, thereby increasing the apparent adsorption capacity of candles.

5.2 Effect of Sulfur Dioxide Concentrations

Effects of gas concentrations were evaluated at three nominal levels: 0.08, 0.16 and 0.32 ppm. Although these levels are greater than commonly encountered ambient concentrations in Alberta, the selection was limited due to the sensitivity level of the monitor. The smallest concentration level that could be read on the chart recorder was mid-point of the smallest division on the chart and this corresponded to a sulfur dioxide concentration reading of 0.01 ppm. Since 0.01 ppm would represent the smallest accurate readable concentration level of sulfur dioxide, the concentration variation at each of the three nominal levels was approximated to be 10 percent at the 0.08 ppm level, 5 percent at 0.2 ppm and about 3 percent at 0.32 ppm. The exposure box temperature was maintained between -1 to -2.5°C during all runs. The data is summarized in Table 5.2 and plotted in Figure 5.2.

The concentrations used in Figure 5.2 are weighted averages determined over the exposure period. With the known speed of the chart recorder, intervals of time of constant sulfur dioxide concentrations were marked to arrive at the weighted average for the test period. This was done to improve the accuracy of experimental data further. The data is represented with least square lines as shown in Figure 5.2.

for Matheson $W = 22.4\ C + 0.17$

...Equation 5.1

and for Baker PbO_2 $W = 12.84\ C + 0.55$

...Equation 5.2

The slope of the lines gives the reactivity, W/C, for the two powders. The units of the reactivity are mg $SO_3/dm^2/ppm$. The dotted portion of the plot extrapolates the experimental data to sulfation rates at zero concentrations of sulfur dioxide. Whether this extrapolation is valid would require further experimental evaluations with a monitor which is more precise and accurate at such low sulfur dioxide concentrations. Within the range of gaseous concentrations studied in this report, the adsorption coefficients were calculated from equations 5.1 and 5.2.

In terms of parts per million of sulfur dioxide and milligrams of sulfur dioxide adsorbed, the adsorption coefficients on a per cylinder basis are:

for Matheson $PbO_2 = 22.4 \times \frac{64}{80} = 17.92$ mg $SO_2/ppm/d$

...Equation 5.3

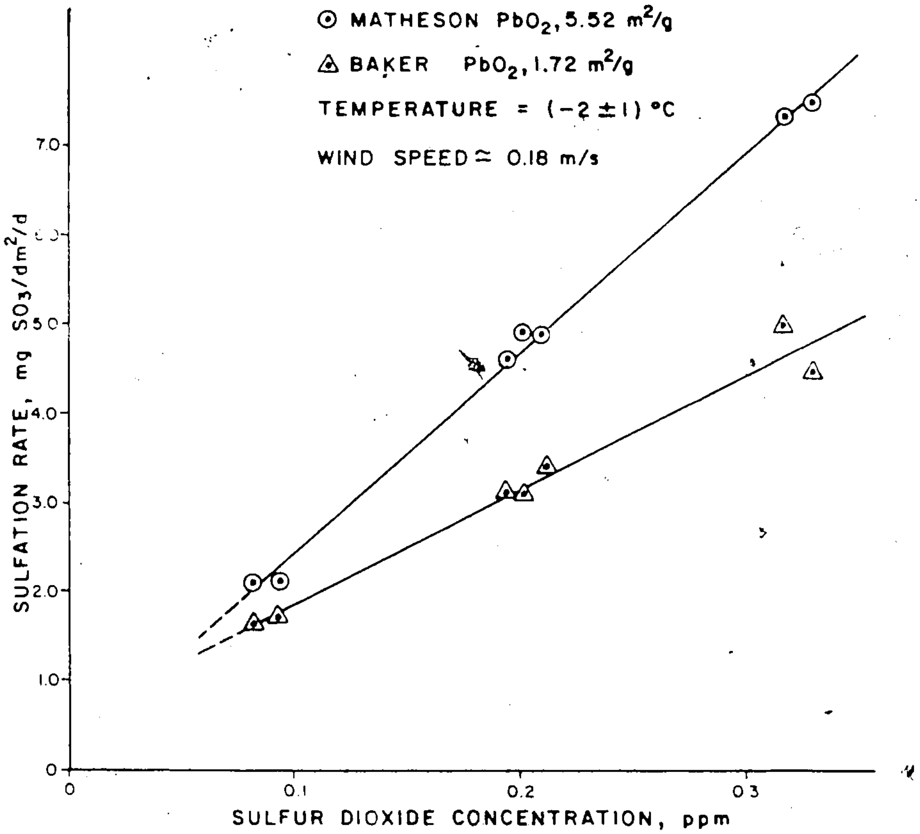


FIG. 5.2 EFFECT OF SO_2 CONCENTRATION ON SULFATION RATES OF CANDLES

TABLE 5.2
EXPERIMENTAL DATA OF SO_2 CONCENTRATION EFFECTS ON SULFATION RATES OF TWO TYPES++ OF CANDLES
Temperature = (-2 ±1)°C

Weighted Conc./Exposure ppm Hours	Cylinders	Sulfation Readings % T	Sulfation Readings SO_4, mg/l	Sulfation Readings Avg. SO_4 mg/l	Sulfation Rate** $mgSO_3/dm^2/d$
0.0936/96	M - 12	43.25	35.0	35.00	2.095
	- 14	43.20	35.0		
	B - 20	55.00	27.4	27.95	1.673
	- 21	53.00	28.5		
.0828/72	M - 40	58.3	25.4	26.00	2.075
	- 41	56.0	26.6		
	B - 36	69.5	20.0	20.30	1.620
	- 37	67.5	20.6		
0.202/48	M - 45	34.7	42.0	40.75	4.878
	- 46	37.5	39.5		
	B - 47	58.0	25.6	25.70	3.077
	- 48	57.75	25.8		
0.21/96	M - 15	10.00*	81.5	81.15	4.857
	- 16	10.20*	80.8		
	B - 18	22.00	56.5	56.50	3.382
	- 19	22.00	56.5		
0.195/97	M - 13	11.2*	78.0	77.25	4.576
	- 28	11.8*	76.5		
	B - 17	25.0	52.5	52.50	3.11
0.318/48	M - 42	18.75	61.5	60.95	7.296
	- 43	19.50	60.4		
	B - 27	34.25	42.5	41.45	4.962
	- 44	36.5	40.4		
0.33/48.5	M - 50	18.00	63.0	63.00	7.464
	- 51	18.00	63.0		
	B - 52	38.50	38.6	37.33	4.423
	- 53	40.00	37.4		
	- 54	37.00	36.0		

* These readings are outside the selected calibration range and may have a slightly higher inherent error margin.

** The sulfation rate has been adjusted to account for a 13% loss of sulfate during the digestion and filtration steps in the analytical method (see Section 5.7)

++ The two types of candles refers to candles made from Matheson and Baber lead dioxides having different surface areas per gram of reagent.

$$\text{and for Baker } PbO_2 = 12.84 \times \frac{64}{80} = 10.27 \text{ mg } SO_2/\text{ppm/d}$$

...Equation 5.4

The adsorption coefficients so obtained were used to arrive at an allowable exposure time versus sulfur dioxide concentrations prevalent in Alberta. This is discussed in the Chapter VI of this report.

5.3 Effect of Wind Speeds

These effects were studied in the closed loop wind tunnel kept at the room temperature of 23 ± 3°C at constant sulfur dioxide concentrations of 0.2 ppm. A set of flat glass plates and a set of sulfation candles were pasted with Matheson lead dioxide having a surface area of 5.52 m^2/g of reagent. An additional set of sulfation candles was prepared using an FC-2x355 lead dioxide reagent having a surface area of 8.3 m^2/g. Each of the plates or the candles had a pasted area of 100 cm^2. The experiments were designed to study the effect of wind speeds on two different exposed surface geometries; a flat and a cylindrical surface, and as well as on candles made from lead dioxide reagents of different surface areas. Table 5.3 summarizes the data obtained during these experiments. The data is plotted on a logarithmic graph paper and a best-fit curve of the form, $y = ax^n$ is fitted to each set of data in Figure 5.3. The least square solution to the above equation for each set of candles and plates is given below:

For candles pasted with,

Matheson PbO_2 $w = 0.41u + 0.75$

...Equation 5.5

FC-2x PbO_2 $w = 0.35u + 0.75$

...Equation 5.6

and for flat glass plates pasted with,

Matheson PbO_2 $w = 0.49u + 0.70$

...Equation 5.7

where $w = \log W$ and $u = \log U$

The slope of the three lines varies between 0.35 to 0.49 with an average slope being 0.42. That is, the average sulfation rate w is proportional to 0.4th power of wind speed.

The sulfation rates for all the candles and plates at each of the wind speeds were within a band-width of 1.5 $mgSO_3/dm^2/d$ or less. This margin is so small that the differences in sulfation rates cannot be conclusively related to having been caused either by the difference in exposed surface geometries or due to the difference in specific surface areas per gram of the lead dioxide reagents. The plots of equations 5.5 and 5.6 show that the sulfation rate does not increase in proportion to an increase in specific surface areas of the lead dioxide reagents. The sulfation rates from the two plots differ insignificantly even though the specific surface area of the FC-2x lead dioxide was 1.5 times the Matheson powder.

TABLE 5.3

EXPERIMENTAL DATA OF VELOCITY EFFECTS ON SULFATION RATES

Temperature = (23 ± 3)°C

Sulfation Device	Velocity/Exposure m/s	hours	Cylinders	Conc.* Factor	Sulfation Readings % T	Solution Volume ml	mg/l SO_4	Sulfation** Rate $mgSO_3/dm^2/d$
Matheson Candles	0.30/20		B - 80	1.034	86.0	250	13.0	3.61
	1.57/47.5		A	1.008	26.0	250	51.2	6.15
	4.36/48.5		B	1.019	35.5	500	41.2	9.57
	5.85/48		C	0.965	26.3	500	51.0	12.65
	8.38/46.5		D	1.015	22.3	500	56.2	13.69
FC - 2X 355 Candles	0.30/17		FC - 9	0.970	89.0	250	12.0	4.18
	1.57/24		FC - 1	0.977	68.0	250	20.5	5.02
	4.36/22.75		FC - 2	0.948	44.6	250	34.0	9.06
	5.85/24		FC - 4	1.042	23.5	250	54.4	12.49
Flat-Glass Plate Coated With Matheson Powder	0.30/24		P_1	0.925	87.0	250	12.6	3.26
	1.57/48		P_2	1.000	32.3	250	44.2	5.29
	1.57/24		P_2	1.010	61.5	250	23.6	5.60
	4.36/24		P_3	1.010	34.0	250	42.6	10.10
	4.36/24		P_3	1.054	31.5	250	45.2	10.26
	5.85/24		P_5	0.980	21.3	250	57.6	14.07
	8.38/27.75		P_6	1.072	38.5	500	38.6	14.92

* Concentration factor is the ratio of actual weighted concentration to 0.2 ppm and the adjusted sulfation rate is obtained by dividing with this factor.

** The sulfation rate has been adjusted to account for a 13% loss in sulfate during the digestion and filtration step in the analytical procedure (see Section 5.7).

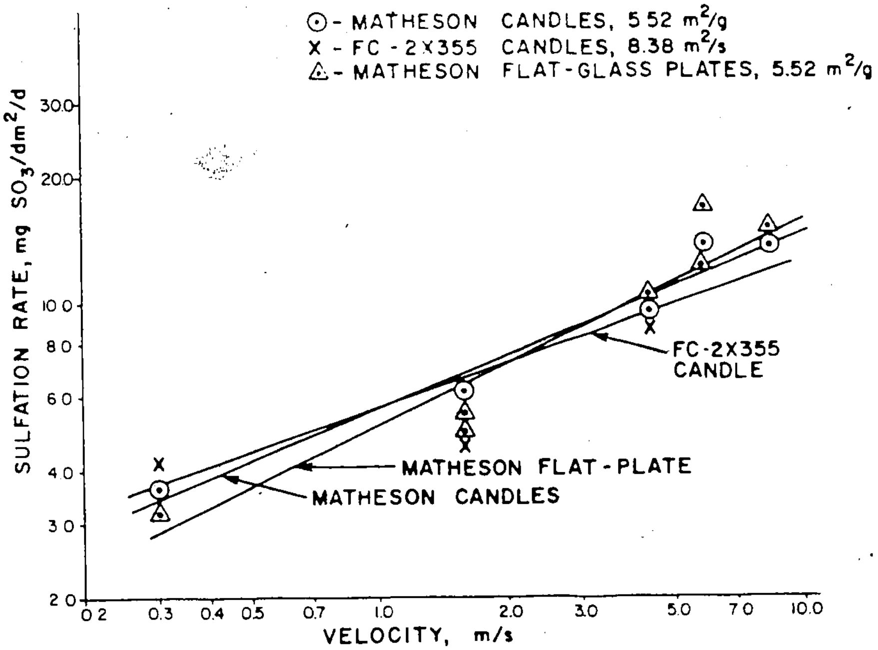


FIG. 5.3 EFFECT OF WIND SPEED ON SULFATION RATE

The experiments, therefore, indicate that the wind speed variations in the range of 0.3 to 8.38 m/s, affect the sulfation rate strongly. Sulfation rate is not directly proportional to the specific surface area (Figure 5.3). This must likely be due to some particle aglomeration occurring when lead dioxide pastes are made up. However, there is a significant difference in rates between pastes made from Matheson powder and from Baker powder (Figure 5.1). It is therefore, recommended that powders used by various laboratories have the same specific surface area.

5.4 Effect of Temperature

The study of temperature effects involved the use of several environmental control chambers each of which was capable of providing temperature control within a certain temperature range. Depending upon the temperature of interest, the exposure box was located in one of the chambers for the duration of the experimental run. In all experiments, the concentration of sulfur dioxide was maintained at 0.2 ppm with a maximum deviation of 0.01 ppm. The exposure periods were generally two days in each run. Any small variations in gas concentrations or exposure periods were taken into account in the calculation of sulfation rates reported in Table 5.4 and plotted in Figure 5.4. During each run, a set of four candles, two Matheson and two Baker, were exposed simultaneously in the exposure box at a constant temperature.

The least square fit to the sulfation rates of Matheson candles is given by equation 5.8 below.

$$W = -8.38 \text{ X } 10\text{-}3\ T_A + 6.78$$

.....Equation 5.8

The Matheson plot in Figure 5.4 indicates higher sulfation at lower temperatures. As the temperature increases, the sulfation rate of Matheson candles decreases. In the range of -40°C to + 40°C, the sulfation rate of Matheson candles decreased at the rate of 0.0084 $mgSO_3/dm^2/d/°K$. The sulfation rate from the least square equation 5.8 at 40°C is approximately 17% lower than that at -40°C. The predicted sulfation rates at the two temperatures (equation 3.13 of Model-1) differ by approximately 10% only. The calculations by Model-1, however, suggest that sulfation rate is greater at higher temperatures contrary to the experimental findings. It is difficult to explain this inconsistency. In any event, it appears that effect of temperature in the described temperature range is small.

