



**Royal Oak
Mines Inc.**

Head Office
2nd Floor - 1425 W. Pender St.
Vancouver, B.C.
V6G 2S3

Tel: (604) 682-8320
Fax: (604) 682-4286

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Mr. Emery Paquin
Director,
Environmental Protection Division
Department of Renewable Resources
Government of the Northwest Territories
600, 5102 - 50 Avenue
Yellowknife, N.W.T.
X1A 3S8

Dear Mr. Paquin:

Re: Information on SO₂ Scrubbing of Roaster Exhaust Gas at Golden Bear Mine

Please find attached two papers covering the scrubbing of a pyrite roaster off gas stream at the Golden Bear Mine in Northwest British Columbia. I hope these will be of value to you as background information.

Regards,

Larry Connell
Manager of Environmental & Metallurgical Services

cc: K. Weston

2600 - 1214.1.5

DEVELOPMENTS IN PASSIVE MONITORING OF AMBIENT SULPHUR DIOXIDE

Henry L. Bertram, C. Bruce Christensen, Violet I. Hannak,
and Nirmal C. Das

Air Analysis and Research Group
Alberta Environmental Centre
Bag 4000 Vegreville, Alberta, T0b-4L0

ABSTRACT

Due to industrialization sulphur dioxide has become one of the major pollutants of concern. Methods of measuring ambient sulphur dioxide fall into two categories; dynamic and passive. Dynamic samplers consist of two types; continuous analyzers which give a continuous reading of the sulphur dioxide level, and filtration type devices which fix the sulphur dioxide by absorption and give an integrated average reading. Both types of dynamic sampler require air to be pumped through the device at a calibrated rate. Passive samplers consist of an absorbent material on some type of substrate which is left exposed to ambient air. Passive devices rely on ambient air currents, gaseous diffusion, or permeation to bring the sulphur dioxide in contact with the absorbent. This allows them to be placed in a location free of power and maintenance requirements. In practice, these devices are exposed for long periods of time, which allows accumulation of a sufficient amount of sulphur dioxide to meet analytical requirements for the detection of low ambient levels. Unfortunately, the low cost of passive samplers has to be balanced against their inability to determine precise ambient levels. By utilizing recent developments in ion selective membranes and diffusion screen technology, improvements in the quantitative reliability of passive samplers is possible. Research by the Air Analysis and Research Group at The Alberta Environmental Centre in developing improved passive samplers has shown promise in enhancing their quantitative reliability. The results of these sampling and analysis techniques and their precision and accuracy studies will be presented.

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INTRODUCTION

Sulphur dioxide measurements in ambient air have been used for the past fifty years (1) to measure the impact of pollution emissions on the environment. The methods used have ranged from impinger solution absorption with wet chemical analysis to automated photometric procedures requiring very sophisticated instrumentation. The least expensive and one of the most widely used procedures is the lead dioxide candle (Fig. 1) as developed by Wilsdon and McConnell (1, 2, 10). This device consists of a paste, prepared from gum tragacanth and lead dioxide (PbO_2) supported by painting it onto a gauze tape which is wrapped around the centre of a glass jar. The advantages of the lead dioxide candle are low cost, lack of maintenance, and absence of electrical power requirements. The candles are simply placed in a protective enclosure (Fig. 2) and left exposed to the air for an extended period of time, such as one to three months. The disadvantages of candles are that the measured levels of sulphate are not linearly related to the time integrated average sulphur dioxide concentration, except under controlled conditions. They are affected by wind velocity, wind direction, temperature, humidity, and ambient concentration in a non-linear fashion. There are also some interferences, such as absorbed hydrogen sulphide which can be oxidized to sulphur dioxide on the candle. An improved sampler having a slightly higher reactivity was developed by Huey, et al (3), and is called the Huey plate (fig. 2). It is prepared by including cellulose fiber in the paste formulation and uses Petri dishes for a support. Huey plates have the advantage of not requiring housing to protect them from the weather.

In order to overcome these disadvantages and retain the advantages of low cost and low maintenance we have developed a monitor (Fig. 3) utilizing passive absorption and diffusion screens to achieve a controlled sampling rate. The principle has been previously applied to the sampling of organic vapors (5), where it has proven very useful for determining integrated average concentrations. Our sampler achieves quantitative sampling over the commonly occurring range of meteorological conditions and is compatible with existing sulphation candles and Huey plates. It is constructed by fastening a diffusion barrier, consisting of two layers of fine screen and perforated plate, over the open side of a Petri dish. The absorbing material is the same as that used in a Huey plate.

Further improvements to the monitor have been achieved by adapting an efficient absorbent which is less hazardous to handle and easier to analyze in the laboratory. Filter pack studies using 25% K_2CO_3 and 10% glycerol on cellulose filter paper (7, 8, 14) are presently being used in dynamic sampling of ambient sulphur dioxide and in a passive permeation type of device as developed by Orr, et. al. (7). Adaptation of K_2CO_3 impregnated filters to our diffusion controlled passive sampler has shown good correlation with the diffusion controlled PbO_2 sampler and improves the precision of the laboratory analysis procedure.

