

551.510.42 : 551.508.95

ROYAL OBSERVATORY, HONG KONG

TECHNICAL NOTE NO. 52

A COMPARISON OF DAILY MEASUREMENTS OF SULPHUR DIOXIDE  
AT KING'S PARK METEOROLOGICAL STATION

by

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NOVEMBER 1979

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## SUMMARY

Levels of sulphur dioxide have been determined at the King's Park Meteorological Station by two methods. In this paper, the methods are described and the sources of errors are considered. Although the means of the readings by the two methods are significantly different, the results are correlated at the 0.1 % significance level.

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## 1. INTRODUCTION

The Royal Observatory obtained a Lear Siegler SM1000 second derivative spectrometer in 1978 to measure the concentration of sulphur dioxide in air. One of the aims was to gain experience from a pilot unit which might later form part of an automatic network of air pollution monitors to be set up by the Hong Kong Government. Also, by using this instrument as a calibration standard it might be possible to show that cheaper instruments could be used with appropriate corrections and precautions in the network.

The Lear Siegler instrument was set up at the Weather Satellite Workshop at King's Park Meteorological Station (elevation 64.8 m above mean sea level) and was linked to a data logger on 4 September 1978. A chemical apparatus for the determination of sulphur dioxide was set up earlier in the main building at King's Park in 1977 but was moved to the Weather Satellite Workshop on 28 February 1979.

In the present study the concentrations of sulphur dioxide determined from the two methods are compared, both before and after 28 February 1979. The basic data used in this study are available at the Royal Observatory.

## 2. DESCRIPTION OF METHODS

The chemical apparatus is assembled and operated according to British Standard 1747 (British Standards Institution 1969). The method is not specific and is a measurement of net acidity absorbed in hydrogen peroxide solution (of approximately 0.03N) through which air has been bubbled for 24 hours.  $\text{SO}_2$  in the air is oxidized to  $\text{H}_2\text{SO}_4$  which is then titrated with sodium carbonate, a standard alkali. The reference pH is 4.5, at which level there is least interference from dissolved carbon dioxide arising from normal atmospheric concentrations. This method has been commonly used in Europe and is sometimes referred to as the OECD method (Perkins 1974).

The Lear Siegler SM1000 is tuned to measure  $\text{SO}_2$  via its strong narrow band absorption of ultra violet radiation at a wavelength of 218 nm. A beam of ultra violet light is modulated about 218 nm at 45 Hz and is directed into an absorption cell, through which ambient air is continuously drawn. At this wavelength,  $\text{SO}_2$  exhibits preferred absorption of radiation. Radiation absorbed at this wavelength contains the exact amount of energy required to produce a transition of  $\text{SO}_2$  from one allowed energy state to another. The change of intensity with wavelength and its derivatives are shown in Fig. 1. The Lear Siegler instrument measures the second derivative of the intensity as it peaks sharply where the narrow band absorption occurs. Since absorption occurs while the wavelength is both increasing and decreasing through 218 nm the output is amplified by a narrow band 90 Hz amplifier. As  $\text{SO}_2$  obeys Beer's Law, the second derivative peak intensity is directly proportional to the  $\text{SO}_2$  concentration (Lear Siegler, Inc. 1976).

One of the advantages of second derivative spectroscopy is that the sharper the narrow band absorption, the higher is the sensitivity of measurement. The presence of broad band absorption by other gases in the same wavelength poses no interference. The determination of concentration is also independent of pressure, temperature and flow rate.