A straight line could not be fitted to the scattered data of Baker candles in Figure 5.4. Further, the sharp decrease in sulfation rate at 232°K could not be explained rationally. Consequently, the temperature experiments were repeated to re-check the sulfation rates at colder temperatures. The repeated experiments were conducted at nominal temperature settings of -5, -20 and -45°C. The actual temperatures in the exposure box averaged -3.75, -16.5 and -41.5°C. The repeated data is also plotted in Figure 5.4, but reported separately in Table 5.5. The repeated data reconfirms the previous findings with respect to Matheson and Baker candles. A possible explanation for the scattered data of Baker candles may be that the effective area of the paste undergoes a change at subzero temperatures. Since all candles are dried at room temperature, the possibility of a small amount of moisture remaining in the paste exists. This moisture at subzero temperatures freezes and may be responsible for reducing the effective surface area available for reaction. The larger surface area of Matheson lead dioxide of 5.5 m^2/g is not affected as significantly as does the surface area of 1.7 m^2/g of the Baker lead dioxide.

Table 5.4

EXPERIMENTAL DATA OF TEMPERATURE EFFECTS ON SULFATION RATES OF TWO TYPES OF CANDLES

Temperature °C/Exposure Hours	Conc. Factor	Cylinders	Sulfation Readings			
			%T	Avg. %T	Avg. SO_4 mg/l	Sulfation Rate $mgSO_3/dm^2/d$
42.5/48	0.983	M-81	44	45	33.6	4.09
		-82	46			
		B-83	72	74.5	17.6	2.15
		-84	77			
45/48	1.019	M-85	43.0	42.75	35.4	4.16
		-86	42.5			
		B-87	75.5	75.5	17.2	2.02
		-88	75.5			
44.5/48	0.989	M-89	41.5	44.0	34.5	4.18
		-90	45.5			
		-91	45.0			
		B-92	76.5	76.5	16.6	2.01
20.5/48++	1.000	M-65	44.0	43.5	34.8	4.17
		-66	43.0			
		B-63	64.5	61.25	24	2.87
		-64	58.0			
21/49++	1.000	M-67	45.5	44.5	34.0	3.99
		-68	43.5			
		B-69	64.0	64.0	22.5	2.64
		-70	64.0			
-2/48**	1.01	M-45	34.7	36.1	40.75	4.83
		-46	37.5			
		B-47	58.0	57.87	25.7	3.05
		-48	57.75			

Table 5.4 (continued)

Temperature °C/Exposure Hours	Conc. Factor	Cylinders	Sulfation Readings %T	Avg. %T	Avg. SO_4 mg/l	Sulfation Rate $mgSO_3/dm^2/d$
-32/48	0.973	M-93	35.25	36.12	40.8	5.07
		-94	37.0			
		B-95	65.5	65.0	22.0	2.70
		-96	64.5			
-32.48	0.985	M-97	38.25	38.5	38.6	4.69
		-98	38.75			
		B-99	67.5	66.4	21.4	2.60
		-100	65.25			
-32.5/48	1.019	M-101	40.5	40.4	37.0	4.34
		-102	40.25			
		B-103	66.0	64.75	22.0	2.59
		-104	63.5			
-32/48	1.011	M-107	36.0	36.75	4.0	4.73
		-108	37.5			
		B-105	67.5	67.75	20.6	2.44
		-106	68.0			
-41/48	1.014	M-109	32.5	33.0	43.6	5.15
		-110	33.5			
		B-111	78.0	77.5	16.4	1.94
		-112	77.0			
-40/48	1.019	M-113	35.0	36.4	40.5	4.76
		-114	37.75			
		B-115	78.0	77.5	16.4	1.93
		-116	77.0			
-41/48	0.975	M-117	40.5	40	37.5	4.60
		-118	39.5			
		B-119	82.5	82.7	14.4	1.83
		-120	83.0			

++ This data set is from Table 5.1. These experiments were conducted at 21°C and because there were no humidity effects, the data provides effects of temperature. Although one of the set from Table 5.1 was chosen, an average sulfation rate of all the data in this Table could also be plotted instead with similar results.

** This data set is from Table 5.2 at 0.2 ppm. The other two sets at 0.2 ppm may be plotted in the temperature effect plot but were omitted to minimize inherent error as explained in the footnote of Table 5.2.

Table 5.5

REPEATED EXPERIMENTAL DATA OF TEMPERATURE EFFECTS ON SULFATION RATES

Temperature °C/Exposure Hours	Conc. Factor	Cylinders	Sulfation Readings			Sulfation Rate* $mgSO_3/dm^2/d$
			%T	Avg. %T	Avg. SO_4 mg/l	
-3.75/51+	1.051	MA 1	30	30.75	45.6	4.88
		MA 2	31.5			
-3.75/69+	0.975	BA 1	36.5	35.75	41.0	3.50
		BA 2	35.0			
-16.5/90	0.949	MA 3	47.75	47.38**	32.0	4.31
		MA 4	47.0			
-16.5/82	0.977	BA 6	28.5	28.5	48.4	3.47
		BA 7	28.5			
-41.5/48++	1.278	MA 9	27	26.5	50.6	4.74
		MA 10	26			
		BA 9	75	75.25	17.2	1.61
		BA 10	75.5			

* Sulfation rate has been adjusted for 13% loss in sulfate during analytical procedure (Section 5.7)

** For this set, the filtrate was diluted to 500 ml due to higher reaction whereas for all other sets it was 250 ml. This would introduce dilution errors.

++ A new calibrated permeation tube was used for this test and difficulties were experienced in maintaining concentrations due to electrical interference.

+. During these runs the 'gain' on the monitor was not adjusted properly and therefore, the concentration readings were fluctuating and had to be estimated.

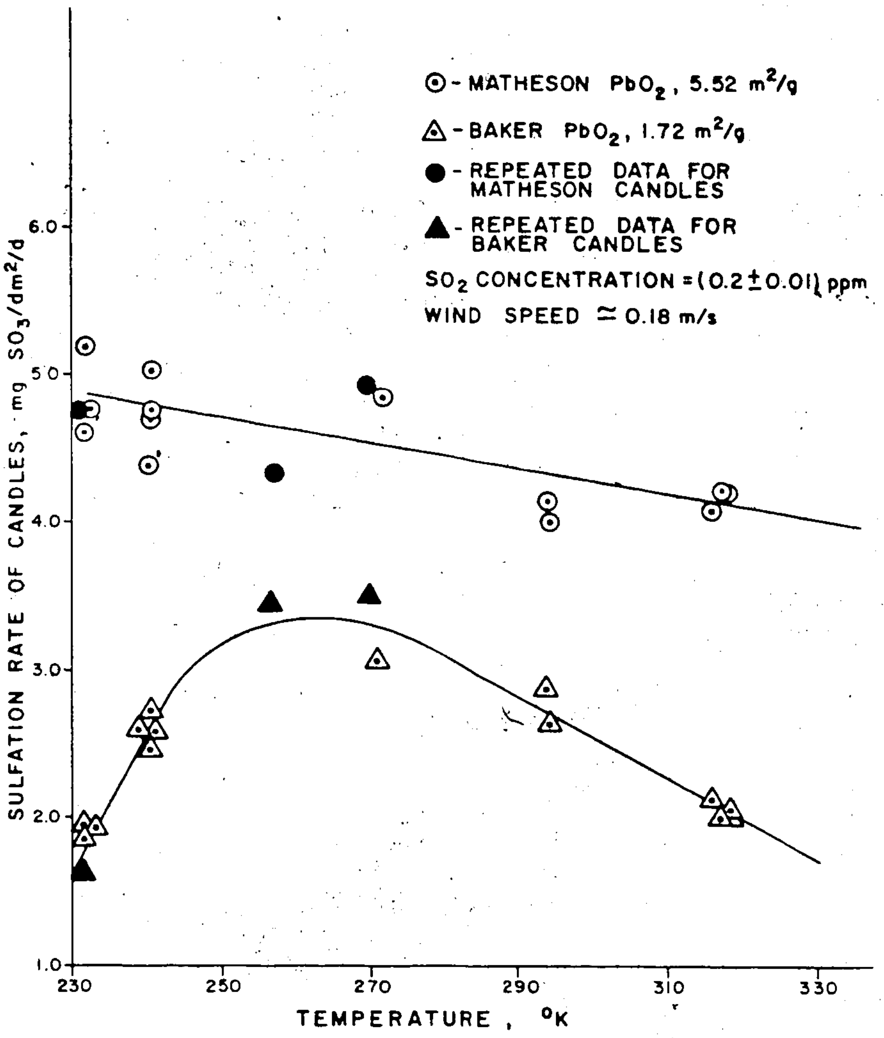


FIG. 5.4 EFFECT OF TEMPERATURE ON SULFATION RATES

The repeat runs were not as reliable as those reported in Table 5.4 due to equipment operational problems experienced in these tests. There were electrical interferences between the monitoring console output signal and the circuitry of the environmental chamber during the frequent switching on and off of the temperature control cycle. This caused sudden variations in the recordings of sulfur dioxide concentrations. Later, leaks developed in the air and water flow lines of the Davis sulfur dioxide analyzer and finally the analyzer pump had to be replaced since it gradually failed to pump the required flows. Eventually most of these problems were corrected but the data obtained in these runs had to be adjusted to correct some of the inaccuracies occurring during the runs.

In summary, apart from the fact that both the predicted and experimental sulfation rates vary little with significant temperature variations, it is difficult to explain the two opposing trends or the scatter in the Baker candle data. A possible explanation of the negative dependency of sulfation rate on temperature is discussed in Chapter VI.

5.5 Validation of Mass Transfer Models

The sulfation rates predicted by either of the two models discussed in Chapter III were compared with the experimental rates obtained from Figures 5.2 and 5.3. The predicted sulfation rates for the plates and candles at various wind speeds were calculated from equations 3.12 and 3.13 of Model-1, respectively. The experimental sulfation rates for candles and plates were computed from equation 5.5

and 5.7 which represent the best fit to the experimental data of Figure 5.3. The predicted rates from Model-1 were calculated at an average sulfur dioxide concentration of 0.2 ppm and average temperature of 25°C, which were the same conditions used in the wind tunnel tests to obtain data for Figure 5.3.

The sulfation rates so obtained were used in the calculation of predicted versus experimental correlation factors at various wind speeds. The correlation factor (C/W) at a wind speed is the ratio of average concentration of sulfur dioxide to the predicted or experimental sulfation rate. The predicted and the experimental data on sulfation rates and correlation factors are listed in Table 5.6. Figures 5.5 and 5.6 show a comparison of the correlation factors for sulfation candles and flat plates, respectively. Figure 5.7 shows a comparison of sulfation rates for candles and flat glass plates.

Model-1 predicts that the correlation factor, C/W is inversely proportional to the square root of the wind speed and this is in agreement with the experimental results. Figure 5.5 shows that for Matheson candles, the predicted and experimental correlation factors agree very well in the wind speed range of 0.3 to 8.4 m/s. For the flat-glass plates, the two correlation factors agree within 25% of each other at a constant wind speed as shown in Figure 5.6. The percentage figure was determined by taking a difference between the correlation factors at a wind speed and dividing the difference by the smaller of the two factors. It is not clear whether the agreement between the predicted and the experimental correlation factors holds true at wind speeds less than approximately 0.3 m/s. For example, the data in Figure 5.2 was collected at an average wind speed of 0.18 m/s in the exposure box and the correlation factor was calculated to be 0.043 at a sulfur dioxide concentration of 0.2 ppm. Even though a temperature difference exists between the data for Figure 5.2 and 5.3, the effect on correlation factors was considered insignificant. The predicted correlation factor of 0.089 from Model 1 is approximately double that indicated by Figure 5.2. A partial explanation of the disagreement between the two factors may be due to the inaccuracies associated with measurement of such low wind speeds. An accurate measurement of velocity profile in the exposure box at these wind speeds was difficult.

Figure 5.3 indicates that the sulfation rate of Matheson candles or flat-glass plates is proportional to an average of 0.42th power of the wind speed. This compares well with Model-1 where the sulfation rate is proportional to the square root of the wind speed. There is insufficient data to establish whether equations 5.5, 5.6 and 5.7 would be true at wind speeds less than 0.3 m/s. In the range of 0.3 to 8.4 m/s, an excellent agreement exists between the predicted and experimental sulfation rates for Matheson candles as shown in Figure 5.7. Model-1, however, predicts lower sulfation rates for flat-glass plates.

Table 5.6

PREDICTED (MODEL-1) AND EXPERIMENTAL CORRELATION FACTORS (C/W) AND SULFATION RATES

Average SO_2 Conc. = 0.2 ppm Average Temperature = 25°C

	Average Wind Speed, m/s				
	0.3	1.57	4.36	5.85	8.38
1. Matheson (6.3 cm diameter X 5.1 cm) Candle					
* Sulfation Rate by Model-1	2.9	6.5	10.6	12.3	14.7
+ Experimental Sulfation Rate	3.4	6.8	10.3	11.6	13.5
**Correlation Factor by Model-1	0.068	0.031	0.019	0.016	0.014
Experimental Correlation Factor	0.059	0.029	0.019	0.017	0.015
2. Flat-Glass Plate Coated With Matheson PbO_2 (12.5 cm X 8.0 cm)					
* Sulfation Rate by Model-1	2.2	4.9	8.2	9.5	11.4
+ Experimetal Sulfation Rate	2.8	6.4	10.5	12.2	14.5
**Correlation Factor by Model-1	0.092	0.040	0.024	0.021	0.018
Experimental Correlation Factor	0.071	0.031	0.019	0.0164	0.0138

* - Sulfation rate units in all cases are $mgSO_3/dm^2/d$

\+ - Experimental rates were obtained from equation 5.5 for Matheson candles and equation 5.7 for the plates

**- Units of correlation factors are $ppm/mgSO_3/dm^2/d$

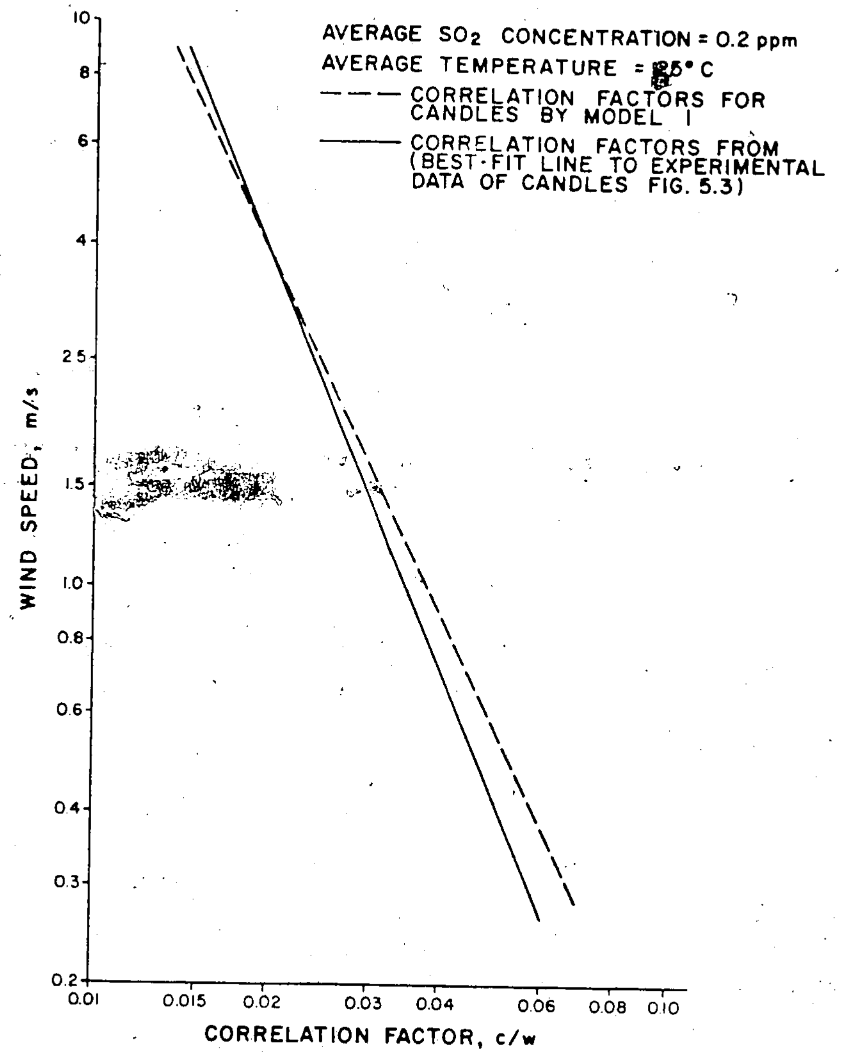


FIG. 5.5 COMPARISON OF PREDICTED (MODEL-I) & EXPERIMENTAL CORRELATION FACTORS FOR MATHESON CANDLES.

