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# THE MEASUREMENT OF ATMOSPHERIC SULPHUR DIOXIDE AND CHLORIDES

BY

M. R. FORAN, E. V. GIBBONS AND J. R. WELLINGTON

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# The Measurement of <sup>ANALYZED</sup> Atmospheric Sulphur Dioxide and Chlorides

M. R. FORAN, F.C.I.C., E. V. GIBBONS, M.C.I.C., and  
J. R. WELLINGTON, M.C.I.C.\*

This paper describes the method used for measuring the relative "activity" of sulphur dioxide at Canadian exposure sites and reports the values obtained over a period of three years. The lead peroxide method was used and factors affecting its variability and correlation with volumetric measurements were investigated in detail at one of the sites. It is concluded that the lead peroxide method is particularly well suited for use in exposure studies at outdoor exposure sites. The different methods used for measuring atmospheric chlorides are discussed, the most promising being a modification of the "wet candle" method and use of rainfall cans. The chloride levels obtained during 1956 at a number of locations in the Halifax area are given. In addition brief reference is made to the performance of two standard metals which have been exposed at each of the sites to provide a measure of the relative corrosivity of the atmosphere. The eight outdoor sites described are used by the Associate Committee on Corrosion Research and Prevention for their outdoor corrosion studies.

SEVEN outdoor exposure sites have been established across Canada by the Division of Building Research of the National Research Council, to provide for the study of the behaviour of materials under outdoor exposure at various locations. These sites are located at York Redoubt (near Halifax), Halifax, Montreal, Ottawa, Saskatoon, Norman Wells in the Northwest Territories and at Rocky Point on Vancouver Island.

These locations provide an east and west coast marine atmosphere, a marine-industrial, industrial, high humidity, low humidity and far northern atmosphere. They are administered by the Division of Building Research and used by the Associate Committee on Corrosion Research and Prevention in their studies on outdoor corrosion. Because of the interest of The Consolidated Mining and Smelting Company of Canada (Cominco) in corrosion research, its outdoor site was made available for exposure testing. This site, known

as the Trail exposure site, is situated at Birchbank in the Columbia River valley approximately six miles north of Trail, British Columbia.

In studies on the weathering of materials it is of prime importance to know the climatic conditions to which the materials have been exposed. Meteorological stations of the Department of Transport, contiguous to the sites, provide data on rainfall, temperature, humidity, sunshine, wind and other related information. While the basic controlling factor in the degradation of materials is climate when assessing their performance, it is also important to know the level of other physical and chemical agents which may have been major factors in their deterioration. Thus, the levels of air contaminants such as sulphur dioxide, chlorides, heavy metals and suspended particulate matter are of special interest.

## **Sulphur dioxide measurement**

Sulphur dioxide has long been recognized as the most common and abundant pollutant in urban and

industrial atmospheres. The measurement of its distribution and abundance has been extensively investigated, particularly in the United Kingdom where special techniques for measuring sulphur dioxide concentration or "activity" have been developed. Because of its acidic nature sulphur dioxide affects the corrosion of metals and the degradation of other building materials.

Atmospheric corrosion and exposure studies of metals and building materials are necessarily long-term investigations. In studying the effects of factors such as sulphur dioxide, it is desirable to know the average level of  $\text{SO}_2$  at each exposure site for each period of exposure. Since exposure sites are frequently located in remote areas, a desirable characteristic of any test method is that it requires no services for its operation and only infrequent attention during use. It should also be inexpensive to set up.

## **Volumetric methods**

A number of methods for measuring the volumetric concentration of sulphur dioxide in the atmosphere have been developed <sup>(1, 2)</sup>. Volumetric methods give instantaneous or frequent periodic indications of the actual concentration of  $\text{SO}_2$  in the atmosphere. However, such instruments are generally costly, require electrical power for their operation, and frequent servicing during use. For corrosion studies a much simpler instrument is required.

## **Lead peroxide method**

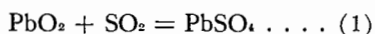
An entirely different method of measuring the sulphur dioxide content of the atmosphere is the lead peroxide method developed in the

\*See pages 6 and 41 for details and authors.

United Kingdom at the Building Research Station of the Department of Scientific and Industrial Research (DSIR) in 1932<sup>(3)</sup>. This method is based on the reaction of gaseous sulphur dioxide with solid lead peroxide to form lead sulphate. This instrument does not measure the volumetric concentration of SO<sub>2</sub> in the atmosphere directly, but presents an integrated measure of the sulphur dioxide "activity" during a period of exposure. This instrument is especially well suited to measuring the relative levels of SO<sub>2</sub> at exposure sites when metals are under test, as is outlined in the following discussion.