### 3. SOURCES OF ERRORS

The Lear Siegler is a specific instrument for SO<sub>2</sub>. It calibrates itself every four hours and is assumed to indicate true values of SO<sub>2</sub>. In this study, LS refers to daily means of measurements obtained from the Lear Siegler instrument and AC refers to daily values from the acidimetric method. Differences between them are expected to be almost entirely due to errors of the latter method and are accounted for as follows :

#### (a) Operational changes

The acidimetric sampler was set up by Royal Observatory staff based on experience gained at similar monitoring stations operated by the Labour Department of the Hong Kong Government. Additional advice was given by the Government Chemist in mid-February 1979 and some improved techniques were instituted. For example, evaporation from the 50 millilitres of sampling solution is rather severe on hot or very dry days in Hong Kong. We were advised to make up the sampled solution back to 50 millilitres with distilled water so that the pH would not be erroneously reduced. Wet chemicals used for titration to the reference pH have been supplied by the Government Chemist since early March to reduce errors arising from solutions with inexact normalities.

Another significant change was moving the acidimetric sampler about 50 metres and installing it in the Weather Satellite Workshop on 28 February 1979 so that it shared the same sampling port and sampled the same air as the Lear Siegler instrument.



TABLE 1. CATEGORISATION OF THE DIFFERENCES IN THE DAILY MEANS OF THE TWO METHODS

Time Period	Month/Year	No. of LS readings in excess of AC readings	No. of LS readings equal to AC readings	No. of AC readings in excess of LS readings	Total
(A)	Sept. 78	5	1	20	26
	Oct. 78	8	0	23	31
	Nov. 78	1	0	29	30
	Dec. 78	2	0	29	31
	Jan. 79	9	0	22	31
	Feb. 79	10	0	18	28
(B)	Mar. 79	26	0	5	31
	Apr. 79	27	0	3	30
	May 79	18	2	11	31
	June 79	23	1	6	30
	July 79	26	0	5	31
	Aug. 79	22	1	8	31

From Table 1 one can see that prior to the operational changes adopted in late February 1979 about 80% of the readings from the acidimetric method were higher than Lear Siegler readings. However, from March 1979 to August 1979, 77% of the Lear Siegler readings were higher, indicating the need to separate the data into two time periods. For convenience the cut-off day was taken as 28 February, the day of co-location and the two time periods are designated (A) and (B) respectively.

There have been further operational changes since 1 March 1979. For example, a Chemtrix 9015 pH meter has been used daily since June. This should have improved the accuracy of titration significantly since subjective judgement of the end point is eliminated. The Chemtrix 9015 pH meter is a fairly sensitive instrument where an addition of only two drops (about 0.06 ml) of 0.04 N acid or base is clearly indicated. This is equivalent to less than  $4 \mu\text{g}/\text{m}^3$  of  $\text{SO}_2$ .

(b) Sampling time :

The acidimetric sampler makes a continuous measurement since air is bubbled through the sampling solution for 24 hours, but for the Lear Siegler instrument the daily value is obtained from the mean of spot readings taken at 20-second intervals.

Sampling periods for the two methods are not always exactly in phase. The Lear Siegler data refers to a 24-hour period commencing at 0900 Hong Kong Time exactly. For the acidimetric method samples are changed manually and the time is generally within 1 hour of 0900 Hong Kong Time.

The Lear Siegler equipment is set to calibrate its span and zero once every 4 hours. The air in the instrument is circulated through an activated charcoal filter to remove all sulphur dioxide. This produces the 'zero' and then a specially calibrated sample in a quartz cell is switched into the optical patch to provide the 'span'. The whole process takes 15 minutes so that the readings during this period are not available for the computation of the daily mean.

Some data were also lost due to down times of either the spectrometer or the data logger, but hourly values were extracted from chart recorders whenever the data logger was unserviceable. The number of hours of missing data are listed in Table 2.

It has been found that rejecting daily values with missing hourly data or shifting the 24-hour averages to coincide more accurately with those from the acidimetric bubbler did not significantly improve the match between the readings of the two sampling methods.