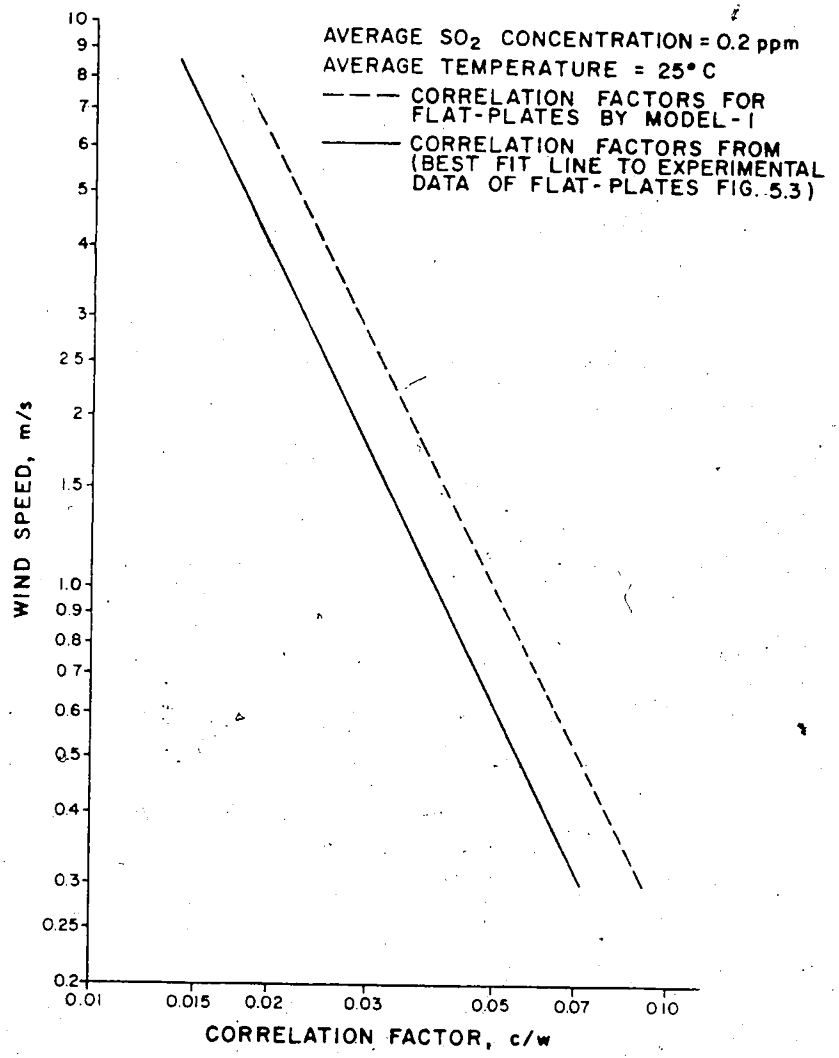


FIG. 5.6 COMPARISON OF PREDICTED (MODEL-I) & EXPERIMENTAL CORRELATION - FACTORS FOR FLAT-GLASS PLATES

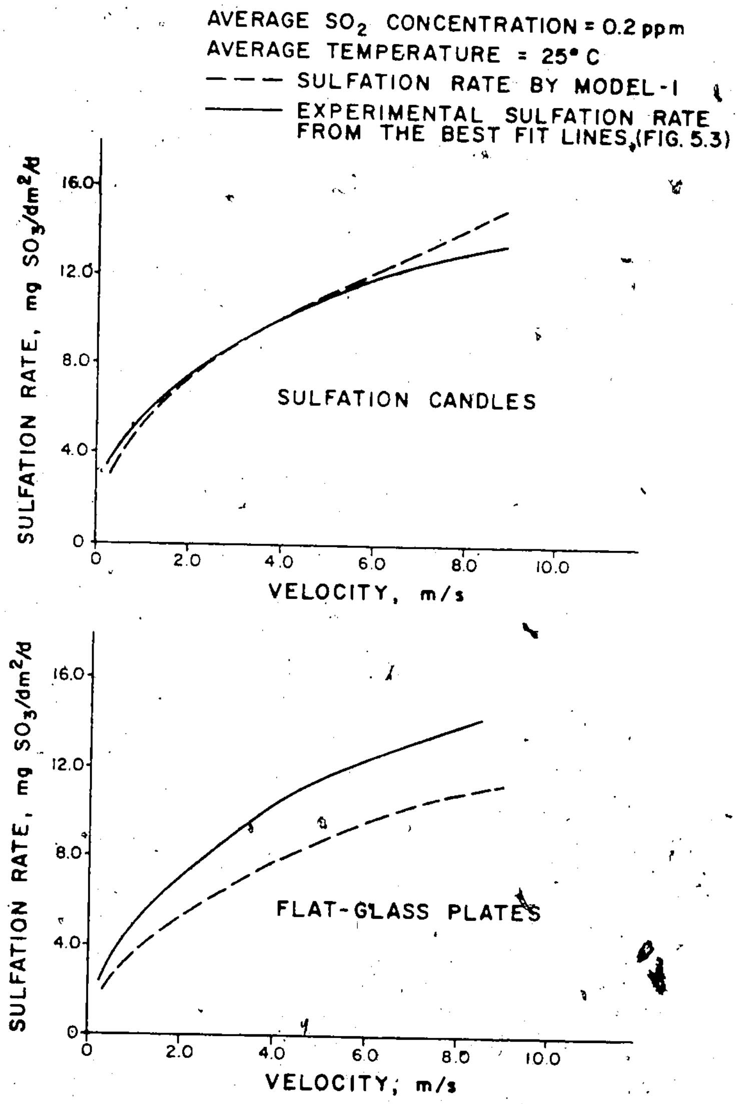


FIG. 5.7 COMPARISON OF PREDICTED AND EXPERIMENTAL SULFATION RATES AT VARIOUS WIND SPEEDS

Model-1 was used further to calculate sulfation rates of Matheson candles at various concentrations of sulfur dioxide while using a constant wind speed of 0.18 m/s. These rates were then compared with the experimental sulfation rates read from Figure 5.2 for the same candles. In both cases, the average temperature was -2°C. The two sets of data are listed below and plotted in Figure 5.8. The predicted sulfation rates were lower than the experimental rates. The difference in sulfation rates is believed to be more due to the difficulty in measuring accurately such low wind speeds. The measurements were at the extreme end of the hot wire anemometer scale. In any case, a logrithmic plot (not shown here) of the experimental data given below indicated that the sulfation rate was proportional to the concentration raised to the power 0.97. This compares well with Model-1 which indicates that sulfation rate is proportional to average sulfur dioxide concentration at a constant wind speed.

Matheson Candle

Average Wind Speed = 0.18 m/s   Average Temperature = -2°C

Sulfur Dioxide Concentration, ppm	Sulfation Rate, $mgSO_3/dm^2/d$ Model-1	Figure 5.2
0.1	1.12	2.4
0.2	2.24	4.65
0.3	3.37	6.9

As discussed in section 5.4, the temperature effects between -40°C and +40°C for both the predicted and experimental sulfation rates were small even though in one case the sulfation rate increased slightly with an increase in temperature whereas in the other, it decreased with an increase in temperature. The predicted sulfation rates were 2.35 and 2.12 at 40°C and -40°C, respectively at a constant wind speed of 0.18 m/s and gas concentration of 0.2 ppm.

Calculation of sulfation rate (Appendix C) by Model-2, which is independent of the effects of gas velocities resulted in sulfation rates of 47.88 mgSO_3/dm^2/d. The sulfur dioxide concentration was 0.2 ppm and the calculations were done at a temperature of -2°C. The calculated sulfation rate is obviously too high and inconsistent with experimental data.

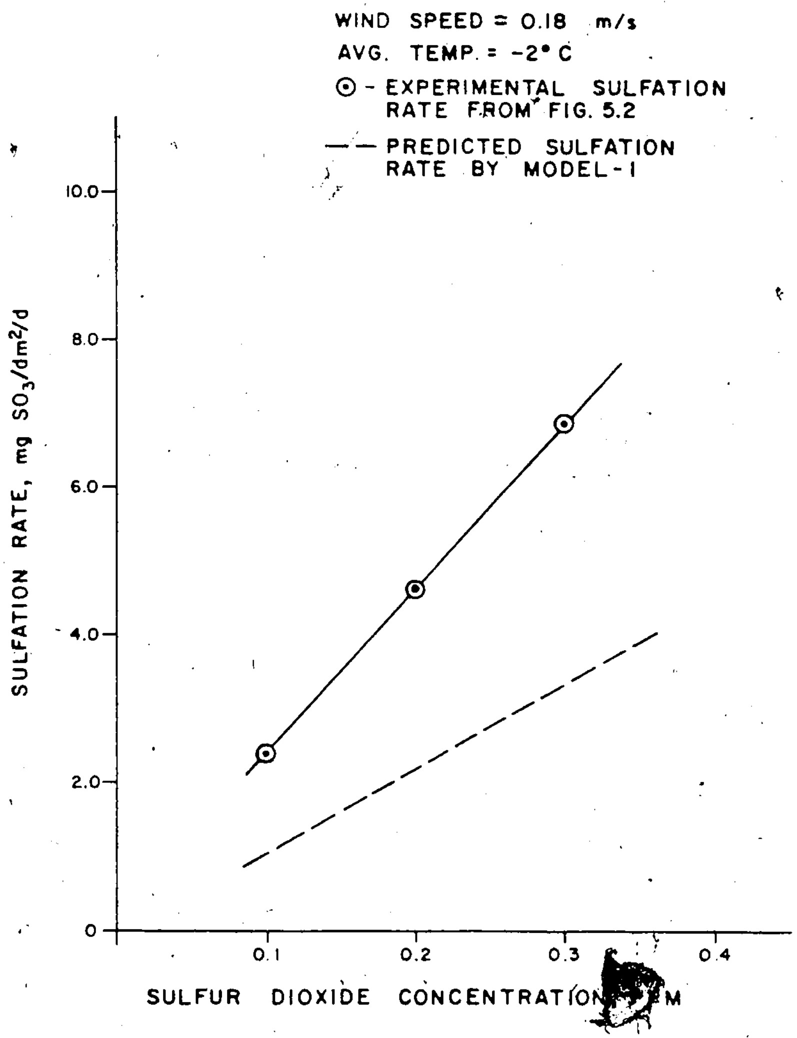


FIG. 5.8 COMPARISON OF PREDICTED AND EXPERIMENTAL SULFATION RATES AT VARIOUS SO_2 CONCENTRATIONS

5.6 Effect of Shelter Shape and Opening Areas

These experiments were conducted in the field at ambient exposure conditions using both the candles and Huey plates pasted with Matheson lead dioxide. The effect of shelter opening areas were evaluated using three cubical shelters whereas the shelter shape effects were determined by a comparison of sulfation rate of candles exposed in a cubical and a cylindrical shelter, both having approximately equal opening areas.

Since the practice of exposing the Huey plates and sulfation candles simultaneously in one shelter has been followed in Alberta at some locations, the field experiments were also conducted in the same manner. The Huey plates were 5 cm in diameter and were mounted on the ceiling of each shelter. The shelter also contained a Matheson lead dioxide cylinder mounted on its base. Three cubical shelters, C-1, C-2 and C-3 were designed with opening areas of 200, 600 and 1180 cm2 respectively. A round shelter R-1, as shown in Figure 2b, of 208 cm^2 opening area was also positioned in the field to determine shelter shape effects. All shelters were mounted on the roof of an air monitoring trailer approximately 3 metre high. The field data so obtained is listed in Table 5.6. The effect of the cubical shelter opening areas on sulfation rate is shown in Figure 5.9 and the effect of shelter shape in Figure 5.10.

Figure 5.9 indicates an approximate 25 percent increase in sulfation rate for cylinders with a six fold increase in the shelter opening area. However, the Huey plates are not affected by the increase in opening areas. Contrary to the findings of Huey [8], who had indicated that Huey plates reacted approximately 20% greater than the candles, the sulfation rates of Huey plates obtained in this study were significantly lower than that of the candles. A possible explanation of this result may be that the ambient air flowing through the shelter comes in contact with the candle first which is much larger in size and occupies a greater volume of the shelter space. Immediate reaction of sulphur dioxide with the much larger coated area of the candle would cause reduction of gas concentrations in air inside the shelter, thereby reducing the sulfation rate of Huey plates mounted just above the candles. Huey plates mounted on a separate receptable outside the cubical shelter and fully exposed to the atmosphere are recommended to arrive at a more reliable comparison of sulfation rates. A larger scatter in the Huey plate data in Figure 5.9 may also be due to such concentration variations in the shelter.