FIG. 1 TOTAL SULPHATION CANDLE AND HOLDER

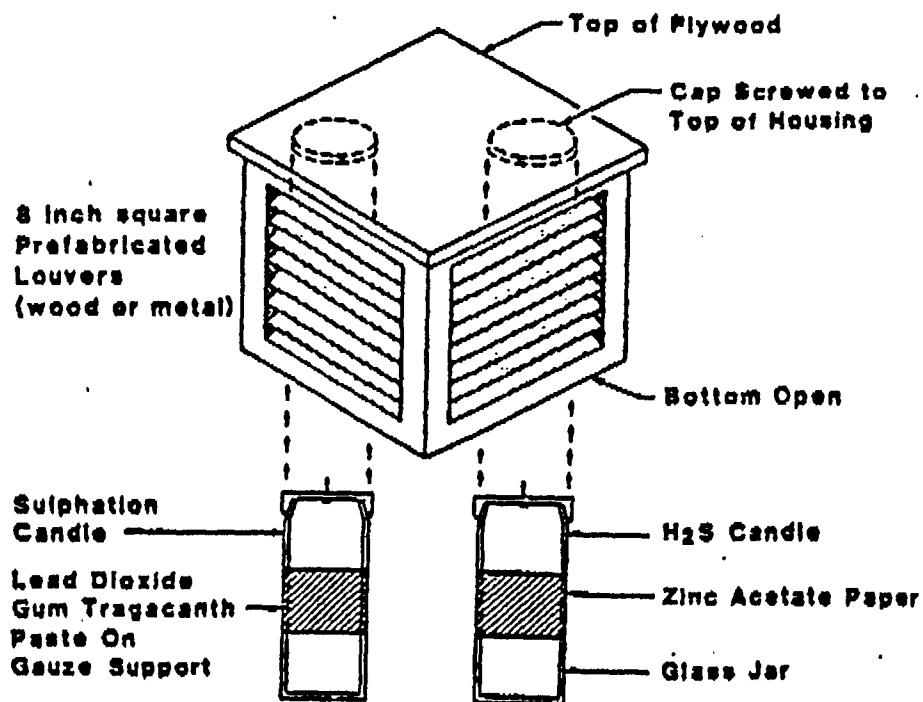


FIG. 2 HUEY PLATE

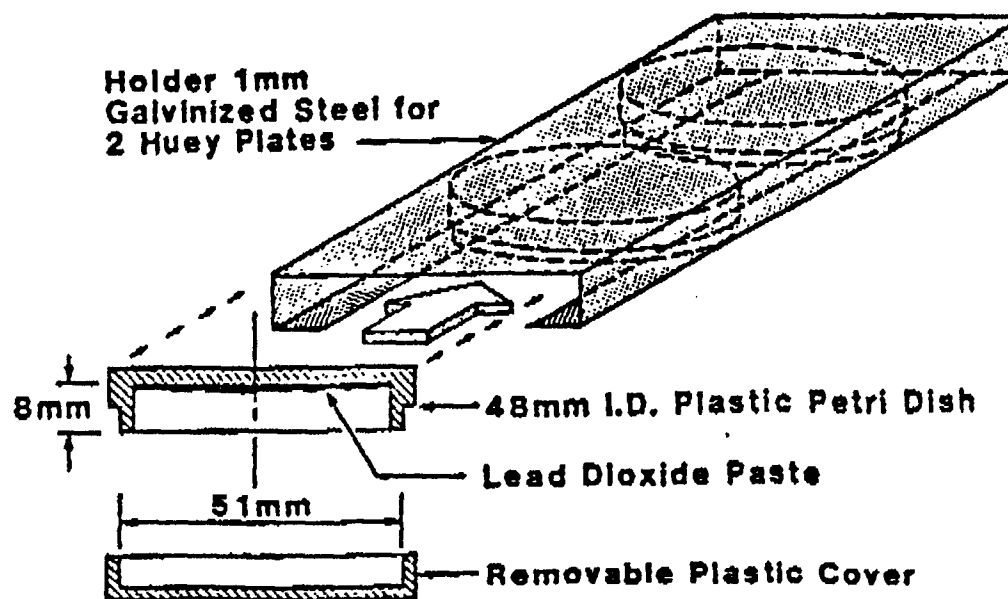


FIG. 3 DIFFUSION SAMPLER

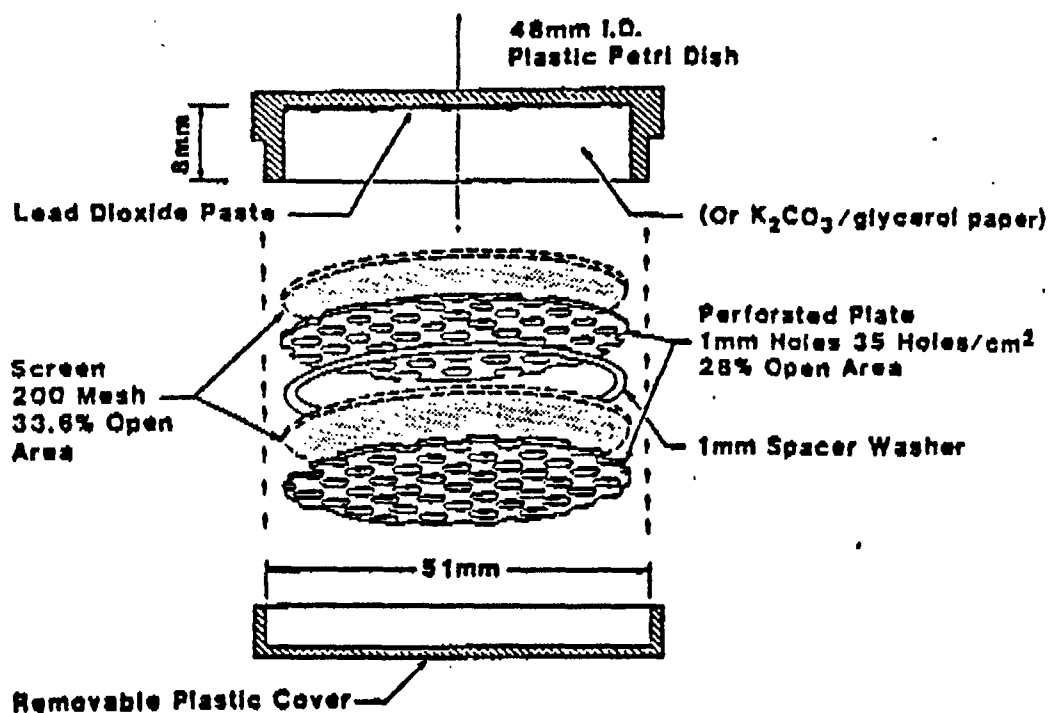
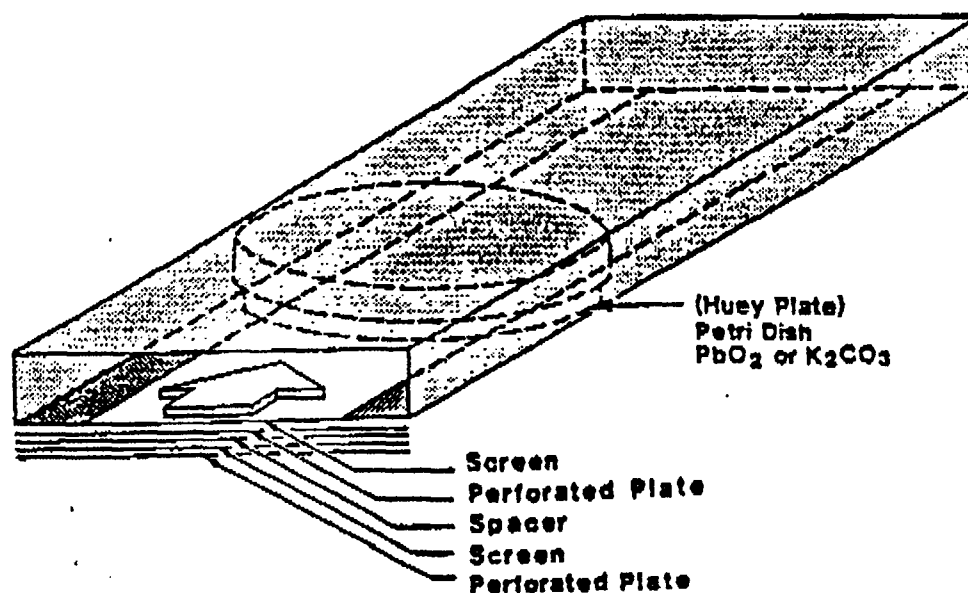


FIG. 4 ALBERTA ENVIRONMENT HUEY PLATE HOLDER WITH ATTACHED DIFFUSION SCREEN MODIFICATION



ANALYTICAL PROCEDURE:

The sampler (fig. 3) was constructed by cutting 50 mm diameter discs from 200 mesh screen (stainless steel, 33.6% open area) and from perforated plate (stainless steel, 1 mm diameter holes, 35 holes per cm^2 , 28% open area), then securing in two alternate layers the screens, and perforated plate along with a 1 mm thick spacer washer to the open side of a Huey plate.

The Huey plates were prepared in the usual fashion (10) from a suspension of PbO_2 (lead dioxide), gum tragacanth and cellulose fiber suspended in water. The suspension was pipetted into a 48 mm diameter Petri dish and dried in an oven.

Efficiency studies were carried out in an absorption chamber, 60 mm inside diameter 30 cm long (Fig. 5) and capable of holding three passive samplers. The incoming gas was mixed by means of a magnetic stirrer located at the bottom of the chamber. The mixing chamber was separated from the absorption chamber by means of a perforated plate (3.5 mm diameter holes, 35% open area).

Reference gases were prepared using a dynacalibrator with NBS certified permeation tubes (permeation rate 3.88 $\mu\text{g}/\text{min}$). Dilution gas flows were monitored using the dynacalibrator rotameter and calibrated occasionally during the run with a 1 litre bubble meter.