In the standard lead peroxide method<sup>(4, 5)</sup>, which has been closely followed at the Canadian exposure sites, a coating of lead peroxide is applied to a 10-cm square of cotton gauze wrapped around a porcelain cylinder. The lead peroxide coated cylinder is exposed to the atmosphere in a louvered box, (Figure 1) which protects the lead peroxide from the direct action of rain but permits free access of air. Instruments are mounted at each site on one of the specimen exposure racks, either five feet above ground or at roof level. The lead peroxide coated cylinders are prepared at Ottawa each month and shipped in air-tight containers to the sites for exposure. The exposed cylinders are returned to Ottawa in the same air-tight cylinders for analysis of lead sulphate content. Results are reported as milligrams of sulphur trioxide per square decimeter of exposed lead peroxide surface per day (mgSO<sub>3</sub>/dm<sup>2</sup>/day). The lead peroxide used thus far has been obtained from the British Fuel Research Station from supplies which are carefully checked against a standard lead peroxide of known reactivity.

Before considering the results obtained at the different exposure sites it is desirable to examine the basic characteristics of the lead peroxide method. It depends on the facility with which gaseous sulphur dioxide is absorbed by a prepared surface of solid lead peroxide according to the reaction,



A desirable feature of the method is that both the absorbent and the product formed are insoluble. In order to ensure reproducible results, it is obvious that the essential physical features of the instrument, i.e., the method of preparation, exposure and analysis, etc., must be rigorously standardized. In this way only, can uniformly reactive lead peroxide sur-

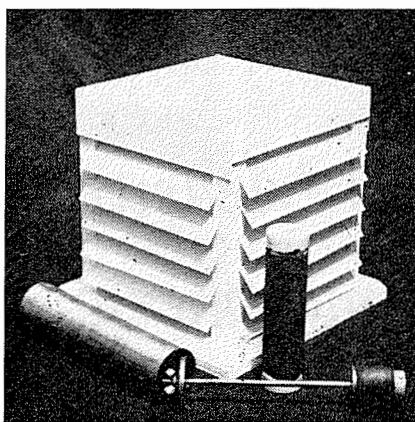


Figure 1—Lead peroxide cylinder and louvered box.

faces be consistently obtained. The reactivity or rate constant  $k$ , is defined as the rate of formation of lead sulphate  $V_{\text{SO}_4}$  per unit area of exposed lead peroxide surface per unit time, divided by the concentration of sulphur dioxide (SO<sub>2</sub>) in the atmosphere, that is,

$$V_{\text{SO}_4} = k (\text{SO}_2) \dots (2)$$

Wilsdon and McConnell<sup>(6)</sup> have shown that  $k$  is independent of SO<sub>2</sub> concentration, up to 1000 ppm, and that, in the standard method,  $k$  is constant if 15% or less of the absorbent (lead peroxide) has been converted to lead sulphate. (This is approximately equivalent to a mean daily rate of sulphation of 13 mg SO<sub>3</sub>/dm<sup>2</sup>/day for a standard cylinder exposed for one month.) They also

TABLE I  
ARRANGEMENT OF 14 LEAD PEROXIDE CYLINDERS AT THE TRAIL EXPOSURE SITE

Cylinder Number	Corner in Which Located	Height Above Ground	Period of Exposure	Type of Cover	Cylinders Prepared and Analysed by
1	Southwest	5'	4 weeks	Cowl	Cominco
2	"	"	"	"	"
3	"	"	1 week	"	"
4	"	"	"	"	"
5	"	"	4 weeks	"	"
6	"	"	"	"	"
7	Northeast	2'	"	"	"
8	"	"	"	"	"
9	"	5'	"	"	"
10	"	"	"	"	"
11	"	"	"	Box	NRC
12	"	"	"	"	"
13	"	"	"	"	Cominco
14	"	"	"	"	"