Figure 5.10 shows that the sulfation rates of candles in round shelters were lower than those obtained in the cubical shelter even though both shelters had approximately equal opening areas. This was contrary to the findings of Lawrence [26], who in his experiments in the wind tunnel found that the percentage of air flow inside the shelters at constant external wind speed was greater for cylindrical shelters than for the cubical shelter, and should therefore result in approximately 10 to 20% greater sulfation rate in the cylindrical shelter. Lawrence found that for a given external air speed, the highest percentage transmission occurs when a face of the shelter is perpendicular to the direction of the air flow. The lowest percentage transmission occurs when a corner of the shelter is into the wind. The round shelter was designed to minimize the directional effects of prevailing winds. However, in this study, unlike the cubical shelter which had long slits of rectangular openings aligned at the same height on all faces, the openings in the round shelter were unaligned and consisted of small slits punched randomly around the circumference. A comparison of the opening dimensions is given below.

	Cubical Shelter	Cylinderical Shelter
Total Number of Openings	16 (4 on each face)	28
Average Length of Each Opening	17.8 cm	5.72 cm
Average Width of Each Opening	0.7 cm	1.3 cm

Even though the opening area is approximately the same, it is now realized that the distribution of a large number of small unaligned openings around the circumference of the shelter may have attributed to a higher resistance to the free flow of ambient air through the round shelter than that encountered in the cubical shelter. This would result in smaller sulfation rates of candles in the round shelter.

Although the amount of data in these experiments is not extensive, but because the data were obtained under field conditions and consistently show a difference in sulfation rates ranging from 2 to 20% for each of these months, arbitrary changes made in shelter geometry and employment of one sulfation device or the other by an agency should be approached cautiously.

TABLE 5.7

FIELD DATA ON SULFATION RATES OF CYLINDERS VERSUS HUEY PLATES USING SHELTERS OF VARYING OPENING AREAS

Exposure Period (days)	Candle & Plate Shelter	Sulfation Reading % T		Sulfation Reading SO_4, mg/l		Sulfation Rate* $mgSO_3/dm^2/day$	
		Candles	Plates	Candles	Plates	Candles	Plates
Oct.4-Oct.26/76 (22 days)	C-1	87.5	-	12.4	-	0.134	-
	R-1	88.9	-	12.0	-	0.131	-
Jan.6-Feb.1/77 (26)	C-1	80.5	95.2	15.2	9.6+	0.140	0.088
	C-2		Rejected Due to Spilling				
	C-3	67.25	93.75	21.0	10.0+	0.193	0.091
	R-1	85.75	96.5	13.0	9.2+	0.119	0.085
Feb.1-Mar.4/77 (31)	C-1	79.25	94.4	15.6	10.0+	0.120	0.077
	C-2	72.0	95.6	18.8	9.5+	0.144	0.073
	C-3	68.75	93.0	20.0	10.2+	0.154	0.078
	R-1	80.0	96.3	15.2	9.2+	0.117	0.071
Mar.4-Apr.13/77 (40)	C-1	74.75	76.0	17.4	17.0	0.104	0.050
	C-2	61.6	71.9	23.0	18.6	0.138	0.066
	C-3	62.75	77.25	23.0	16.5	0.138	0.039
	R-1	80.12	65.5	15.2	21.6	0.09	0.051
Apr.13-May 4/77 (21)	C-1	86	83.6	13.0	14.0	0.148	0.079
	C-2	80	90.6	15.2	11.4	0.173	0.129
	C-3	82.75	79.0	14.2	15.8	0.162	0.089
	R-1	92.2	80.0	11.0	15.2	0.125	0.068

---

* The sulfation rate has been adjusted to account for a 13% loss in sulfate during digestion and filtration step in the analytical procedure (Section 5.7)

+ These readings for Huey plates (Figure 5.11) fall outside the selected calibration range and their precision is lower than other readings in this Table. The sulfation rates of these plates were calculated from extrapolated calibration curve.

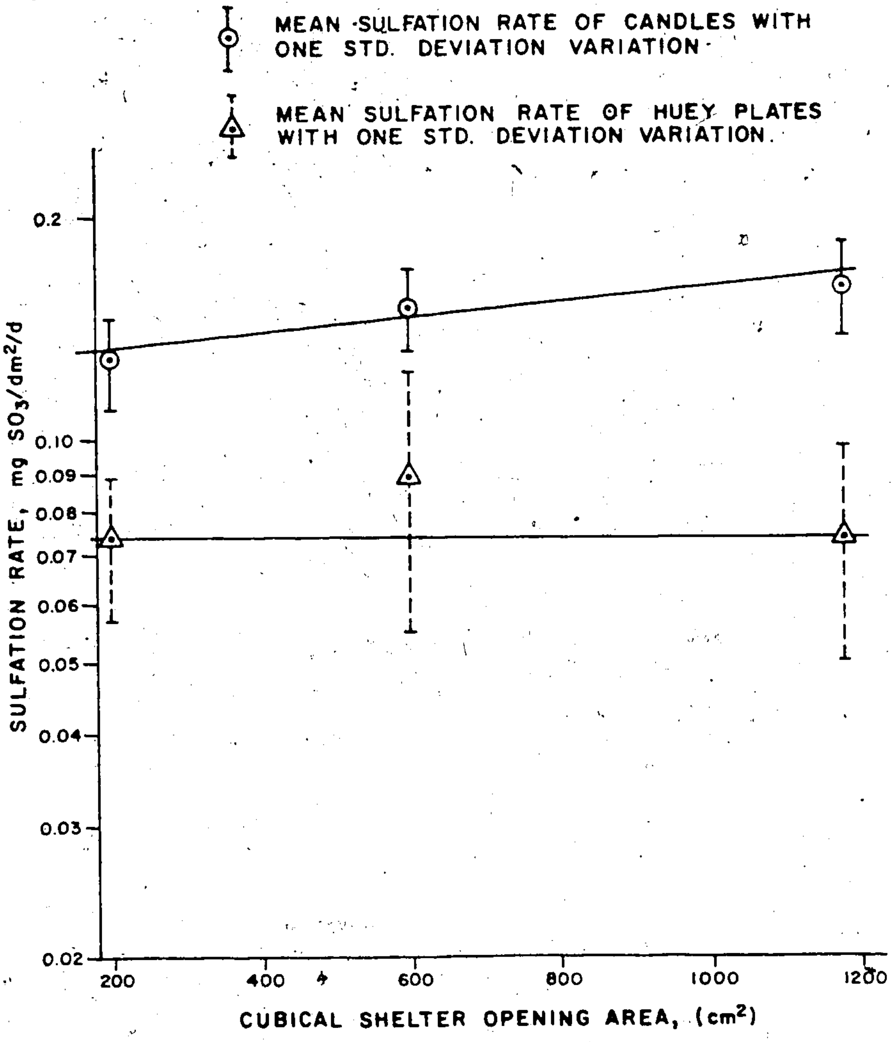


FIG. 5.9 EFFECT OF SHELTER OPENING ON SULFATION RATE

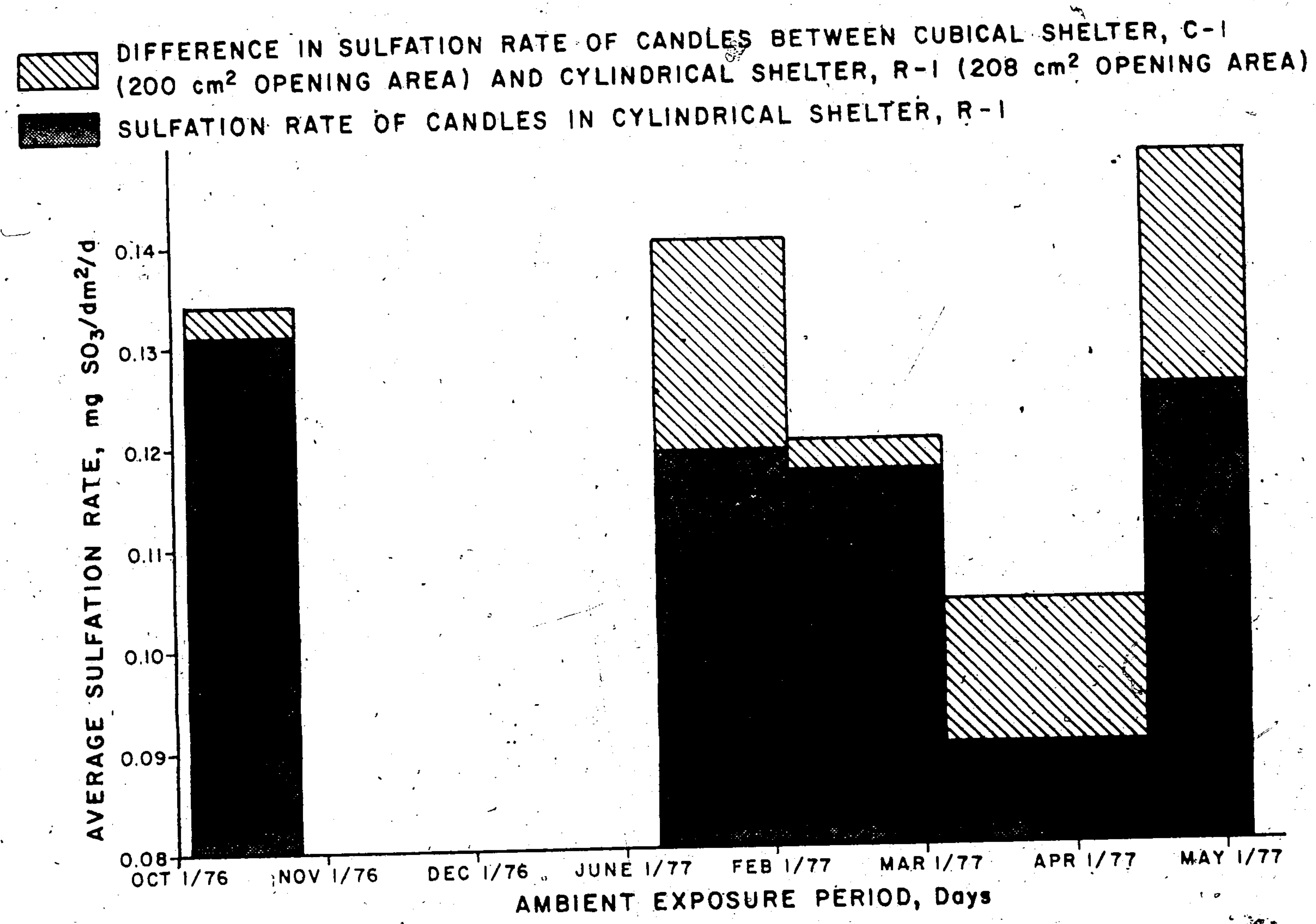


FIG. 5.10 EFFECT OF SHELTER GEOMETRY ON SULFATION RATE OF CANDLES

5.7 Analytical Accuracy and pH Effects

Accuracy of a measurement technique refers to a degree of difference between observed and known, or actual values [38]. The accuracy of the turbidimetric method was determined by conducting a sulfate recovery analysis and a study of solution pH effects. In the recovery analysis, samples of lead sulfate reagent of known sulfate concentrations were digested and analysed according to the turbidimetric method, and percentage recovery was calculated. As reported in Section A of Table 5.7, the average recovery was 87 percent of the total sulfate initially present as lead sulfate. This means that of the lead sulfate formed on sulfation candles exposed in the atmosphere, only 87 percent is recoverable by the turbidimetric method after digestion. A 13 percent loss occurs during the digestion and filtration step. This is confirmed further by the 100% recovery of sodium sulfate standards as reported in Section B of Table 5.5. Two known standards were mixed to obtain two sets of composite samples; the concentration for the first set being 17.46 ppm, which is near the lower sensitivity level of the analytical method and that of the second set 50 ppm, being near the upper level. The average recovery for both sets was almost 100 percent indicating that after the digestion step, there was no loss in sulfate recovery when standards are prepared using sodium sulfate as done in this study.

A study of the pH effects on measured sulfation levels was undertaken since many laboratories in Alberta were analyzing the sulfation devices at different pH levels, the two typical values being pH of 4.5 and 2.5. A study by See and Solomon [31] had indicated differences of up to 30% in the measured sulfation levels at pH of 6.1 and 2.8. The differences were observed between two series of standards, one series prepared at pH of 6.1 and the other at pH 2.7.

TABLE 5.8

ACCURACY OF TURBIDIMETRIC METHOD

A. Digestion and Analysis of Lead Sulfate Samples of 30 ppm and 60 ppm Sulfate Concentration

Sample Number	Pre-Digestion Sulfate Concentration 30 ppm		60 ppm	
	% T*	ppm*	% T*	ppm*
1	58.5	25.4	25.0	52.5
2	57.0	26.2	24.5	53.2
3	56.0	26.8	24.0	53.8
4	58.5	25.4	26.0	51.2
5	57.5	26.0	25.0	52.5
6	57.0	25.6	24.0	53.8
	Avg.	25.9		52.83
	S	0.548		0.989
	CV	2.1%		1.87%

$$\% \text{ Recovery} = \frac{25.9}{30} \times 100 = \frac{52.83}{60} \times 100$$

$$= 86.3 \qquad = 88.05$$

B. Recovery of Sodium Sulfate Standards

Sample Number	Added Standard #5 to #6 17.46 ppm		Added Standard #8 to #10 50 ppm	
	% T*	ppm*	%T*	ppm*
1	75	17.4	27	50
2	75.2	17.5	26.5	50.6
3	73.0	18.2	25.5	51.8
4	74.0	17.8	26.8	50
5	76.5	16.6	26.4	50.5
6	76.0	17.0	26.8	50.0
	Avg.	17.41		50.48
	S	0.567		0.700
	CV	3.2%		1.3%
Recovery	=	99.7%		101%

* - Refers to spectrophotometer readings, that is, percent transmission and corresponding concentration of sulfate from the calibration curve.

A plot of data obtained from these tests resulted in two lines intersecting at a point representing 0.25 mg sulfate such that the curve at pH 6.1 gave lower absorbances for equivalent levels of sulfate less than 0.25 mg. The reasons for the differences were the varying solubility of barium sulfate at various pH levels. However, if the standards are run at the same pH as the samples, See et al. indicated that the dissolved barium sulfate would be compensated for and the observed results would be correct. But the review of common-station study conducted in Alberta had indicated that, in some cases, laboratories were not adjusting the pH level of the standards or were adjusting the sample pH level different than that of the standards. Therefore, it was decided to evaluate the pH effects in the same manner, that is the standards, or the calibration curve, were at a different pH than the samples. In this study, the samples were, therefore, adjusted to pH levels of 4.5 and 1.5, although the calibration curve was obtained at a pH of 1.5. The pH 1.5 was selected to ensure complete reaction of excess carbonate such that effervescence of the carbon dioxide would not interfere with spectrophotometer readings.

The analyses were conducted at the two pH levels using field samples. The candles exposed in the field were stripped, digested, and filtered, and the resultant solution was adjusted to pH 4.5 and the solution volume was made up to 250 ml. An aliquot of the solution was adjusted to a pH of 1.5 with concentrated HCl. In all cases approximately a drop or two of HCl was necessary to adjust the pH of the aliquot to 1.5, thereby ensuring no dilution effects. The data is tabulated below.