Times, temperatures, and barometric pressures were recorded and used to correct the sulphur dioxide concentrations and to calculate the overall dosage received by the sampler.

Analysis of lead dioxide candles and Huey plates were carried out with an auto analyzer (10), using an automated methyl thymol blue colorimetric procedure. Blanks were run at the beginning of each set of analysis. Duplicate and spiked samples were included in order to maintain the quality control by determining the precision and accuracy of the procedure. The samples were also analyzed by an ion chromatographic method. The two analysis procedures were in good agreement. Potassium carbonate absorption filters were extracted by soaking the filter overnight in 100 ml of aqueous 0.2% hydrogen peroxide solution (to oxidize the sulphite to sulphate), followed by ion chromatographic analysis using continuous suppression.

RESULTS AND DISCUSSION

Efficiency testing has shown the SO_2 sampling device to be capable of analyzing the range of ambient concentrations of concern. Lower wind velocities would cause boundary layer depletion effects; these would be expected to occur at velocities less than about 15 cm/s according to boundary layer theory (5). The layer of gas in the boundary of the sampler is depleted of sulphur dioxide by the absorbent when it becomes stagnant. This restriction would only affect indoor air sampling where the sampler is stationary in a pool of stagnant air. Outdoor air rarely has a velocity less than 15 cm/s and so the boundary layer would not be expected to become stagnant. Average outdoor air velocities are from 5 to 10 m/s for Alberta.