TABLE 2  
AVERAGE RATE OF SULPHATION OF LEAD PEROXIDE CYLINDERS

Group 1		Group 2		Group 3	
Cylinder	mg SO <sub>3</sub> dm <sup>2</sup> day	Cylinder	mg SO <sub>3</sub> dm <sup>2</sup> day	Cylinder	mg SO <sub>3</sub> dm <sup>2</sup> day
3	0.851 ± 0.04*	1	0.784 ± 0.04*	7	0.704 ± 0.04*
4	0.850 ± 0.04	2	0.782 ± 0.04	8	0.698 ± 0.04
Mean 3,4	0.851 ± 0.03	5	0.794 ± 0.04	Mean 7,8	0.701 ± 0.03
		6	0.763 ± 0.04	13	0.689 ± 0.04
		9	0.760 ± 0.04	14	0.680 ± 0.03
		10	0.775 ± 0.02		
Mean 11,12	0.857 ± 0.03	Mean	0.776 ± 0.02	Mean 13,14	0.680 ± 0.03

\*95 per cent confidence limits based on average standard error for this set of data.

TABLE 3  
95 PER CENT CONFIDENCE LIMITS OF A SINGLE DETERMINATION

Cylinders 1,2,5,6,9,10,13,14	0.09
" 7, 8,11,12	0.07
" 3, 4	0.24

deduced, on theoretical grounds, that an increase in temperature of 1°C should increase the reactivity by 0.4%, and showed experimentally, that  $k$  was proportional to the one-fourth power of the velocity of the air past the lead peroxide surface. However, the air velocities obtainable in their laboratory were considerably lower than normal wind velocities and their  $\text{SO}_2$  concentrations appreciably higher than those commonly found outdoors. Subsequent laboratory and field studies (7, 8) have failed to show a significant relationship between reactivity and wind velocity. It has been reported that relative humidity does not have any significant effect on the reactivity (8). In summary, then, the rate of sulphation of lead peroxide cylinders should be directly proportional to the concentration of sulphur dioxide in the atmosphere.

In 1955 a special series of tests was set up at the Trail exposure site to establish the suitability of the lead peroxide method for use in corrosion and other outdoor exposure studies. Because of Cominco's long-term interest in atmospheric pollution, special facilities and experience were available at this site. In this series of tests, 14 lead peroxide cylinders were exposed simultaneously for four-week intervals over a period of two years. The type of cylinder and the procedure used followed established Cominco practice, which, although closely patterned on the original DSIR lead peroxide technique, differed slightly from the procedure previously described. The cylinders were protected by cowls (Figure 2) rather than louvered boxes, and locally available lead peroxide was used. A recording Thomas autometer was available at the Trail exposure site and this instrument, which provides a continuous, periodic (20-minute interval) record of the sulphur dioxide content of the atmosphere, in ppm, was operated in conjunction with the lead peroxide test cylinders.

The results obtained (Table 2) with the 14 lead peroxide cylinders will be discussed later. The 20-minute Thomas autometer readings, corrected for temperature and atmospheric pressure, were totalized and the average monthly concentration of  $\text{SO}_2$ , in ppm, at the exposure site was obtained. These data, for the 26 four-week periods during the interval from February 8, 1955 to February 5, 1957, together with the average rate of sulphation, in  $\text{mg SO}_3/\text{dm}^2/\text{day}$ , of six Cominco cowl-type lead

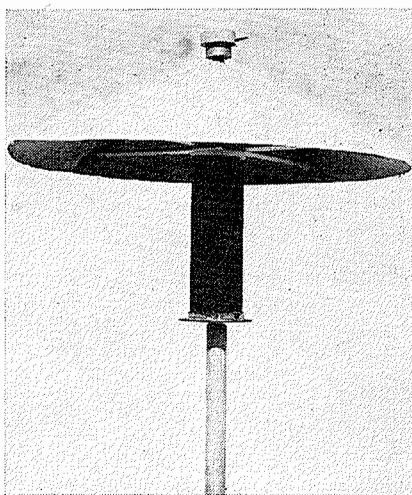


Figure 2—Lead peroxide cylinder and cowl protector.

peroxide cylinders (Group 2 in Table 2), are shown in Figure 3. Also shown in Figure 3 are the random variations and 95% confidence limits of the coefficient  $b$ . The relationship between the regression coefficient  $b$  and the rate constant  $k$  is obtained by transposing equation 2,

$$(\text{SO}_2) = \frac{1}{k} V_{\text{SO}_4} \\ = b V_{\text{SO}_4} \dots (3)$$

Equation 3 was used to facilitate the correlation of  $V_{\text{SO}_4}$ , which is considered to be the independent variable, with  $(\text{SO}_2)$ . Figure 4 is a plot of  $(\text{SO}_2)$  (the autometer readings) vs  $V_{\text{SO}_4}$  (the lead peroxide figures) for the 26 individual periods. The slope of this line, which is the average of the regression coefficient  $b$ , was determined to be 0.028 by statistical methods, with 95% confidence limits