Cylinder	mg/l Sulfate pH 4.5	 pH 1.5	 % Difference*
RE-1	12.2	12.6	3.2
CE-1	12.8	13.6	5.9
CR-1	17.0	17.8	4.5
CR-2	19.6	21.5	8.8

* Percentage based on correct result at pH 1.5.

The measured sulfation rate is approximately 6 percent greater at pH 1.5 than at pH 4.5 for field samples. It was observed that the adjustment of solution pH to 4.5 can cause large errors due to the effervescence of carbon dioxide still remaining in the solution. Upon addition of the precipitating reagent, a froth tends to form in the spectrophotometer cell and unless more than 10 to 15 minutes is allowed for the froth to disappear, the spectrophotometer readings would be affected.

The results obtained above merely indicate the potential of errors when a non-standardized analytical technique is followed by different laboratories. The error potential increases when the analytical techniques are completely different. In any event, since adjusting the samples and the standards to same pH compensates sulfate solubility variations [31], analysis can be conducted at either pH 4.5 or 1.5, but analysis at pH 1.5 is recommended because it minimizes interferences due to excessive effervescence by ensuring a more complete reaction of excess carbonate at lower pH.

5.8 Minimum Reproducible Detection Limit (MRDL)

During the common station study evaluation, the lack of a non-standard calibration method of laboratory spectrophotometers was determined to be one of the sources of error in the measured sulfation results. In a report [27] by the Environmental Protection Agency, 93% of the reproducibility variation in a test result was attributed to laboratory bias with the other 7% due to repeatability variation. Most of the apparent laboratory bias variation was rather a day effect primarily caused by dubious daily spectrophotometer re-calibration procedures. The report concluded that restricting the usage of the calibration curve to its upper region can halve the analytical procedure's percentage error contribution to the reproducibility variation. Although this report was produced to improve the source sampling method for oxides of nitrogen, the inferences drawn about the calibration of the spectrophotometer were considered to be equally applicable to the turbidimetric method. An attempt was, therefore made to conduct precision analyses [38] of the spectrophotometer calibration curve at various concentration levels. According to reference [38], precision refers to the reproducibility among replicate observations. The reference [38] describes the procedure for determination of precision in terms of standard deviation and coefficient of variation (CV) and this procedure has been followed here. Another reference [39] that discerns between the use of standard deviation and coefficient of variation as tools for determining precision in air pollution measurements indicates that typically acceptable values for the CV are between 5 - 10%.

TABLE 5.9

DETERMINATION OF SPECTROPHOTOMETER CALIBRATION CURVE PRECISION

Sample Number	Sulfate Concentrations from Calibration Curve, mg/l					Statistics		
	Run 1	Run 2	Run 3	Run 4	Run 5	Avg., x̄	S*	CV(%)**
1			Indeterminate					
2	5.5	4.5	3.5	3.0	4.0	4.1	0.96	23.5
3	8.5	7.5	9.5	6.2	7.0	7.7	1.02	16.7
4	11.5	10.5	8.0	8.8	10.8	9.9	1.46	14.7
5	14.2	14.8	14.8	15.6	16.0	15.08	0.72	4.7
6	20.5	19.0	20.8	20.8	19.5	20.12	0.82	4.1
7	28.5	30.2	29.2	29.5	29.8	29.44	0.64	2.2
8	39.0	40.8	39.2	39.0	40.8	39.76	0.95	2.4
9	49.8	47.5	51.0	50.5	49.8	49.72	1.34	2.7
10	60.8	61.0	60.8	61.5	59.5	60.72	0.74	1.2
11	69.5	80.0	66.2	66.8	69.5	70.4	5.58	7.9

---

* - Standard Derivation

** - The coefficient of variation (CV) as a measure of dispersion is computed by CV = $(s/\bar{x}) \times 100$.

The spectrophotometer calibration data is included in Appendix B but sulfate concentrations corresponding to percent transmission of each run are given in Table 5.8. The coefficient of variation at each concentration level was then determined to provide an indication of precision at that level. A plot of CV versus concentration level is shown in Figure 5.11. Corresponding to an arbitrarily selected variation of 6% in precision, a concentration range of 15 to 70 mg/l sulfate was used to obtain most of the results included in the previous sections of this chapter. In some cases an extrapolation of the calibration curve was employed. Figure 5.11 clearly shows a very rapid decrease in precision for concentrations below 15 mg/l sulfate. This error may be further exaggerated if more than one operator, that is, various laboratories are involved. Although lower sulfate concentrations are detectable by the turbidimetric method, a 15 ppm limit is the minimum reproducible limit within 6% deviation. The 95% confidence range at this level is 13.2 to 16.8 ppm.

In order that ambient sulfation results be compatible between various laboratories using turbidimetric method, it is recommended that a series of calibrations be conducted by each laboratory as done in this section and a precision analysis made. An agreed range of calibration curve should then be used by all laboratories and any sampling data falling outside this range rejected.

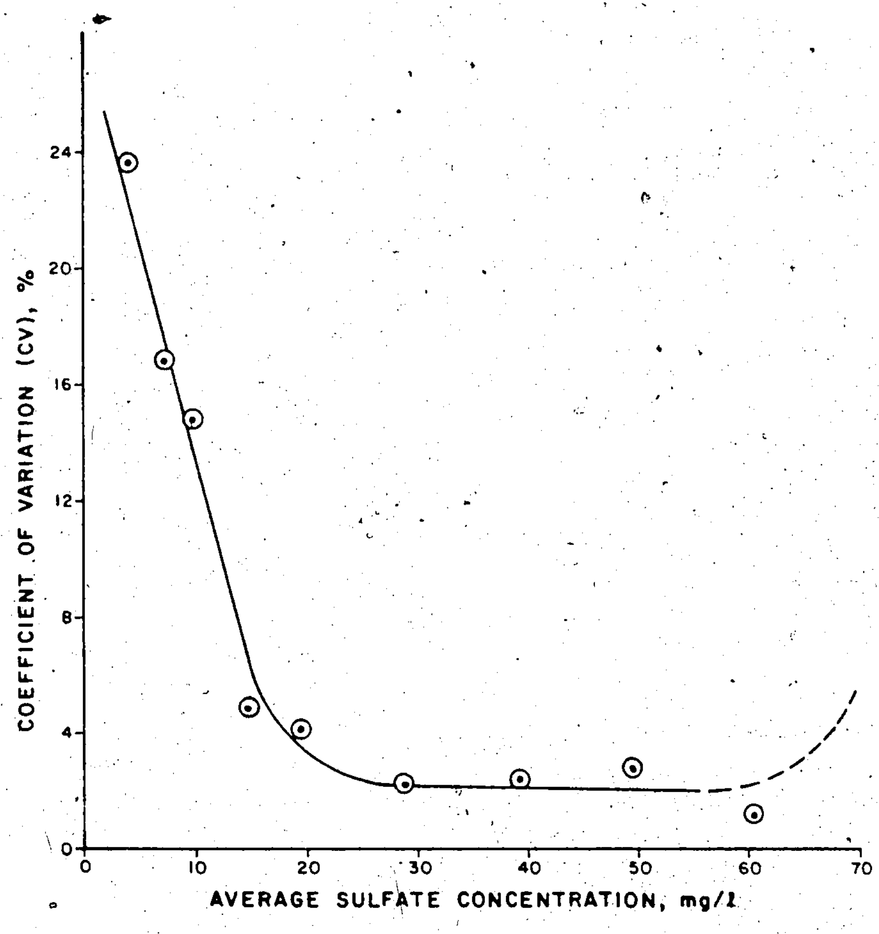


FIG. 5.11 PRECISION ANALYSIS OF CALIBRATION CURVE

CHAPTER VI

DISCUSSION

The sulfation rate of lead dioxide candles in Alberta are, in general, less than 0.3 mg $SO_3/dm_2/d$ at most monitoring stations [28]. An exa[illegible] of typical field data is illustrated in Table 5.7 of Chapt[illegible] The monitoring was conducted in the refinery row area of the City of Edmonton primarily during the winter months when ambient concentrations of sulphur dioxide are somewhat higher than in the summer months. Approximately 50% of the data in Table 5.7 indicates sulfation levels of candles around 15.0 mg/l or less. The remainder of the results are slightly higher. However, since sulfation rates in summer months are half as much or less as in the winter months [4,36], somewhat similar to the past experience in Alberta, the precision analysis of Section 5.8 show that almost all of the data on a yearly basis, is analysed near or below the minimum reproducibility detection limit (MRDL) of the turbidimetric method. The differences in the seasonal sulfation rates in Alberta may or may not be as high as indicated in references [4,36] since accurate measurements were difficult at such low sulfation rates. At the MRDL of 15 ppm, the 95% confidence interval permits a variation of up to 26% in the sulfation rate, that is

$$(16.8 - 13.3)/13.3 = 26\%$$

This variation at 95% confidence level can be reduced further to approximately 10% if the candles or plates are exposed for periods in excess of the typical one month so that the reacted sulfation levels are high enough to be in the mid-calibration curve range. At higher sulfation levels, measurements are more accurate and standard deviation is smaller. However, before exposing the candles or plates for longer periods, it is necessary that information about the adsorption capacity of sulfation candles be obtained. Various investigators [3, 14, 24, 29] have indicated that the sulfation rate of the candles remains linear with sulfur dioxide concentration only until a certain percentage of the initial amount of lead dioxide on the candle has reacted. Wilsdon and McConnell [3] indicated effectively no change in the rate of adsorption of sulfur dioxide until at least 15% of the lead dioxide had been consumed. This was an estimated figure based on very limited data and corresponds to an equivalent mean daily rate of sulfation of 13 as compared to that in Alberta of 0.3 mg $SO_3/dm^2/d$. Hickey and Hendrickson [24] in the first kinetic study of the sulfation reaction conducted experiments to determine this percentage, referred to as the "critical loading percentage" as described in Section 2.3.2. In order that the proportionality is maintained under different exposure conditions, information of the critical loading percentage and a basis for determining the maximum exposure period are required. This would ensure a standard design basis to obtain either a representative correlation factor between the sulfation rate of candles and ambient concentrations of sulphur dioxide or to compare different sets of sulfation data for establishing long-term trends. In this study the critical loading percentage of the Matheson lead dioxide powder was obtained by comparing it's surface area with the surface areas of the powders investigated by Hickey and Hendrickson. By interpolation the critical loading percentage was calculated as in the following.

Lead Dioxide	Specific Surface, m^2/g	Critical Loading Percentage
Matheson	5.52	6.71+
Baker	1.72	++
ACS 0.72 μ [24]	4.48	4.8
Baker 0.49 μ [24]	6.82	9.1

The maximum allowable exposure period for Matheson candles was determined from equation 2.2, using a maximum ambient concentration of 0.015 ppm* of sulfur dioxide prevalent in Alberta. That is,

$$M_C = (1873)\ (6.71)/(0.015)^{*}\ (17.92)^{**}\ (100)$$
$$= 467 \text{ days} \qquad \text{...Equation 6.1}$$

During the maximum exposure period, the sulfation rate remains constant since the exposure period was calculated using critical loading percentage. A similar calculation for Huey plates of surface areas between 19.64 ± 0.01 cm^2 was made. The plates were prepared by Alberta Environment and contained a minimum of 1.65 gm of the Matheson lead dioxide. Allowing exposure of plates to similar gas concentration, a conservative estimate of allowable exposure period was calculated to be

$$M_P = \left(\frac{1873}{7} \times 1.65\right)\ (6.71)/(0.015)\ (17.92)\ (100)$$
$$= 110 \text{ days} \qquad \text{...Equation 6.2}$$

$+\ 6.71 = [(9.1 - 4.8)\ (6.82 - 4.48)] \times (5.52 - 4.48) + 4.8\ m^2/g.$

++ - Indeterminate since Hickey [24] did not use powders in this range of specific areas.

* Estimated maximum 24-hour running average of SO_2 around gas plants in Alberta. In almost all cases, monitored concentrations of SO_2 were well below this level. The figure was arrived at by a random review of records of monitored data with the Alberta Environment.

** Adsorption coefficient in equation 5.3.

since critical loading percentage is inversely proportional to particle size [24], that is, the smaller the particle size, the larger the critical loading percentage, the allowable exposure period can be extended even further with lead dioxide powders having smaller particle size or greater surface area. In terms of specific surface area, lead dioxide with areas equal to or greater than about 9 m^2/g exhibited a marked increase in adsorptive capacity as compared to lead dioxides with smaller surface areas [24]. This corresponds to a particle size of 0.36 microns.

Considering that one month exposure periods during common station study generated sulfation rates at or below the minimum reproducible detection levels of the analytical method and that extended exposure periods are permissible, an improvement in the accuracy of sulfation results can be realized by extending the exposure periods to at least 3 month periods. This would allow sufficient increase in the accumulation of reaction product, thereby decreasing analytical errors inherent in the analyses of samples having sulfation levels near the MRDL. In turn, 3 month exposure periods would reduce the monitoring load and yet provide a better estimate of long-term sulfation trends of a region.

The use of Huey plates instead of cylinders is also feasible for 3 month exposure periods for concentrations of sulfur dioxide prevalent in Alberta. The effect of this change will be to reduce the cost of monitoring and the cost of operating the stations. The data collected in this manner would be representative of the 3 month period and attempts to calculate sulfation rates on a monthly basis by dividing with a factor of 3 would be correct only if ambient concentrations of sulfur dioxide remain constant from one month to the next in a 3 month period. And such an assumption may not hold true.

Ambient monitoring of sulfur dioxide concentrations in a region using continuous monitors could indicate whether sulfur dioxide concentrations remain constant in a 3 month period. In any event, the 3 month period could be chosen to represent a season and the data obtained would provide reliable seasonal variations.

Experimental evaluation of the effects of environmental parameters indicates that gas concentrations and wind speeds affect the sulfation rate of the static devices far more than the influence of humidity and temperature variations. Unless the reactive surface of lead dioxide paste was wet, the sulfation rate remained unaffected under various humidity conditions. This fact is in concurrence with the findings of other investigators [4, 25]. Sulfation rates at colder temperatures are marginally higher. There have been no previous experimental evaluations in a laboratory of the temperature effects at the sub-zero temperatures. Hickey [24] studied the temperature effects at 25°C and 45°C but was unable to maintain constant temperatures due to the exothermic reaction. The exposure period was too short and was limited to approximately 5 minutes. The study concluded no discernible effects at those temperatures. Wilsdon and McConnel [3] theoretically postulated that an increase in temperature of 1°C should yield an increase in the reactivity by 0.02%. This is contrary to the experimental evaluations of this study where a temperature decrease led to a slight increase in sulfation rate at the rate of 0.0084 $mgSO_3/dm^2/day/°K$. An attempt to plot the Arhenius equation from the temperature data in this study results in a positive slope instead of the expected negative slope for the lead dioxide reaction with sulfur dioxide. A possible mechanism of the reaction may involve physical adsorption of sulfur dioxide at lead dioxide surface before chemisorption and formation of the final product. The concentration of lead dioxide is assumed constant.

$$SO_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (SO_2^*)_A \xrightarrow{k_o} PbSO_4$$

...Equation 6.3

The amount of physical adsorption decreases rapidly as the temperature is raised. The pseudo-steady complex is chemiadsorbed forming lead sulfate as governed by,

$$R_o = k_o P_A^*$$

...Equation 6.4

where $P_A^* = k_f/(k_b + k_o) P_A$

...Equation 6.5

and P_A, P_A^*, represent initial and intermediate-complex concentrations of sulfur dioxide. The experiments to evaluate temperature effects were conducted under dynamic flow conditions at constant concentrations of sulfur dioxide and the insensitivity of the chemical reaction to temperature changes indicates that chemical reaction is not rate controlling.