FIG. 5 TESTING CHAMBER FLOW DIAGRAM

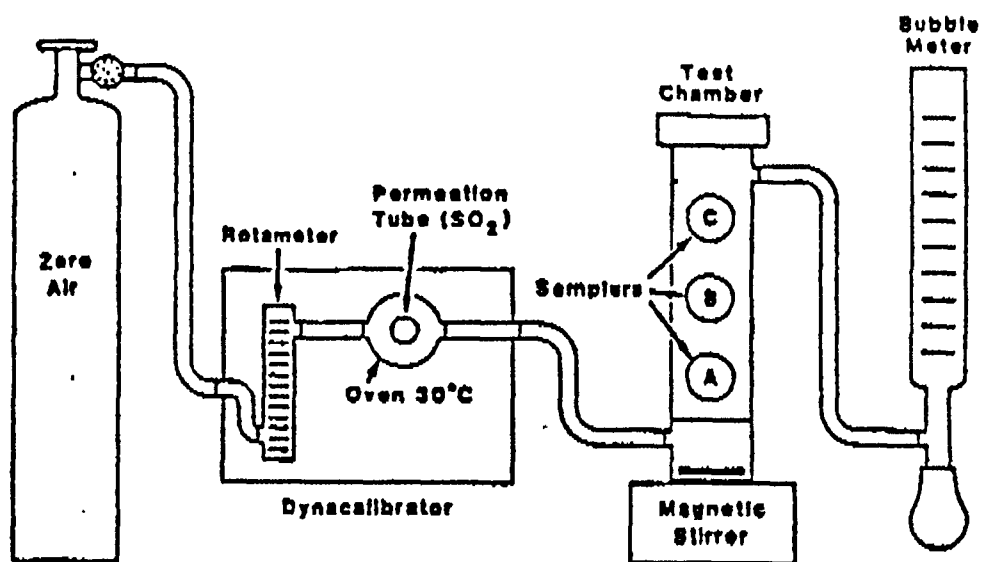
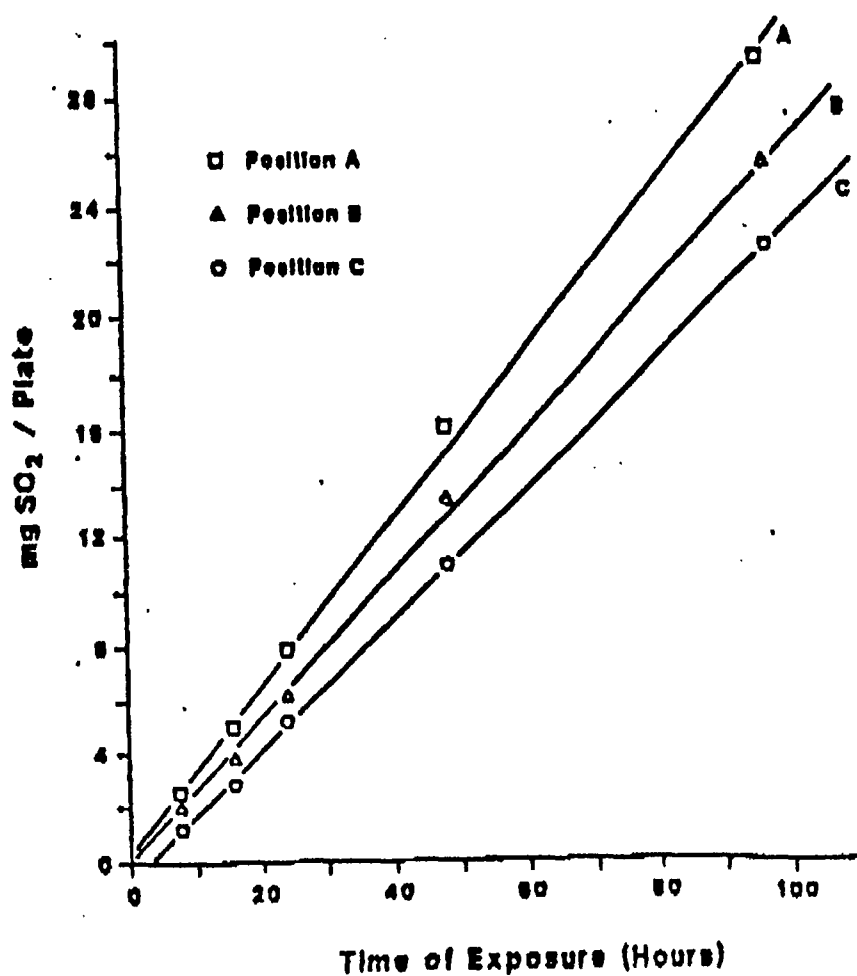


FIG. 6 LEAD DIOXIDE DOSAGE - RESPONSE GRAPH

mg of SO₂ Absorbed vs Time of Exposure

Singh and Otto (15) have evaluated the variables affecting PbO_2 candles and found that the candles respond linearly to SO_2 concentration, proportionately to the .42 power of the wind velocity, and only slightly to humidity and temperature changes. These results were corroborated by Sickles and Michie (6). Neither group investigated the boundary layer depletion effect of low wind velocities. Particle size affects the capacity of the plate to respond linearly to dosage, but is not rate limiting when the plates are used for ambient concentrations and exposure times of 1 to 3 months. One of the recommendations of Singh and Otto was to introduce a resistance, which is independent of wind velocity, to the transport of SO_2 to the PbO_2 surface. They suggested a layer of inert porous material be placed over the PbO_2 . This is similar to the method used by Orr et al of Ontario Ministry of Environment in which a polycarbonate membrane is placed over the absorbent to control the rate of diffusion (permeation) to the absorbing medium. Potassium carbonate was used as the absorbent. Our approach has been to use a stainless steel diffusion screen to act as the resistance eliminating the effect of wind velocity. As well, we have evaluated K_2CO_3 as an adsorbing medium because of its superior analytical precision which is mostly due to the elimination of the large sulphate blanks. For PbO_2 the blanks are similar in magnitude or larger than the normally measured values for many Alberta stations.