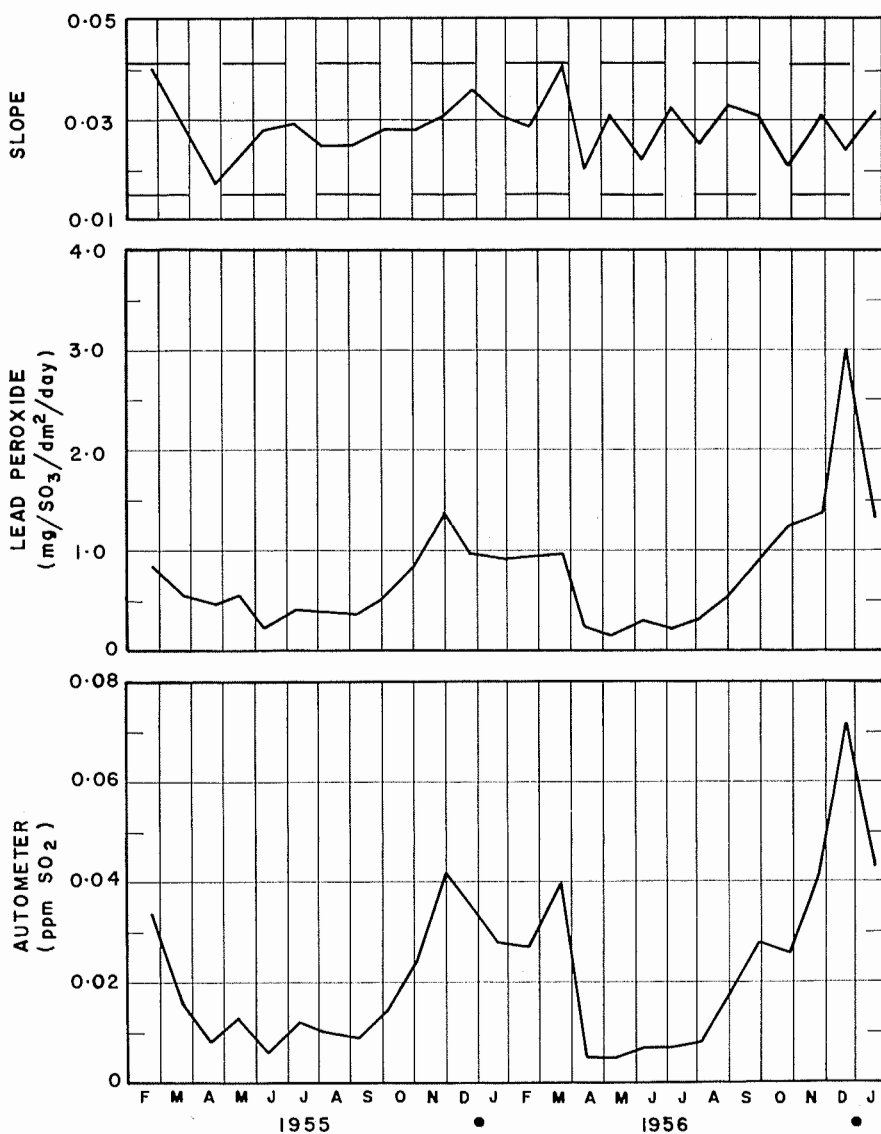


Figure 3— $\text{SO}_2$  levels at Birchbank. Autometer vs lead peroxide cylinders.