TABLE 2. NUMBER OF HOURS OF MISSING DATA FROM  
THE LEAR SIEGLER SM1000

Month/Year	Number of hours
Sep/78	66
Oct/78	30
Nov/78	2
Dec/78	0
Jan/79	0
Feb/79	0
Mar/79	2
Apr/79	1
May/79	0
Jun/79	0
Jul/79	0
Aug/79	0

(c) Sampling loss

In order to test whether some SO<sub>2</sub> can pass through an acidimetric bubbler without being absorbed, an experiment was carried out whereby two bubblers were operated in series for two days. There was no measurable change in the acidity in the second bubbler. So it was assumed that there is no significant loss of SO<sub>2</sub> through non-absorption.

(d) Sampling rate

The daily volume of air pumped through the acidimetric sampler is required to be between 1.5 m<sup>3</sup> and 2.75 m<sup>3</sup> by the British Standard. In operation, it has been found to be generally around 1.7 m<sup>3</sup> per day. In the Lear Siegler, the suction pump operates at a higher rate of around 2.9 to 5.8 m<sup>3</sup> per day. Hence short durations of high concentrations may not be reflected in the same way in both methods.

(e) Chemical interference

The acidimetric method is non-specific and is affected by any other acidic or alkaline pollutant. Appreciable interference from ammonia has been identified by the Government Chemist, though concentrations are not sufficient to explain all the differences. The World Health Organization also cautions that interference by ammonia may be appreciable if the true SO<sub>2</sub> concentration is less than 100 µg/m<sup>3</sup> (World Health Organisation 1977). No interfering acids have been identified.

Vegetation in the immediate neighbourhood of both sampling sites during time periods (A) and (B) consists of short grass with no noticeable acid or alkaline emissions. Both buildings face south. The Hok Un Power Station is located about 2 km to the east-southeast.

In an attempt to locate possible sources of acidic or alkaline interference from any particular direction, Table 3 was constructed. Each cell represents the mean difference between the Lear Siegler and the acidimetric bubbler for a particular wind direction. An unusually large mean would indicate a possible source of interference in that direction, but none was found.

TABLE 3. MEAN DAILY DIFFERENCE (AC-LS) < 0 AND (AC-LS) > 0 FOR DIFFERENT WIND DIRECTIONS (SEPTEMBER 1978 - AUGUST 1979)

DIRECTION	(AC-LS) < 0 (BASES AFFECTING)	(AC-LS) > 0 (ACIDS AFFECTING)
CALM	.0 ( 0)	.0 ( 0)
010	-20.0 ( 2)	40.3 ( 4)
020	-29.2 ( 5)	52.6 (10)
030	-27.5 ( 2)	33.4 ( 7)
040	-30.3 ( 4)	55.0 ( 8)
050	-45.0 ( 3)	32.8 ( 5)
060	.0 ( 0)	38.3 ( 4)
070	-14.0 ( 3)	30.6 ( 5)
080	-33.3 ( 4)	36.8 ( 9)
090	-33.5 (27)	43.4 (22)
100	-49.3 (69)	31.6 (40)
110	-69.2 ( 5)	33.8 (25)
120	-50.0 ( 1)	26.3 ( 3)
130	-13.0 ( 2)	14.0 ( 3)
140	-26.0 ( 3)	39.0 ( 1)
150	-30.0 ( 3)	5.0 ( 1)
160	-26.0 ( 4)	20.0 ( 2)
170	-11.5 ( 2)	10.0 ( 1)
180	-5.0 ( 1)	.0 ( 0)
190	-33.7 ( 3)	7.0 ( 1)
200	-51.3 ( 3)	3.0 ( 2)
210	-41.0 ( 7)	7.0 ( 1)
220	-27.8 ( 4)	16.7 ( 3)
230	-27.0 ( 2)	12.5 ( 4)
240	-16.3 ( 3)	8.0 ( 1)
250	-38.7 ( 6)	12.3 ( 4)
260	-13.0 ( 2)	17.0 ( 1)
270	.0 ( 0)	19.0 ( 2)
280	-77.0 ( 1)	.0 ( 0)
290	-46.0 ( 1)	.0 ( 0)
300	.0 ( 0)	.0 ( 0)
310	.0 ( 0)	.0 ( 0)
320	-78.0 ( 1)	.0 ( 0)
330	.0 ( 0)	23.5 ( 2)
340	.0 ( 0)	.0 ( 0)
350	-64.0 ( 1)	.0 ( 0)
360	-31.0 ( 3)	27.2 ( 5)

Note : The number of counts is in brackets.