EFFECT OF DOSAGE

The diffusion sampler responded linearly to dosage over the range 0.1 to 3 mg/plate tested (fig. 7, 8). The concentration range tested is comparable to the range of values encountered for Huey plate exposures in the province. The response was independent of the absorbent used (PbO_2) (table 1) and confirms that the rate limiting step is transport of SO_2 to the absorbent through the diffusion screen. The linearity of response to concentration requires further testing to confirm that the results of Singh and Otto are also applicable to our diffusion sampler.

EFFECT OF WIND VELOCITY

Diffusion screen technology has been shown to eliminate the dependence on wind velocity for velocities greater than 15 cm/s (5). At velocities less than 15 cm/s the boundary layer becomes depleted and the resistance increases. The effect of SO_2 depletion in the boundary layer at low wind velocities is shown in (fig. 8) where the calibration factor (eq. 1) is plotted against the wind velocity. The wind velocities tested were very low 0.25 to 1 cm/s. (.0025 to 1 m/s) and as expected the C.F. increases at lower velocities.

$$\text{Eq 1. Calibration Factor (C. F.)} = \frac{\text{Concentration of } \text{SO}_2, \text{ } \mu\text{g/L}}{\text{SO}_2, \text{ adsorbed/cm}^2/\text{day}}$$