The effects of temperature predicted by Model-1, however, indicate that the sulfation rate increases slightly at higher temperatures, contrary to the experimental findings. The important point to note is that regardless of how the temperature variations affect the sulfation rate, the temperature effects are very small and with the analytical technique used in this study, more precise determination was difficult.

A significant increase in the rate of sulfation with an increase in gas velocity would indicate that mass transfer through the fluid film is rate controlling. The plots in Figure 5.3, represented by Equations 5.5 to 5.7, indicate an average sulfation rate increase of 1.51 $mgSO_3/dm^2/d$ for each 1.0 m/s increase in wind speed in the range of 0.3 to 8.33 m/s. That is, the effect of wind speeds on sulfation rate is significant. A logarithmic plot of the experimental data for Matheson candles in Table 5.3 indicated that the data can be approximated by the power law equation,

$$W = \text{Constant} \times U^{0.4}$$

...Equation 6.6

Model-1 predicts that the sulfation rate is directly proportional to the square root of the wind speed. This indicates a good agreement between equation 6.6 and Model-1. The strong effect of the wind speed, therefore, indicates that gas phase resistance is the predominant rate controlling step. Further, a comparison with equation 2.5, which was derived from simultaneous measurements of sulfur dioxide and mean wind speed in the field is reasonably good allowing for differences in the two environments. Equation 2.5 indicates that at constant concentration, the sulfation rate is proportional to wind speed raised to the power 0.55. The sulfur dioxide levels for equation 2.5 were monitored with the lead dioxide method using cubical shelters to house the sulfation candles, and the winds speed were obtained from anemometers at a nearby weather station.

The mass transfer correlations for flow of gases transverse to cylinders and parallel to plates are shown in Figure B-3, of Appendix C and the Figure was taken from reference [40]. The figure indicates that within the range of Reynolds numbers of 0.7×10^4 - 3.8×10^4 for cylinders and 1.4×10^4 - 7.6×10^4 for plates used in this study, the convective mass transfer correlations for cylinders and plates at a fixed Reynolds number are within 20% or less. This would explain why in Figure 5.3 the sulfation rates for candles and plates at each wind speed were so close to each other.

Since gas phase resistance is controlling, velocity effects are significant, that is, the sulfation rate is proportional to the square root of wind speed. It should be possible to reduce and perhaps eliminate velocity influences by placing a velocity independent controlling resistance in series with the resistance in the gas phase. One approach to this would be to place a layer of inert, porous material such as a surgical gauze or a porous, non-adsorbent membrane of suitable material over the pasted layer of lead dioxide such that sulfur dioxide reaching the reactive surface would be essentially permeating the gauze or membrane without introducing velocity effects at a negligible velocity.

It is realized that rate controlling steps can change in the course of reaction and can overlap one another at certain stages. But such changes occur generally due to changes in the composition of the reacting mixture as well as changes in the particle size with the progress of a reaction. Since during this study the concentrations of the sulfur dioxide were maintained constant in all experiments and the maximum exposure periods, as calculated by equation 2.2, were not exceeded during experiments, the change in rate controlling step is not believed to have taken place due to either of the two reasons. As it was not the object of this study to determine the reaction mechanisms, additional kinetic studies would be necessary to define reaction mechanism further.

The above discussions have been to this point mainly related to the significance of the individual environmental parameter. However, how would each of these parameters affect the sulfation rate relative to each other in the field remains to be discussed. An attempt was made to provide a common basis of comparison such that the relative significance of wind speed, gas concentration, temperature and humidity in the range of values prevalent in Alberta could be determined. Equations 5.1, 5.5 and 5.8 were used for each respective parameter and the sulfation rates for Matheson candles were calculated at the upper and the lower limit of the selected range of each parameter. The two rates are then divided resulting in a fraction less than 1.0. The smaller the fractional value, the more sensitive is the sulfation rate to variation of that parameter in the specified range.

The average wind speed in Alberta over a long period, typically a month, was selected as being the same as used by Liang et al. [14]. That is, the average wind speed is assumed to be no higher than 2.2 m/s and lower than 0.67 m/s. This is considered a reasonable range because sulfation instruments are generally set at a height of one to two metres above ground, where the wind speeds are low. A temperature range of -30 to +30°C was used which encompasses the complete range of yearly temperature variations in Alberta, with few exceptional days. Similarly, the range of sulfur dioxide concentrations was selected between 0.001-0.015 ppm. Due to the fact that recorded ambient concentrations on a daily basis in Alberta are very frequently zero, the selected concentration range refers to the maximum recorded 24-hour averages likely to occur in any part of Alberta. This data was obtained from a random review of the Department records around a few gas plants. The ratio of sulfation rate is unaffected by whether the range of parameters are based on a monthly or daily basis. However, a larger or smaller range than the ones selected above would affect the following analysis. With respect to humidity variations since the sulfation rate remains unaffected as shown in Figure 5.1, the ratio of sulfation rates at any two humidities would be 1.0. The ratio of sulfation rates of Matheson candles was now calculated at wind speeds of 0.67 and 2.2 m/s from equation 5.5, and was found to be 0.61. Similarly, this ratio at temperatures of +30 and -30°C from equation 5.8 is 0.89 and at sulfur dioxide concentrations of 0.001 and 0.015

ppm, from equation 5.1 is 0.38, respectively. That is,

C: U : T_A : Humidity :: 0.38 : 0.61 : 0.89 : 1

The above analysis merely indicates the relative significance of various parameters affecting sulfation rates assuming that variations in each parameter at a site in Alberta would be as extreme as indicated by each parameter range. However, since ambient concentrations of sulfur dioxide have been shown to decrease significantly with increase of wind speeds for wind speeds less than 2.5 m/s [32], the significance of wind speed and concentration affects are related and would tend to compensate individual affect on sulfation rates under ambient conditions. Further, on a long-term basis, the average range of variation of each parameter is expected to be smaller than those selected above and the relative significance deduced above would change. This would especially be the case for gas concentrations since the selected range merely represents the maximum daily concentrations. In summary, it can be stated that the gas concentration and the wind speed effects are significantly more influential and that the effects of temperature and humidity are negligible for conditions prevalent in Alberta.

The determination of a universally applicable correlation factor (C/W) is difficult due to uncertainty of several factors such as change in day-to-day emissions of sulfur dioxide, change in the wind speed distribution throughout the day and the stability conditions of the atmosphere. However, experimental data indicates that the correlation factor remains constant at a constant wind speed with changes in gas concentration (Figure 5.2) and varies sharply with changes in wind speed at a constant gas concentration (Figure 5.7). Figure 5.2 also indicates that due to the effect of different specific surface areas on sulfation rate, the correlation factors would be different for different lead dioxide reagent. The sensitivity of correlation factors to fluctuations in wind speed indicates that these factors should be used only over a small range of wind speeds. Therefore, if the selected range of average wind speeds of 0.7-2.0 m/s is applied to figure 5.5 and 5.6, the average correlation factors obtained from the experimental data for cylinders and plates are 0.0337 and 0.0375 with ±25% deviation over the selected range. This compares very well with the Huey [8] suggested factor of 0.035, and the field measured values [4,6] between 0.02-0.04. The predicted correlation factors by Liang et al. from Model-1 were 0.023 to 0.041 in the above wind speed range.

However, if the wind speed effects on the candles or plates could be virtually eliminated by covering the reactive lead dioxide surface with a porous, non-adsorbent gauze such that sulfur dioxide reaching the reactive surface would be essentially at zero velocity at all times in the field, a reliable correlation factor from field data could be obtained provided that for some period of time a continuous monitor is operated at the same location as the static device. Such an information could be used to compare the correlation factor from the field data with that predicted by Model-1. This hypothesis is based on the experimental data of this study which indicates that the correlation factor remains constant at a wind speed with changes in gas concentration. Since wind speed effects could be eliminated by covering the reactive surface with a gauze, it would seem reasonable that even if ambient gas concentrations vary, the correlation factor would not vary.

Since it has been shown that experimentally determined sulfation rates are proportional to 0.4th and 0.97th power of wind speed and gas concentration as compared to the 0.5 and 1.0 power of the two parameters by Model-1, respectively, the assumption of gas phase resistance as the predominant controlling step is justified. Model-2 is independent of wind speed effects and the sulfation rate is assumed to be proportional to the square root of the concentration of gas, contrary to the experimental findings in this study.

The field experiments of Section 5.6, although limited in data, consistently show a difference in sulfation rates due to differences in shelter geometry for each month during the 5 month test period. The results indicate that arbitrary changes made in shelter geometry or employment of different sulfation devices could introduce sources of error in the measured data. The round shelter as designed in this study resulted in lower sulfation rates contrary to the findings of Bowden [7] and Lawrence [26]. A round shelter designed as illustrated in [26], would be needed to confirm results obtained by Lawrence and Bowden.

The sulfation rates of Huey plates were found to be lower than the candles, contrary to the findings of Huey [8]. The possible reasons for our results are already discussed in Section 5.6. It is, therefore, recommended that the Huey plates be exposed in separate receptacles instead of with the cylinders in cubical shelters.

The experimental results obtained during the evaluation of analytical accuracy and pH effects indicate a sulfation loss of 13% during the digestion step. A correction factor accounting for the sulfation loss was incorporated in the data of Chapter V as indicated in the footnotes of various tables. The results of the pH effect evaluations indicate approximately a 6% increase in measured sulfate levels when the aliquot was adjusted from a pH 4.5 to pH 1.5. However, See and Solomon [31] in their work found that large errors up to 30% in the measured sulfate levels can occur if the samples are adjusted to a different pH than the standard calibration curve. See et al. evaluated the differences in measured sulfate levels at pH 6.1 and 2.8. The errors are largest at the low levels of sulfate due to low reproducibility. See et al. indicated further that if standards and samples are adjusted to the same pH, the errors caused by the different solubility of barium sulfate at different pH levels do not occur and the analysis can be conducted at either pH. However, at higher pH, large errors can occur due to effervescence of carbon dioxide still remaining in the solution. For this reason, it is recommended that analysis be conducted at pH 1.5.

See and Solomon [31] also found that analytically reproducible results were not obtainable below 75 g sulfate even with two aliquot from the same solution. They used an aliquot size of 5 ml containing the above amount of sulfate. The conversion of 75 g/5 ml sulfate to ppm gives exactly the same MRDL of 15 mg/l SO_4 as found in this study using an independent precision analysis approach. This corresponds to a sulfation rate of 0.104 mg SO_3/dm^2/day on a 30-day basis.

In the turbidimetric method, the reproducibility of the analytical results depends on the sulfate concentration of the filtrate after adjustment of filtrate to pH 1.5 (Appendix B). For this reason, only the concentration of sulfate per litre in the filtrate is used as the minimum reproducible detection limit.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The work done in this study leads to the following conclusions and recommendations.

1. The minimum reproducible detection limit of sulfate concentrations by the turbidimetric method is 15 mg/l SO_4. The method can detect sulfate concentrations below the above limit but the reproducibility is difficult and unreliable. The 15 mg/l sulfate concentration corresponds to a sulfation rate of 0.1 $mgSO_3/dm^2/d$ averaged over a 30-day period. The calibration curve should be used within the 15 to 70 mg/l SO_4 range, preferably avoiding the reading of the curve at either extreme. Precision analysis (Section 5.8) by each participating laboratory should be conducted to verify the calibration range. The turbidimetric method is a simple, useful and inexpensive method that can provide consistent results within the specified limits.
2. A large number of sulfation rates obtained during the common station study (Appendix A) were less than 0.1 $mgSO_3/dm^2/d$. Although the sulfation rates at other sites in Alberta, or during the winter season, may be somewhat higher at some of the sites than the above mentioned minimum rate, generally the sulfation levels obtained during a one month exposure period are too low to be analysed reproducibly by the turbidimetric method. Therefore, to obtain better quality data with the turbidimetric method, it is recommended to extend the exposure period of the sulfation devices to a minimum of 3 months.

3. Huey plates and sulfation candles contain a sufficient amount of lead dioxide for an exposure period of 3 months. The significant effect of specific surface area on sulfation rates mandates that the lead dioxide reagent used by various companies have the same specific area per gram of the reagent. Since a marked increase in adsorptive capacity has been indicated for lead dioxides having surface areas greater than 9 m^2/g [24], other lead dioxides with greater specific surface areas, instead of the Matheson reagent, can be used if necessary, to allow even longer exposure periods.
4. Huey plates and candles should not be exposed simultaneously in the same shelter, due to the possibility of interference between the two devices as discussed in Section 5.6. Huey plates mounted on a separate receptable are recommended to arrive at a reliable comparison of sulfation rates between plates and candles.
5. Among the environmental factors considered, sulfur dioxide concentrations and wind speeds affect the sulfation rates significantly. Humidity has no effect unless condensation at the coated surface occurs. Humidity and temperature effects are negligible for conditions prevalent in Alberta. The wind effects result in an average sulfation rate increase of 1.51 mg $SO_3/dm^2/d$ for each 1 m/s increase in wind speed in the range of 0.3-8.4 m/s. Considering that sulfation rates in Alberta are generally less than 0.3 mg $SO_3/dm^2/d$, the wind effects are very significant.

6. In the field, it should be possible to reduce and perhaps eliminate the wind speed effects on sulfation rate by covering the reactive lead dioxide surface with a porous, non-adsorbent gauze such that only the variations in the gaseous concentrations of ambient air would affect the sulfation rate. If a continuous sulfur dioxide monitor is operated concurrently with a static device, more reliable correlation factors are possible.
7. Since the Huey plates have adequate capacity for longer exposures, the plates could be used instead of the candles. As the field evaluations of Huey plates and candles in this study were not very extensive and were not conducted under proper exposure conditions, such as separate receptacles for the two devices and 3-month exposure periods, a further field evaluation is necessary before the sulfation candles are rejected for field use.
8. The experimental sulfation rates were found to be proportional to 0.4th and 0.97th power of wind speed and gas concentration as compared to 0.5th and 1.0 power of the two parameters by Model-1, respectively. This indicates that gas phase resistance is the predominant rate controlling step. Within the wind speed range of 0.7-2.0 m/s, the average correlation factor for cylinders and plates is 0.0355 ppm/mg $SO_3/dm^2/d$ within ± 25 percent.
9. After the completion of digestion and filtration steps of the turbidemetric method, only 87 percent of sulfate present initially is recoverable. An adjustment in sulfation rates to account for the 13 percent loss should be made.