(f) Other instrumental considerations

The standard range of the Lear Siegler equipment is specified to be 0 - 0.5 ppm (0 - 1309  $\mu\text{g}/\text{m}^3$ ). It has been noted that on a few occasions the upper limit is exceeded when 3-minute averages are taken. Although the computer programme reads these over-shoots as the top of the range, it is obvious that the estimate of the true level may be biased towards the low side.

The noise level is specified to be 0.005 ppm (13.1  $\mu\text{g}/\text{m}^3$ ) and is a measure of the standard deviation about the mean of short duration fluctuations of the instrument output which are not caused by changes in  $\text{SO}_2$  concentration. Since the output is a positive DC voltage the noise of the SM1000 may contribute positively near true-zero concentrations.

The minimum detectable concentration (MDC) of the Lear Siegler instrument is 0.010 ppm (26.2  $\mu\text{g}/\text{m}^3$ ). This is defined as twice the noise level. The acid-peroxide titration method is generally applicable to  $\text{SO}_2$  concentrations in the 0.01 ppm to 10 ppm range but the lowest detectable level is seldom specified and is dependent on operational practice.

The daily zero drift of the Lear Siegler equipment is within  $\pm 0.020$  ppm (52.4  $\mu\text{g}/\text{m}^3$ ) and the daily span drift is within  $\pm 5.0\%$  at 80% of full scale and  $\pm 20.0\%$  at 20% of full scale. The effects of drift are reduced as far as possible by a computer programme which calculates the average voltage of 12 to 15 points on the zero mode and on the span mode and uses the two averages in evaluating the  $\text{SO}_2$  readings during the next 4 hours. There should be no problems of drift with the acidimetric method.

#### 4. RESULTS

Comparisons were made between daily readings of the acidimetric method and the Lear Siegler during the following periods :

Time Period	No. of readings	Remarks
(A) 5 Sept 1978 - 28 Feb 1979	177	Chemical sampler in main building, Lear Siegler sampler in Weather Satellite Workshop
(B) 1 Mar 1979 - 31 Aug 1979	184	Both instruments in Weather Satellite Workshop

A Student's *t* test was conducted to determine whether there is any significant difference between the mean values of the readings from the two sampling methods in either time period. Readings from the two different sampling methods for any one particular day may be regarded as a paired sample with difference  $D_i = LS - AC$ . The sample mean difference  $\bar{D}$  was assumed to be normally distributed with standard deviation  $S_{\bar{D}}$ , where

$$S_{\bar{D}}^2 = \frac{\sum D_i^2 - (\sum D_i)^2/n}{(n-1)n} \quad (\text{Snedecor and Cochran 1971}).$$

Parameters for the test are listed in Table 4.

TABLE 4. ANALYSIS OF THE DIFFERENCE BETWEEN THE SAMPLING METHODS

	Time Period	
	(A)	(B)
Mean difference $\bar{D}$ ( $\mu\text{g}/\text{m}^3$ ) (LS - AC)	-22.1	+28.6
Standard deviation of differences $S_{\bar{D}}$	3.310	2.750
$t = \frac{\bar{D}}{S_{\bar{D}}}$	-6.696	10.40

A table of the distribution of *t* indicates that for each time period the means of the sampling methods are different at the 0.1% significance level. The foregoing test demonstrates that equivalent Lear Siegler  $\text{SO}_2$  levels cannot be inferred directly from readings of the acidimetric method.

The next step is to determine if the results are correlated well enough to warrant the formulation of regression equations. The correlation coefficients are given in Table 5.