FIG. 7 DOSAGE RESPONSE GRAPH
mg of SO_2 vs Time of Exposure K_2CO_3 Plate

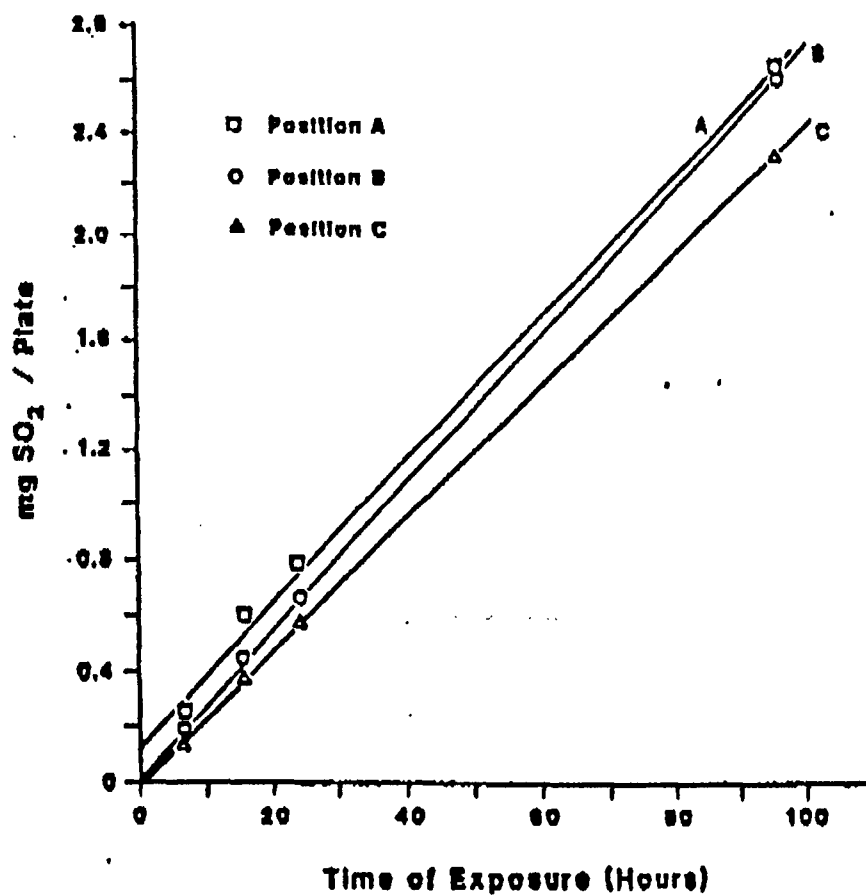


FIG. 8 SO_2 DEPLETION AT LOW WIND VELOCITIES

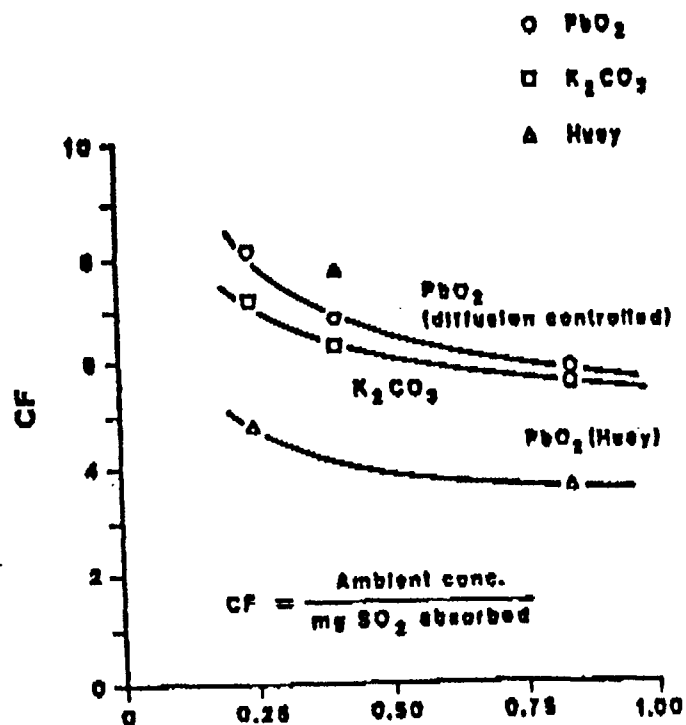


TABLE 1
Effect of Wind Velocity

Rm#	Position	mg/SO ₄ /plate	SO ₂ μg/L	C.F.	Air Velocity cm/s	C.F.
				μg SO ₂ μg SO ₄ /d/plate		μg SO ₂ /l μg SO ₄ /cm ² /d
PbO ₂ Diffusion						
R13	A	1.58	13.06	8.26	0.24	0.477
	B	1.28	10.60	8.27		
	C	1.05	8.60	8.20		
R14	A	1.07	7.35	6.86	0.42	0.396
	B	0.82	6.41	7.82		
	C	0.63	5.69	9.03		
R15	A	0.63	3.72	5.90	0.84	0.341
	B	0.58	3.44	5.93		
	C	0.53	3.18	6.01		
PbO ₂ Huey						
R18	A	2.70	12.68	4.69	0.24	0.271
	B	1.56	8.60	5.51		
	C	0.79	6.24	7.90		
R17	A	0.87	7.46	8.57	0.42	0.495
	B	0.96	6.69	6.96		
	C	0.82	5.84	7.11		
R16	A	1.15	3.75	3.26	0.83	0.188
	B	1.04	3.24	3.11		
	C	0.88	2.78	3.15		
K ₂ CO ₃ Diffusion						
K3	A	1.76	12.52	7.13	0.25	0.412
	B	1.35	9.90	7.33		
	C	1.11	7.88	7.10		
K4	A	1.16	7.39	6.37	0.42	0.369
	B	0.99	6.37	6.43		
	C	0.87	5.49	6.31		
K5	A	0.65	3.69	5.68	0.84	0.328
	B	0.60	3.41	5.68		
	C	0.56	3.16	5.64		

The SO₂ concentration seen by the samples is calculated by subtracting the amount absorbed by the upstream sampler.

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As the diffusion screen controls the rate of transport, and as long as the concentration on the absorbent side is close to zero, the sampler is independent of the type of absorbent used (eq. 2). (Fig. 7, 8) confirms this, giving nearly identical C. F. for PbO_2 and K_2CO_3 . This is expected if $C_o = 0$ for both absorbents.

Eq. 2 Fick's law $m = DA(C_{\infty} - C_o) / l$

m = mass flow rate, D = diffusion coefficient (of SO_2), A = area of diffusion channels, l = length of the diffusion channels, C_{∞} = ambient concentration, C_o = absorbent surface concentration.

The transport of SO_2 through the gas phase is the rate controlling step. The diffusion screen resistance is in series with the resistance to transport through the boundary layer and becomes rate controlling as long as it is significantly larger. The use of mechanical screens would allow for increasing or decreasing the resistance by adding or removing a layer of diffusion screen. This could be used to achieve the optimum range of linear response, while still sampling a sufficient amount of SO_2 to be analyzed. These conclusions would be applicable to other pollutants where a suitable absorbent is available to maintain $C_o=0$. The degree to which SO_2 is removed from the air stream is illustrated in (fig. 9) and table 1. The bulk concentration in the air stream decreases from 13.06 to 10.60 $\mu g/l$ as it passes over a sampler at a velocity of 0.24 cm/s.

EFFECT OF TEMPERATURE HUMIDITY AND PARTICLE SIZE

These variables were not studied as their effects have been previously been investigated (15, 6).

Humidity is not expected to affect the diffusion rate of SO_2 through the screens(5). PbO_2 was shown to be independent of humidity effects (15). When K_2CO_3 is used as an absorbent, glycerol is added to maintain a level of moisture, due to its humifacant properties, which minimizes any variability due to humidity.

Temperature changes have only a small effect on the diffusion rate and would only introduce minor variability. As there is no phase change over the temperature range -40 to +40 C, the temperature effect on reaction rate would be small(15).

Particle size only effects the loading capacity of the sampler. When the sampler is used within the proper concentration range and exposure time particle size does not effect the response (12).

PERMEATION SAMPLERS

Silicone permeation membranes were tested using a manganese trichloride absorbing solution (16) in a glass sampling vessel. Because the sampling rate of a permeation membrane is much lower than diffusion rates, most of the ambient samples were not detectable. As well the fragile nature of the sampler made shipping and handling difficult. There was also some deterioration in the membrane when exposed to hydrogen peroxide.

CONCLUSION AND RECOMMENDATIONS

The use of diffusion screens would enable PbO_2 or K_2CO_3 plates to be used for ambient SO_2 analysis independent of wind velocity. This method of sampling would determine more precise integrated average SO_2 concentrations than the existing sulphation candle procedure. More rigorous testing of higher wind velocity effects is still required.