10. Since adjusting the samples and standards to same pH compensates barium sulfate solubility variations but potential for analytical error due to effervescence of carbon dioxide is greater at a pH 4.5 than at pH 1.5, it is recommended that the pH of the standards and solutions be adjusted to 1.5 before conducting sulfate analysis.
11. The lead dioxide candles and plates should be prepared and analysed as described in Sections 4.1.5 and 4.2.2 of this report.
12. With the above recommendations the common station study should be attempted again to recheck the consistency of results between various laboratories. For the refinery row area in Edmonton, if ambient sulfur dioxide concentrations and wind speeds are also measured at the same time, a check of the derived correlation factor could be made.
13. Additional studies are required to evaluate the effect of the shelter geometry and shelter opening areas on sulfation rates.

NOMENCLATURE

B	Frequency or pre-exponential factor
b	Width of flat glass plate as defined in the derivation between equation 3.6 and 3.7
C	Concentration of sulfur dioxide, ppm
ΔC_A	Concentration gradient, mole/cm^3
C_A, $C_{A,o}$	Sulfur dioxide concentration in air and gel phase, mole/cm^3
$\overline{C}_A$	Average sulfur dioxide concentration at gel phase, mole/cm^3
C_B	Initial lead dioxide concentration in gel, mol/L
d	Diameter of sulfation candles, cm
D	Diffusivity of sulfur dioxide in air, cm^2/s
D_{eff}	Effective diffusivity of sulfur dioxide in gel, cm^2/s
E	Activation energy
f	Function of Reynolds number in equation 2.3
ΔG	Change in free energy of a reaction, KCal/mole
H	Height of sulfation candle, cm
k	Reaction velocity constant in equation 3.3
k_c	Convective mass transfer coefficient, cm/s
k_f, k_b, k_o	Rate constants for reactions in equation 6.3
K	Correlation factor relating sulfur dioxide concentration to sulfation rate, ppm/mgSO_3/dm^2/d
l,d	Characteristic length of flat plate or diameter of Huey plate, cm
M	Exposure period of sulfation devices, days
M_1, M_2	Molecular weight of a metal and its oxide, respectively
M_c, M_p	Maximum Exposure period of sulfation candles and Huey plates, respectively, days.

N_A	Mass flux, moles/cm^2/s
P	Critical loading percentage, % (equation 2.2)
Q	Adsorption coefficient, mgSO$_2$/ppm/d
R	Gas constant in equation 3.3
R_o	Rate of reaction as defined by equation 6.4
Re_d	Reynold number based on the diameter of sulfation candle as defined in equation 3.11, dimensionless
Re, Re_x	Reynold numbers for flat plate with a length or characteristic dimension x, as defined in equations 3.13 and 3.9, respectively
S_c	Schmidt number as defined in equation 3.9, dimensionless
Sh_{av}	Average Sherwood number (equation 2.3)
Sh_x, Sh_d	Sherwood numbers based on characteristic dimension x or d, respectively (dimensionless)
t	time as defined in equations 3.14 to 3.17
t'	temperature, °C
T	Percent transmission of light during spectrophotometer measurements
T_A	Absolute temperature of reaction, °K
U	Wind speed, m/s
W	Sulfation rate, mgSO$_3$/dm^2/d
W_1	Rate of mass transfer by equation 3.10, mole/cm^2/s
W_A	Rate of mass transfer, mole/s
Y_p	Refers to sulfation rate of plates coated with Matheson lead dioxide, mgSO$_3$/dm^2/d
Z	Refers to the location of reaction front in Model-2 and at time t, is denoted by $Z_{f(t)}$

Greek Symbols

α	As defined by equation 3.22
ρ, ρ_0	Gas density at temperatures of t' and 0°C, respectively.
ρ_1, ρ_2	Gas density of a metal and its oxide, respectively
μ, μ_0	Gas viscosity at temperatures of t' and 0°C, respectively
τ	Length of test period in days in equation 3.21.

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APPENDIX A

COMMON REFERENCE EXPOSURE STATION RESULTS

TOTAL SULFATION RESULTS - BY CANDLES, $mgSO_3/dm^2/d$
1974

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1*	.206	.058	.015	.025	.023	.116	.025	.136	.121	.139	.055	-
2*	.207	.277	.098	.090	.086	.017	.103	.100	.127	.111	.106	.075
3	.124	.133	.064	.025	.052	.098	.094	.075	.056	.043	.072	-
4	.150	.171	.073	.062	.041	.029	.039	.058	.038	.009	.046	.039
5++	.173	.122	-	-	-	-	-	-	-	-	-	-
6	.059	.235	.046	.067	.078	.134	.070	.081	.060	.099	.082	.124
7*	.046	.163	.034	.015	.165	.159	.114	.045	.051	.193	-	-
8	.091	.047	-	.024	.081	.042	.025	.044	.091	.103	.127	.086
9++	.071	.079	.029	-	-	-	-	-	-	-	-	-
10*	.189	.137	.073	.073	.217	.157	.144	.126	.366	.084	-	-
11	.183	.157	.011	.072	.027	.011	.083	.028	.063	.102	-	-
12++	-	-	-	-	.072	.063	.061	.055	.065	.0574	.063	.0502

* - Sign test indicates biased results for these labs.

++ - Very little data and therefore rejected.

Sign Test:

To determine if two data sets are consistent, one simple test of a significant bias is to check the sign of the differences in the data set values. If the differences among all of data set values are negative, one has considerable doubt about the lack of a bias as it would be expected that on the average, half would be positive and half negative if no bias were present. For example, if two data sets had 10 values and 9 out of 10 differences were negative or positive, the chance of this happening when there was no bias present is very small. Unless some outside check of the results is available, that is, against some reference standard, it is not possible to assume that one data set is not biased and the other set is biased.

In this analysis, the common station data for each laboratory in the preceeding table were subtracted from all other laboratories and if a large number of signs of differences in the data set values were found to be of one kind, that particular laboratory was considered biased. Laboratories marked by an asterisk (*) are biased whereas those marked (++) have very few data points to conduct proper evaluation.

APPENDIX B

CALIBRATION PROCEDURES

A. Spectrophotometer and pH Meter

A Bosch-spectronic 20 spectrophotometer was used in these studies to determine the sulfate concentrations of the exposed samples. A stock solution containing 1000 mg/l SO_4 was prepared by dissolving 1.479 g of anhydrous sodium sulfate in 10% sodium carbonate solution. The mixture was diluted to one liter with the sodium carbonate solution.

Aliquots of 2, 4, 8, 10... ml (as shown in Table B-1) of the stock solution were diluted to approximately 900 ml with 1% sodium carbonate solution and adjusted to a pH 1.5 by adding diluted HCl, prepared by mixing equal volumes of acid and distilled water. Each of the solutions was diluted to a liter in a volumetric flask with distilled water. The concentrations of standard solutions so prepared are shown in column 2 of Table B-1.

A 50 ml portion of each of the standard solutions was placed into a matching set of nessler tubes and a fixed amount (approximately 1.0 g) of Sulfaver IV reagent was added. The samples were mixed and stirred to precipitate sulfate. A 5 minute period was allowed to elapse before reading the percent transmission. The spectrophotometer was set at 100% transmittance at 420 nm using distilled water blanks before reading any of the standard solutions. The zero reading was adjusted as well.

During these studies the spectrophotometer calibration was checked by reading percent transmittance of at least two standard solutions before processing any set of test samples.

TABLE B-1

DATA FOR CALIBRATION OF SPECTROPHOTOMETER

Sample Number	Standard Conc., SO_4(mg/l)	Calibration Readings, % T					Average % T
		Run 1	Run 2	Run 3	Run 4	Run 5	
1	2.0	100	99	100	100	100	99.8
2	4.0	95.5	96.5	97.5	98	97	96.9
3	8.0	92.5	93.5	91.2	95	94	93.3
4	10.0	88	89.5	93	92	89	90.3
5	15.0	83.2	82	81.8	80	79	81.2
6	20.0	69.0	72.2	68.0	68.2	71	69.7
7	30.0	53.2	50.5	52	51.5	51	51.6
8	40.0	38.1	36.0	37.8	38	35.8	37.1
9	50.0	27.0	29	26	26.5	27	27.1
10	60.0	19	18.8	19	18.5	19.8	19.0
11	70.0	15.0	12	16.2	16	15	14.8
12	80.0	11.2	10	13.2	13	12	11.9
13	100.0	8.0	6.5	7.5	8.	8.0	7.6

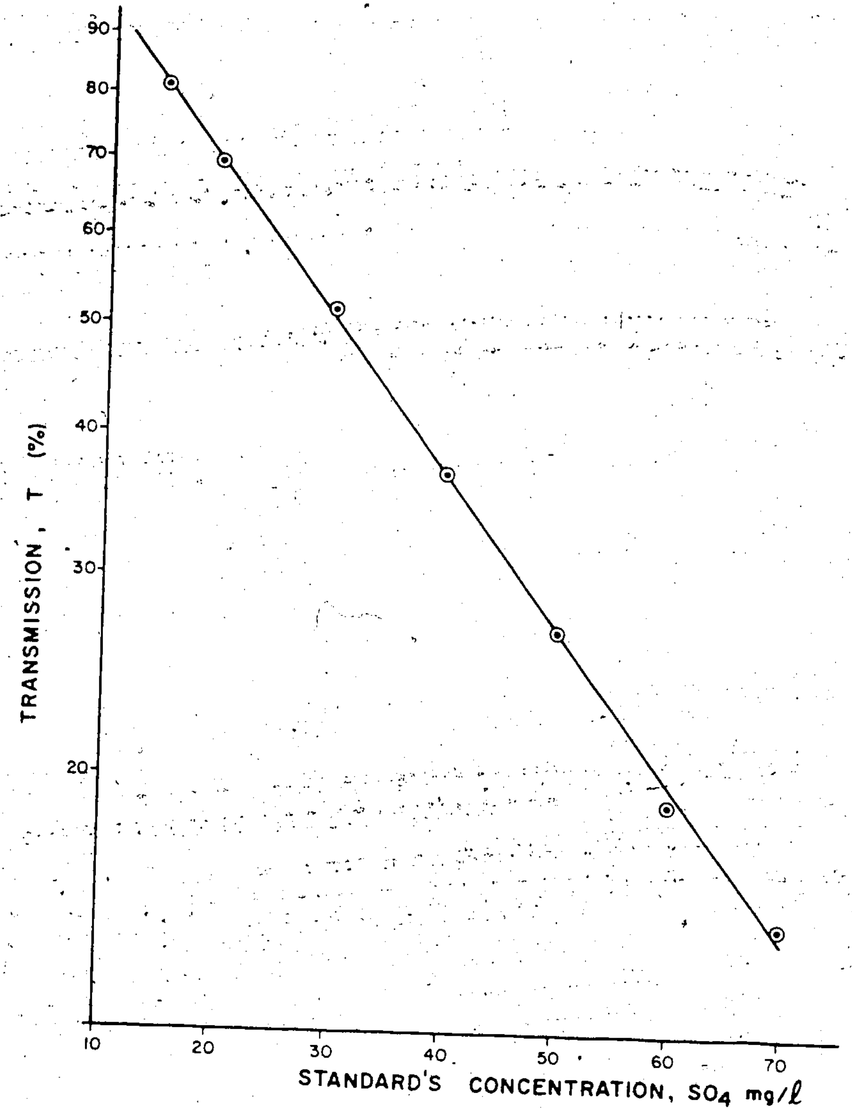

FIG. B-1 SPECTROPHOTOMETER CALIBRATION

Table B-1 shows percent transmittance variation for each of the standard solutions during the five runs. A calibration curve was prepared by plotting an average percent transmittance versus mg/l SO_4 concentration as shown in Figure B-1. The calibration data was used statistically to determine the precision criteria as discussed in Section 5.8.

The pH meter was calibrated each time by using a set of three standard solutions of pH 4, 7, 9. There was hardly any change noticed in the pH meter calibrations during the course of these experiments. The solution in the reference pH electrode needed touching up from time to time.

B. Rotameter Calibrations

In this study the two rotameters used in the monitoring console circuit (Figure 4.3) were calibrated as a set against a calibrated wet test meter. Rotameter No. 1 was installed to provide a very small constant flow rate to sweep any permeated gas in the oven and rotameter No. 2 would measure the diluted mixture. Since the purpose was to generate gaseous mixture of known concentrations, individual calibration of each rotameter was considered unessential. The calibrations were conducted by placing the rotameters exactly as shown in Figure 4.3 with the exception that the oven did not contain a permeation tube and the exposure system was replaced with a calibrated wet test meter.

The flow rate in rotameter No. 1 was maintained at a constant float setting of 5 while varying the float setting of rotameter No. 2. The rotameter setting (16, 5) in Table B-2 represents rotameter No. 2

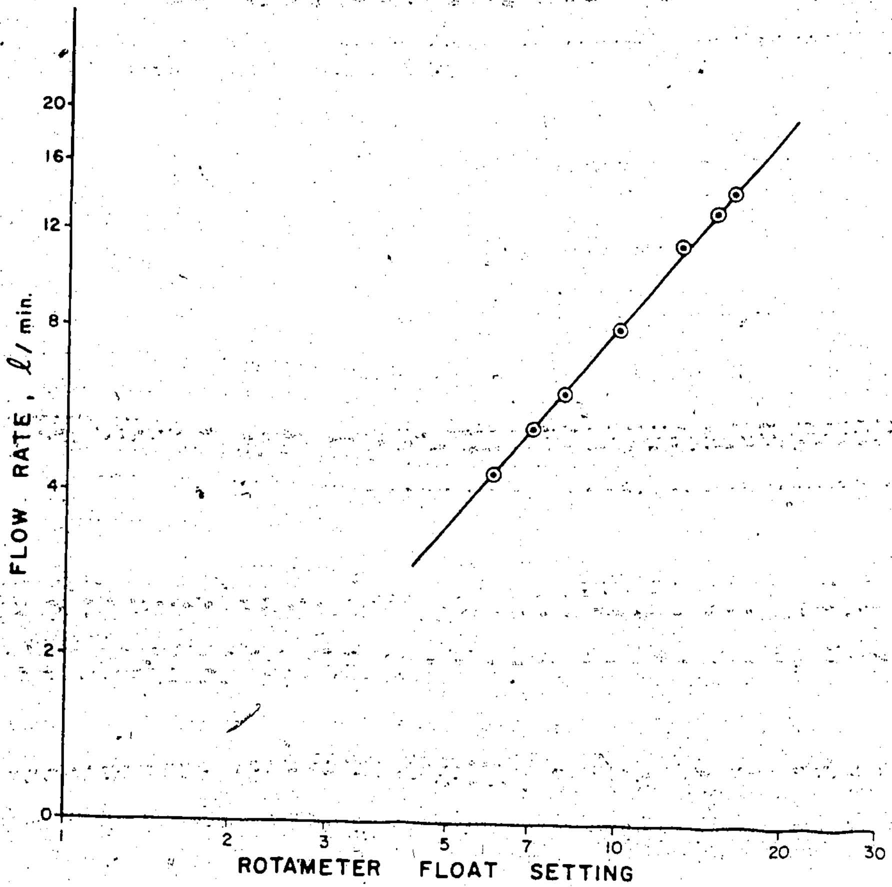

FIGURE B-2 ROTAMETER CALIBRATION

set at 16 and rotameter No. 1 at 5 on their respective scale. A stop watch was used to determine the flow rate of air through the wet test meter in litre per minute. Temperature corrections were not necessary since the whole apparatus was operated at room temperature throughout the duration of the study. A calibration curve plotting flow rate in litre per minute on the y-axis and rotameter No. 2 settings along the x-axis is shown in figure B-2. Rotameter No. 1 setting was maintained constant throughout the range of calibrations.