TABLE 5. CORRELATION BETWEEN THE TWO SAMPLING METHODS

	Time Period	
	(A)	(B)
Mean of Acidimetric readings ( $\mu\text{g}/\text{m}^3$ )	87	59
Mean of Lear Siegler readings ( $\mu\text{g}/\text{m}^3$ )	65	87
Correlation coefficient (r)	0.485	0.750
Regression equation	(LS) = .597 (AC) + 13.2	(LS) = .907 (AC) + 34.0
Standard Error (standard deviation) ( $\mu\text{g}/\text{m}^3$ )	41.1	36.9

From a table of levels of significance for correlation coefficients, one concludes that they are significant at the 0.1% significance level for both periods. The regression equations were formulated and are also included in Table 5.

For time period (A) the correlation, whilst highly significant, is poor. By co-locating the instruments and introducing improved techniques for the acidimetric method, the correlation was improved to 0.750. Even so, this indicates that 44% of the variance is still not accounted for. The improved acidimetric method will indicate daily  $\text{SO}_2$  levels within about  $37 \mu\text{g}/\text{m}^3$  on about 68% of the days. This calibration applies only to this particular site and operation conditions with no changes in land use in the neighbourhood and with no new sources or sinks of either acids or alkalis.

Figures II and III show the scatter diagrams for time periods (A) and (B). Intervals of one and two standard errors are marked. Points outside two standard errors from the regression equations for both time periods are listed in Table 6. On 17 of the 19 days, the Lear Siegler reading exceeded that of the acidimetric method. Although there are no significant remarks in the log book on these 17 days, it is noted that nearly all occurred over or immediately after weekends when large number of people use the neighbouring football playground. It is also noted that out of the 19 days, 10 are within



time periods of 3 days. This may imply the existence of spells of alkali interference on the acidimetric bubbler over two or three days during or after weekends.

TABLE 6. PERCENTAGE ERRORS OF SOME EXTREME POINTS

Date	Time Period	Lear Siegler Reading (LS)	Acidimetric Reading (AC)	Error $(\frac{AC-LS}{LS} \times 100\%)$
1/10/78 (Sun)	(A)	141	35	-75.2
7/10/78 (Sat)		211	121	-42.7
8/10/78 (Sun)		240	36	-85.0
12/1/79 (Fri)		120	33	-72.5
24/1/79 (Wed)		168	112	-33.3
10/2/79 (Sat)		146	58	-60.3
17/2/79 (Sat)		236	159	-32.6
19/2/79 (Mon)		171	122	-28.7
3/3/79 (Sat)	(B)	102	152	+49.0
5/3/79 (Mon)		42	87	+107.1
19/3/79 (Mon)		167	68	-59.3
6/4/79 (Fri)		124	20	-83.9
4/5/79 (Fri)		117	0	-100.0
7/5/79 (Mon)		311	171	-45.0
8/5/79 (Tue)		254	82	-67.7
28/5/79 (Mon)		135	19	-85.9
29/5/79 (Tue)		155	24	-84.5
14/6/79 (Thu)		191	72	-62.3
7/7/79 (Sat)		230	76	-67.0

## 5. CONCLUSION

Whilst the sampling of daily  $\text{SO}_2$  levels by an acidimetric bubbler may yield very different readings from Lear Siegler readings, the results from the King's Park experiment indicate that, provided care is exercised, the acidimetric method may be used to obtain equivalent Lear Siegler readings within certain limits. The standard error may be determined by calibration against a Lear Siegler instrument and, provided it is within acceptable limits, the acidimetric method results may be converted to equivalent Lear Siegler readings by using an experimentally determined regression equation.