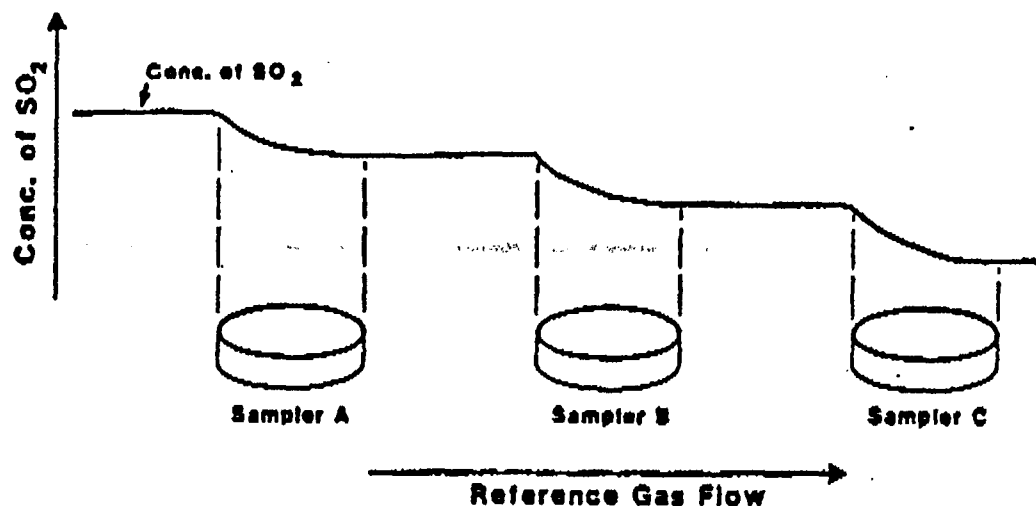
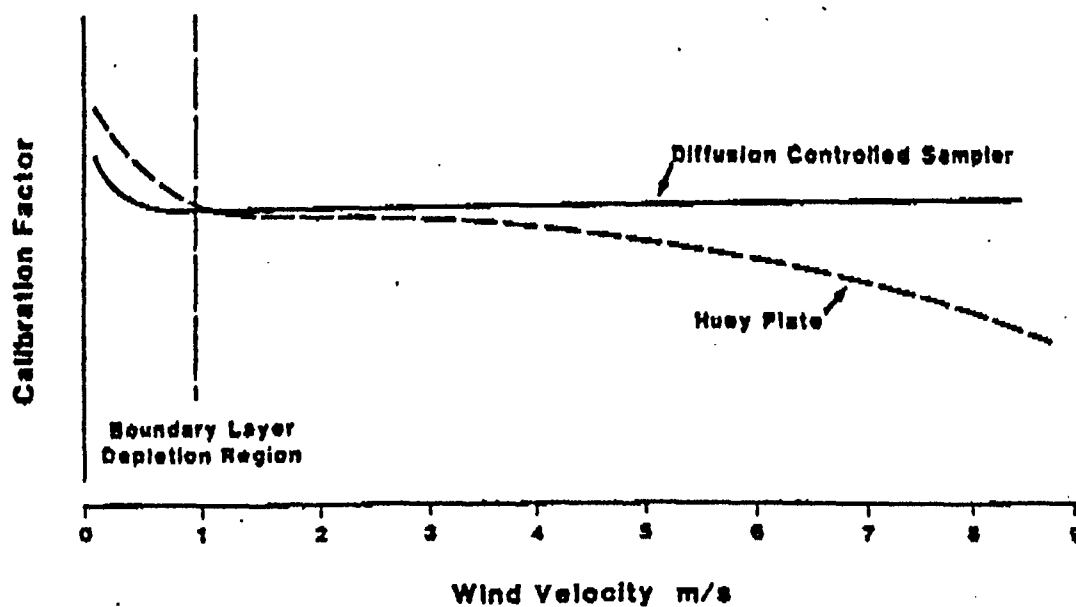
The use of K_2CO_3 would eliminate the large blanks encountered in PbO_2 candle and Huey plate analysis. This would allow accurate determination of lower levels of SO_2 and be useful for the monitoring of pristine areas. The accurate determination of SO_2 levels in pristine areas is necessary to assess dry deposition of acidic sulphate.

The use of a diffusion controlled sampler would eliminate shelter geometry effects common in sulphation candle monitoring.

Boundary layer depletion would not be significant for outdoor air monitoring.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Yan K. Lau and Bonnie Magill for their helpful discussion and review of the draft copy. This project has required the assistance and cooperation of all members of the Air Analysis and Research Group and the authors gratefully acknowledge their contributions.

FIG. 9 TESTING CHAMBER SO_2 GRADIENT**FIG. 10 ILLUSTRATION OF THE EFFECT OF WIND VELOCITY ON THE CALIBRATION FACTOR (THEORETICAL)**