C. Permeation Tube and Monitoring Console

The objective of this calibration was to obtain the concentration of sulfur dioxide per chart division of the chart recorder used in the monitoring console. This was achieved by determining the permeation rate of the permeation tubes followed by computations using the calibrated rotameter flow rates.

Generally, the permeation tubes are made by sealing a condensable vapour as a liquid in Teflon tubes. Following an initial induction period, the material in the tube permeates through the wall of the tube at a uniform rate.

The permeation rate of each tube was determined by placing it in a constant temperature bath for several intervals of time. During each time interval lasting for one to two days, the weight loss of the permeation tube was recorded. An AID Model 300 portable calibration system was used to provide a constant temperature bath. The permeation rate of each tube was obtained by calculating an average rate of weight loss over several intervals of time. The permeation rate varied less than 10 % over different intervals of time. During the permeation rate tests, the clean air flow rate was held constant. Figure 4.3 describes the calibration system for the tubes if the exposure system was removed and the effluent gas vented. A column of water may be used to scrub sulfur dioxide before venting it to atmosphere. Having determined the permeation rate at a constant temperature, the clean air flow rate was varied by adjusting the rotameter float setting. This would provide an effluent gas mixture of varying concentrations of sulfur dioxide. The exposure system containing the chart recorder is now connected to record the output corresponding to each flow rate setting. Corresponding to each rotameter setting shown in Table B-2, the concentration of sulfur dioxide gas was determined by the following equation:

$$C = \frac{R}{F} \times \left(\frac{24.12}{MW}\right) \qquad \text{...Equation B.1}$$

where C = Sulfur dioxide concentration, ppm (volume per volume)

R = Permeation rate of each tube, ng/min

F = Air flow rate at each setting, L/min

24.12 = Molar volume at 21°C and 1 atmosphere, L/mol

and MW = Molecular weight of sulfur dioxide, g/mol.

The quantity in parenthesis in equation B.1 converts the permeation rate from a weight per unit time to a volume per unit time. The permeation rate is constant throughout the life of the tube as long as the temperature of the tube is held constant.

The sulfur dioxide concentrations in ppm were divided by the corresponding number of chart divisions to obtain ppm per division. Once the ppm per division at constant temperature and over a range of flow rates was obtained, the temperature of the bath and the gas flow rates could be varied to obtain gaseous mixtures of desired concentrations. This would also provide the range of concentrations at a constant temperature that can be generated by varying the clean air flow rates. The system is therefore well-defined and calibrated. Table B-2 shows such a calibration for one permeation tube.

Example: Calculation of sulfur dioxide concentration using Equation B.1

(a) Permeation Rate Calculation:

Given: average weight loss over 68 hour period = 0.0238 g

Therefore,
$$R = \frac{0.0238 \text{ X } 10^9 \text{ ng}}{68 \text{ X } 60 \text{ min}}$$

$$= 5833 \text{ ng/min}$$

(b) Therefore, if the rotameter flow at a setting of (13, 5) was 11.31 L/min, the concentration of sulfur dioxide from equation B.1, is

$$C = \frac{5833}{11.31} \times \frac{24.123}{64} \times \frac{1}{10^9}$$

$$\frac{\text{ng}}{\text{min}} \times \frac{\text{min}}{\text{l}} \times \frac{1}{\text{mol}} \times \frac{\text{mol}}{\text{g}} \times \frac{\text{g}}{10^9\ \text{ng}}$$

$$= 0.1944 \text{ ppm}$$

The corresponding output at the chart recorder was 9.7 divisions, therefore the

$$SO_2 \text{ conc/div} = \frac{0.1944}{9.7} = 0.02$$

Other values in Table B-2 were calculated similarly.

TABLE B-2

CALIBRATION DATA FOR ROTAMETERS AND MONITORING CONSOLE

AT CONSTANT TEMPERATURE = 25°C

Rotameter Setting	Flow Rate (L/min)	Chart Div	SO_2 Conc. (ppm)	ppm/div
(16, 5)	14.16	8	0.155	0.019
(15, 5)	13.31	8.25	0.165	0.020
(13, 5)	11.31	9.7	0.194	0.020
(10, 5)	7.97	13.75	0.276	0.020
(8, 5)	6.09	19.2	0.361	0.019
(7, 5)	5.2	23.5	0.422	0.018
(6, 5)	4.3	28.5	0.511	0.018

The above table indicates that provided the flow rate settings were maintained between (16, 5) and (8, 5), the conc/div reading of 0.02 would be valid within 5 percent.

APPENDIX C

A. Mass Transfer Model Calculations

1. Calculation of sulfur dioxide diffusion in air at 25°C and atmosphere pressure. Sulfur dioxide concentrations vary between 0.08 to 0.032 ppm in the gas mixture.

   From Table K in the Appendix of reference [30], the values of σ and ϵ/k are obtained.

	mol.wt.	σ, in °A	ϵ/k, in K
SO_2	64	4.290	252
Air	29	2.617	97

Therefore, $\sigma_{AB} = (\sigma_A + \sigma_B)/2 = 3.95$

$$\epsilon_{AB}/k = (\epsilon_{A/k} \times \epsilon_{B/k})^{0.5} = 156{\cdot}3$$

and $\epsilon_{AB}/kT = 156.3/298 = 1.906$

From Table J in reference [30], the collision integral;

$$\Omega = 1.094$$

Therefore, at an atmospheric pressure of 27 inches or 0.904 atmosphere, the diffusion coefficient is given by equation,

$$D_{AB} = \frac{0.001858(T)^{1.5}\,(1/M_A + 1/M_B)^{0.5}}{P \quad \sigma_{AB}^2 \;\; \Omega}$$

$$= \frac{0.001858\ (298)^{1.5}\ (1/64 + 1/29)^{0.5}}{0.904 \times (3.95)^2 \times 1.094}$$

$$= 0.138\ \text{cm}^2/\text{s}$$

2. Standard data at 25°C and 1 atmosphere,

$\mu_{air} = 0.018$ centipoise $= 1.8 \times 10^{-4}$ g/cm.sec

$\rho_{air} = 0.001293$ g/cm^3

diameter of candle = 6.30 cm

height of candle = 5.08 cm

3. Model-1, Gas Phase Resistance Controlling

At a wind tunnel setting = 2, which corresponds to a wind speed of 1.575 m/s,

$$Re_d = \frac{dU\rho}{\mu} = \frac{6.3 \times 1.575 \times 0.001293 \times 10^2}{1.8 \times 10^{-4}}$$

$$\text{cm} \times \frac{\text{cm}}{\text{s}} \times \frac{\text{g}}{\text{cc}} \times \frac{\text{cm} \times \text{sec}}{\text{g}}$$

$$= 7171.2$$

and Schmidt no., $S_c = \dfrac{\mu}{\rho D_{AB}}$

$$= \frac{1.8 \times 10^{-4}}{0.001293 \times 0.138}$$

$$\frac{\text{g}}{\text{cm} \times \text{sec}} \times \frac{\text{cc}}{\text{g}} \times \frac{\text{sec}}{\text{cm}^2}$$

$$= 1.003$$

Sherwood no. from equation 3.11 of Chapter III is,

$$Sh_d = \frac{2}{(d/2H + 1)\ \text{In}\ (1 + 2H/d)} + 0.6\ S_c^{1/3}\ Re_d^{1/2}$$

$$= \frac{2}{(6.3/10.16 + 1)\ \text{In}\ (1 + 10.16/6.3)} + 0.6\ (1.003)^{1/3}\ (7171.2)^{1/2}$$

$$= 1.285 + 50.863$$

$$= 52.1489$$

From equation 3.13 for reactive candle, the sulfation rate,

$$W = C \frac{8424\ D\ Sh_d}{T_A\ d}$$

$$= \frac{0.2 \times 8424 \times 0.138 \times 52.1489}{298 \times 6.3}$$

$$= 6.568\ \text{mgSO}_3/\text{dm}^2/\text{d}$$

The remaining calculations are similarly performed at wind speeds of 0.30, 4.36, 5.85 and 8.38 m/s. For flat plates, Reynold number is calculated by using the length of plate equal to 12.5 cm instead of the diameter of the candle and equations 3.12 are used for calculation of sulfation rate.

B. Model 2 - Gel Phase Diffusion Resistance Controlling

Equation 3.23 is used for sulfation rate calculation in this Model:

$$W = 4.7 \times 10^6\ (D_{eff}\ \bar{C}_A\ C_B/1.13\ (\pi)^{0.5}\ \tau\ )^{0.5}$$

where $D_{eff} \simeq 0.1D$

and C_B = 3.35 g-moles of lead dioxide per liter assuming

1 mm gel thickness and 8 gm PbO_2/dm^2

Therefore,

$$W = 4.7 \times 10^6\ (0.0138 \times \left(\frac{0.2 \times 10^{-6} \times 273}{22.4 \times 271}\right) 3.35/1.13 \times 2\ (\pi)^{0.5})^{0.5}$$

$$= 47.88\ \text{mgSO}_3/\text{dm}^2/\text{d}$$

C. The mass transfer correlations for cylinders and plates from reference [30] are represented by curves 3 and 5 in figure B-3 respectively. Table 5.3 provides the respective equations.

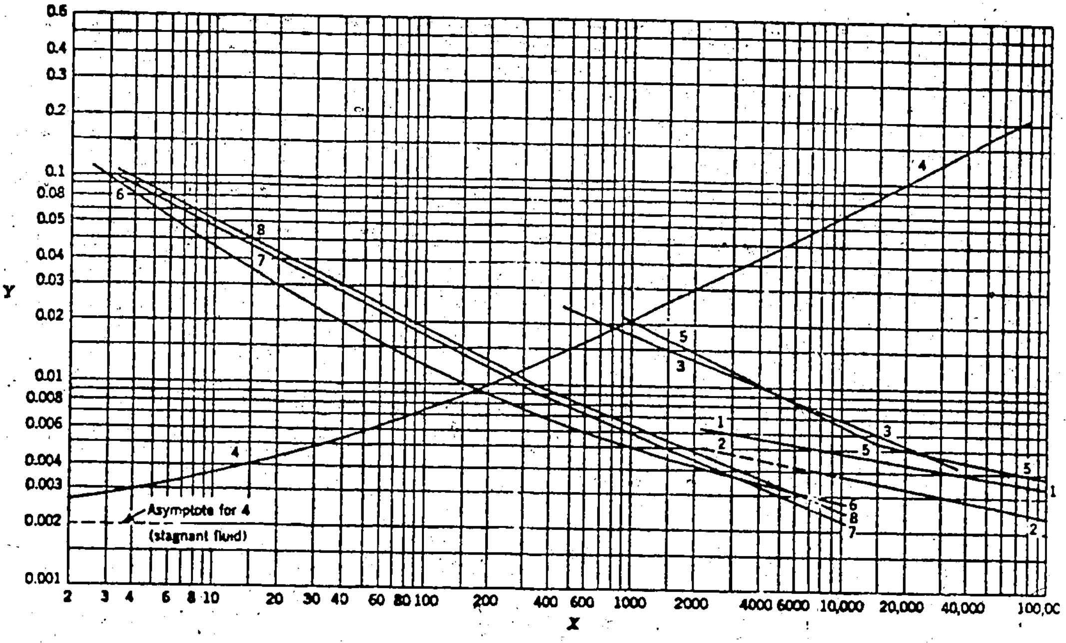

Figure B-3 Mass and Heat-Transfer Correlations.

TABLE 5-3 DATA FOR FIGURE B-3

Curve	Situation	Operation	X	Y	Sc range
1	flow inside pipes	mass transfer	Re	$j_D = \frac{k_G'P}{G_M}(\mathrm{Sc})^{2/3}$ $= \frac{k_x}{L_M}(\mathrm{Sc})^{2/3}$	0.6–3000
2	flow inside pipes	heat transfer	Re	$j_H = \frac{h}{c_pG}(\mathrm{Pr})^{2/3} = \frac{c_f}{2}$	
3	flow of gases transverse to cylinders	mass transfer	Re′	$j_D = \frac{k_G'P}{G_M}(\mathrm{Sc})^{0.56}$	0.6–2.6
		heat transfer	Re′	$j_H = \frac{h}{c_pG}(\mathrm{Pr})^{0.56}$	
4	flow of gases past single spheres	mass transfer	$\mathrm{Re}''(\mathrm{Sc})^{2/3}$	$\frac{k_cd_p}{D_{AB}}(10^{-3})$	0.6–2.7
		heat transfer	$\mathrm{Re}''(\mathrm{Pr})^{2/3}$	$\frac{hd_p}{k}(10^{-3})$	
5	flow of gases parallel to plates	mass transfer	Re‴	$j_D = \frac{k_G'P}{G_M}(\mathrm{Sc})^{2/3}$	0.6–2.1
		heat transfer	Re‴	$j_H = \frac{h}{c_pG}(\mathrm{Pr})^{2/3}$	
6	flow of liquids through packed solids	mass transfer	Re''/ϵ	$j_D(10^{-1}) = \frac{k_x}{L_M}(\mathrm{Sc})^{0.58}(10^{-1})$	164–10,700
7	flow of gases through packed solids	mass transfer	Re″	$j_D(10^{-1}) = \frac{k_y}{G_M}(\mathrm{Sc})^{0.66}(10^{-1})$	0.6
8	flow of gases through packed solids	heat transfer	Re″	$j_H(10^{-1}) = \frac{h}{c_pG}(\mathrm{Pr})^{0.66}(10^{-1})$	

$\mathrm{Re}' = \frac{d_c v_\infty \rho}{\mu}$

d_c = cylinder diameter, in ft

G_M = molar mass velocity, in lb mole/hr ft²

$\mathrm{Re}'' = \frac{d_p v_\infty \rho}{\mu}$

d_p = sphere diameter, in ft

L_M = molar liquid mass velocity, in lb mole/hr ft²

$\mathrm{Re}''' = \frac{l v \rho}{\mu}$

l = distance from upstream edge, in ft

$G = \rho v_\infty$ = mass velocity

ϵ = void fraction