# NARROW BAND ABSORPTION

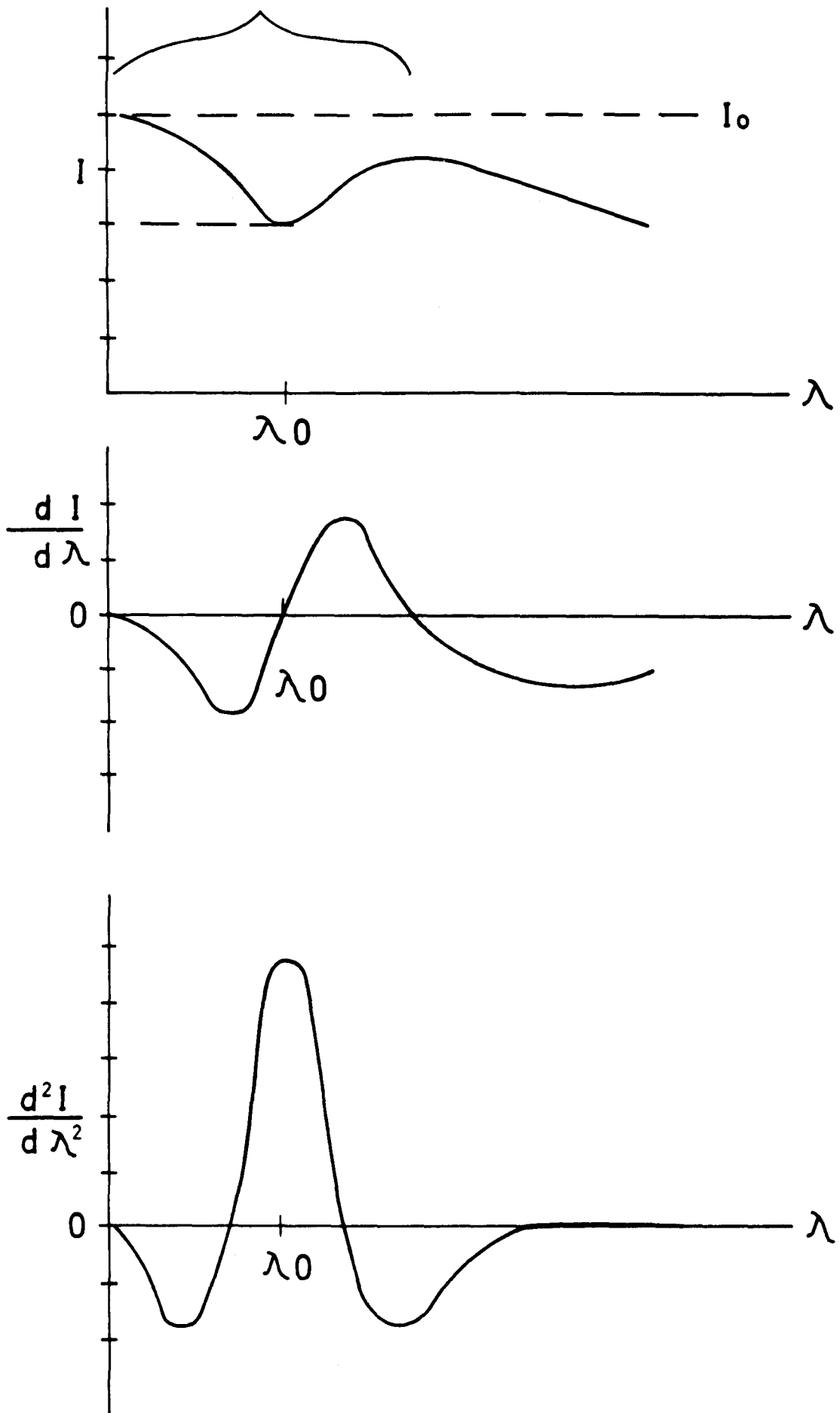


FIG. 1 INTENSITY DISTRIBUTION AND ITS DERIVATIVES

FIG. 2 SCATTER DIAGRAM OF 177 SO<sub>2</sub> CONCENTRATION PAIRS  
IN TIME PERIOD ( A )