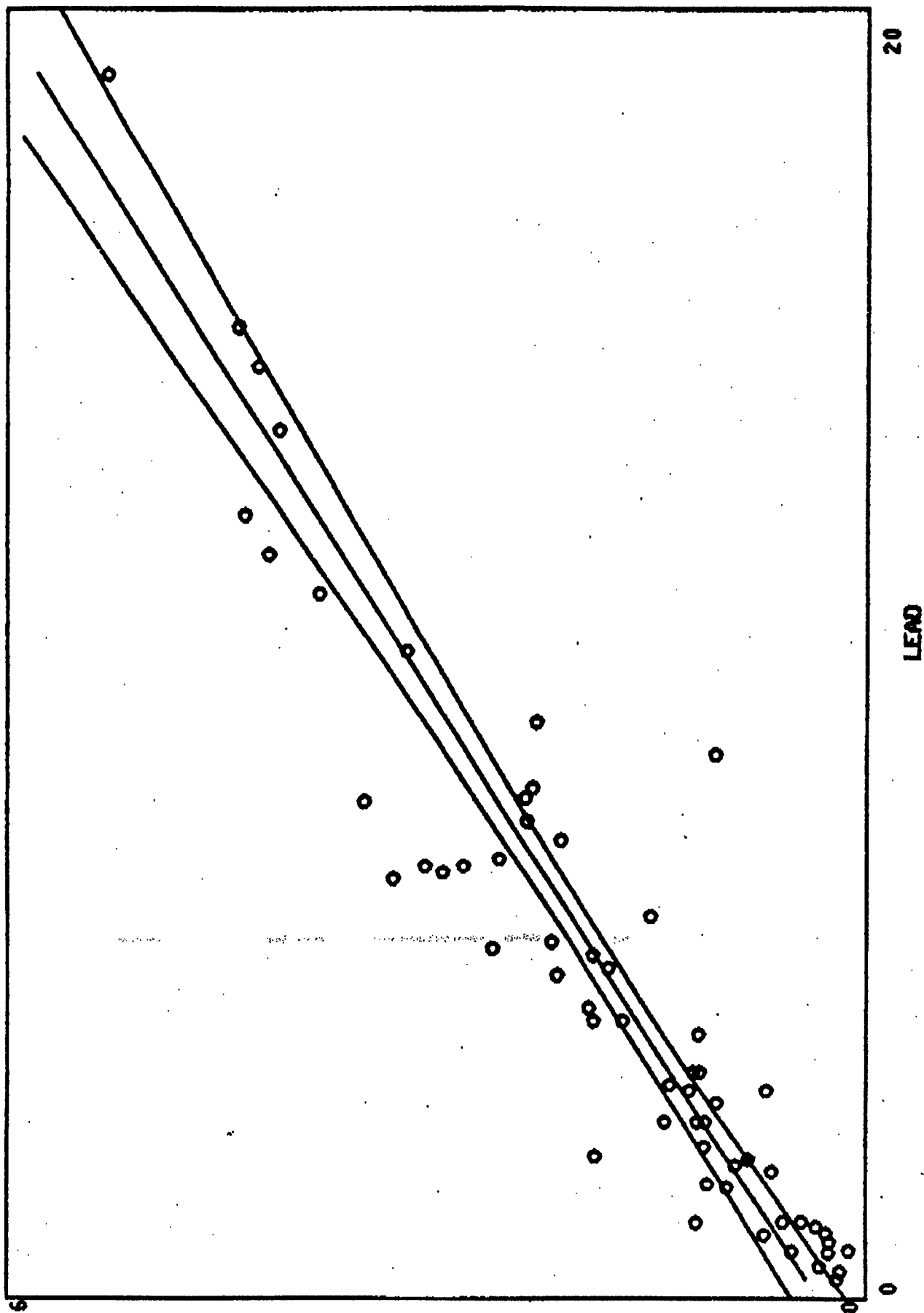
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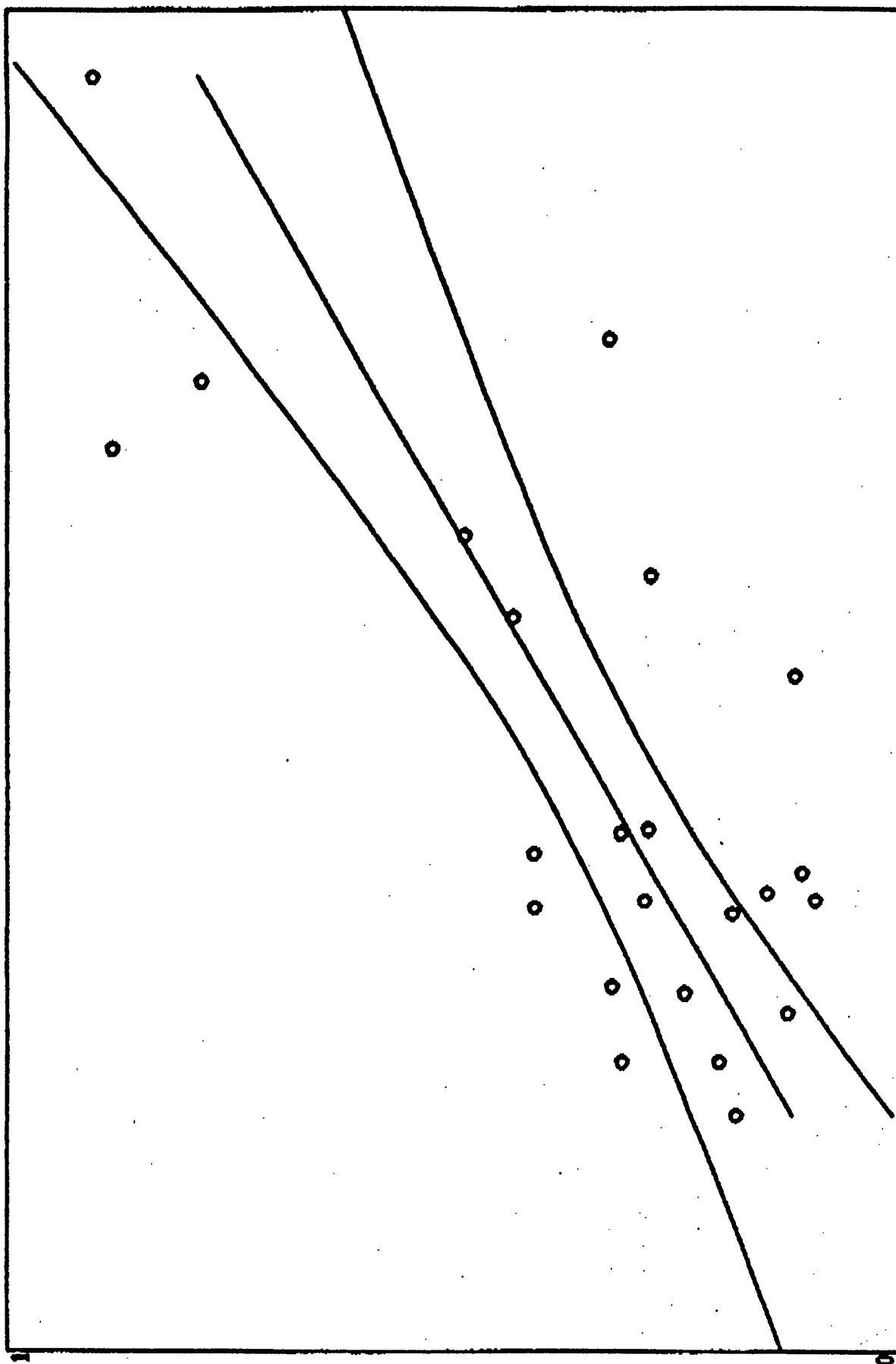
Correlation of Open H_2CO_3 plots (Lead Correlation = 90%)

Potassium Carbonate vs Huey Plate



Correlation of Diffusion plots

Diffusion vs Huey at 4 & 11



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