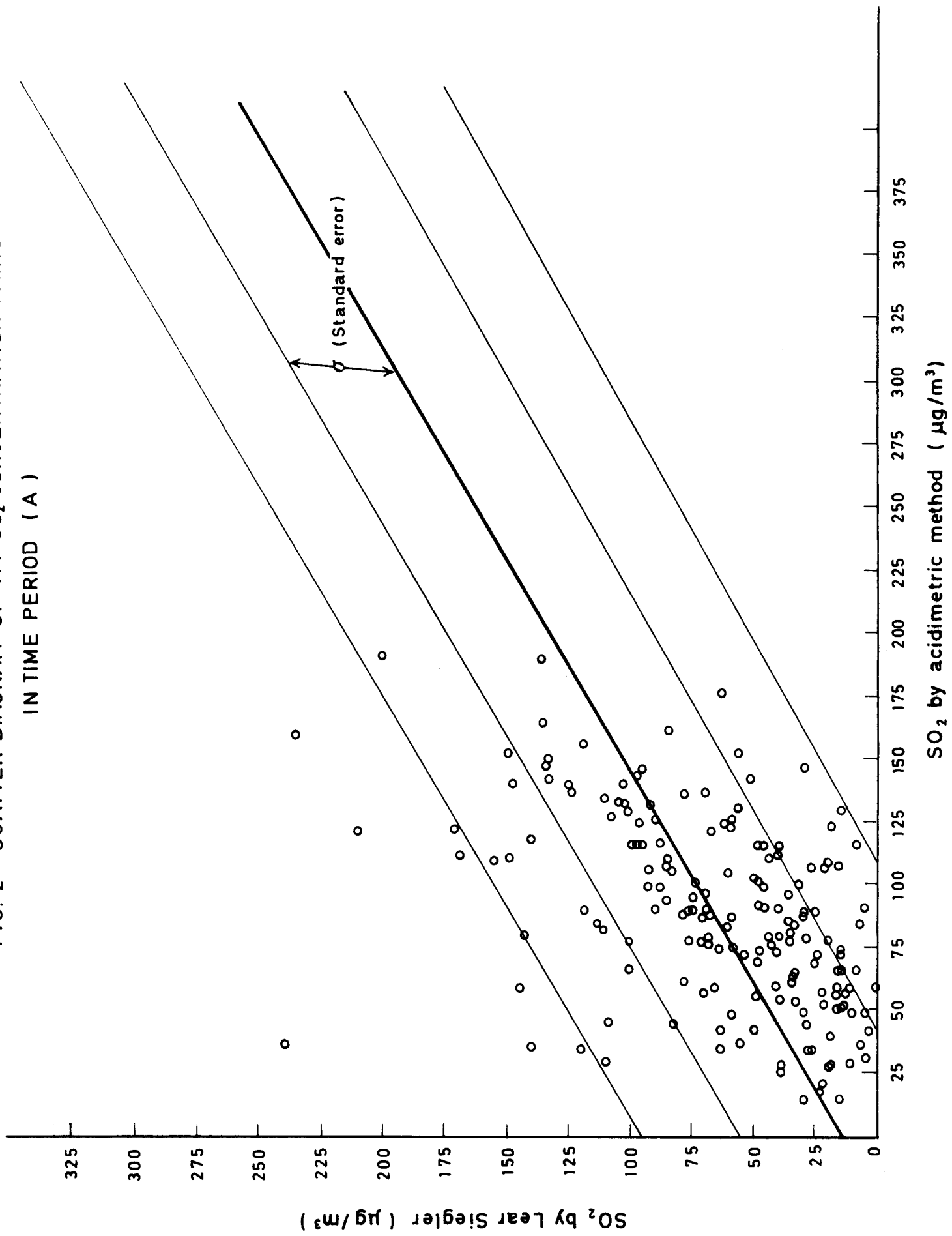
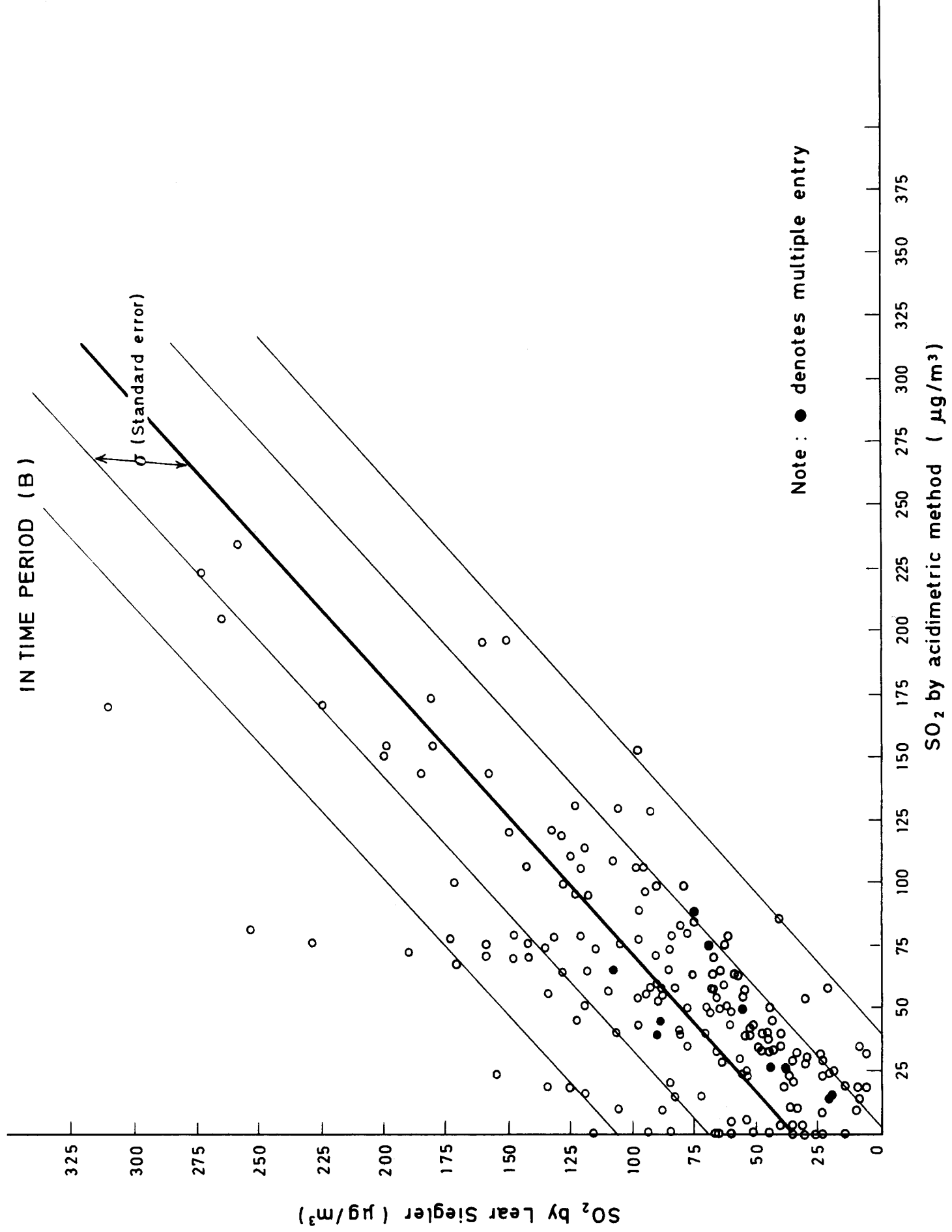


FIG. 3 SCATTER DIAGRAM OF 184 SO<sub>2</sub> CONCENTRATION PAIRS



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