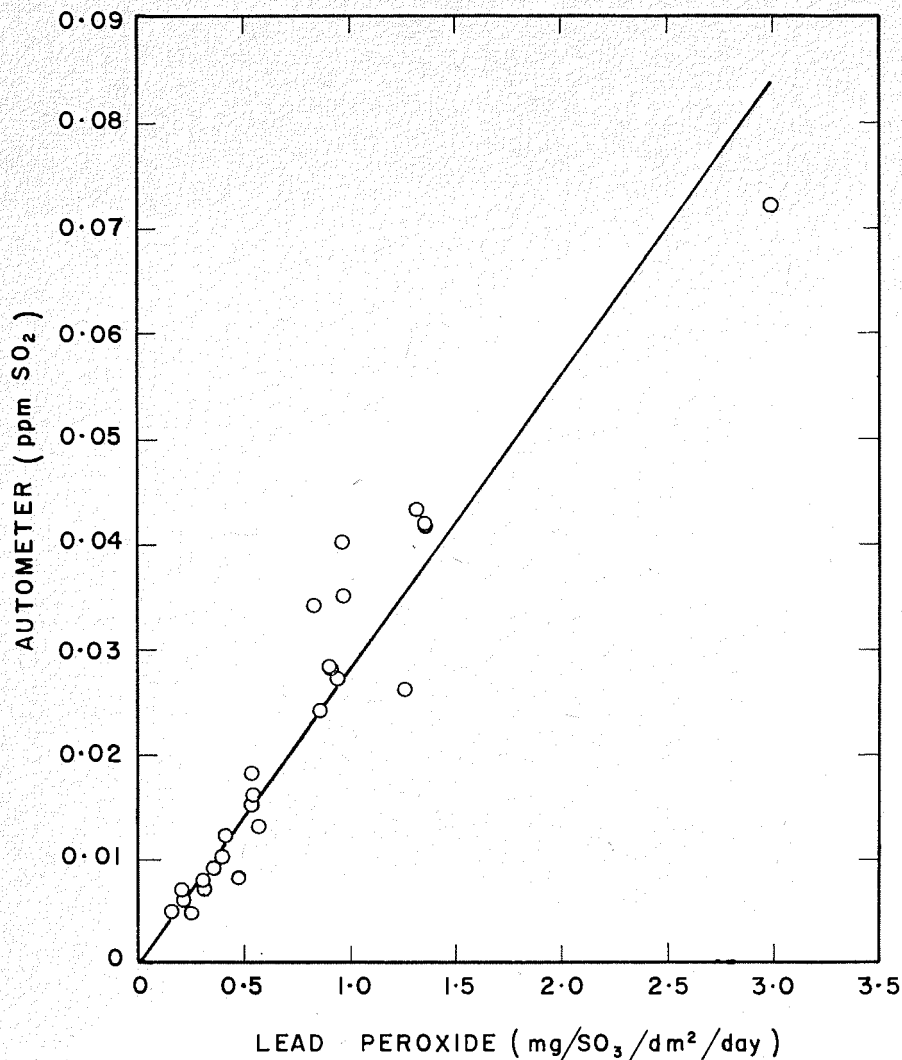


Figure 4—SO<sub>2</sub> levels at Birchbank. Autometer vs lead peroxide cylinders. Cylinder stations 1,2,5,6,9,10.

of +0.002. The correlation coefficient was determined to be +0.94.

It is therefore clear that the sulphur dioxide "activity" figures obtained by the lead peroxide method correlate very closely with the average SO<sub>2</sub> content of the atmosphere, as determined volumetrically. Hence the lead peroxide method may be considered to be, from this point of view, eminently suited to determining the relative sulphur dioxide "activity" at the various sites at different times, using a standardized procedure. This conclusion assumes that climatic conditions at other exposure sites will not affect the rate constant  $k$  any differently than at the Trail site, and while this point should be checked, in view of the excellent correlation obtained, it would seem safe to conclude that this is generally so.

Practical considerations require that the degree of reproducibility

and precision of the lead peroxide method be known, as well as the effect of differences in position at the site, both horizontally and vertically, the effect of type of shelter provided, etc. Accordingly, the 14 lead peroxide cylinders referred to previously were arranged as shown in Table 1. In order to facilitate the statistical evaluation, a standard exposure period of four weeks was selected, rather than a variable length monthly interval. All 14 cylinders were exposed, with appropriate replacements, during the interval from May 31, 1955, to January 8, 1957. The average rate of sulphation of cylinders 1 to 14, is shown in Table 2. In Table 2 the cylinders have been grouped according to rate of sulphation—there is a significant difference between groups, but the differences within each group are not significant. In Table 3 the 95% confidence limits of a single determination are given.

The difference shown between the three confidence limits are statistically significant. The relatively high figure for cylinders 3 and 4 reflects an increase in analytical errors due to low values of sulphation.

The data show that although there was no significant difference in rate of sulphation across the width of the exposure site (approximately 100 feet), the distance above ground level is significant—the average of cylinders 7 and 8 (2 ft. above ground level) being some 10% lower than the average of Group 2 cylinders. Consequently, weekly exposure of fresh cylinders (No's 3 and 4) resulted in a slightly higher, 10% rate of sulphation than the standard four-week exposure period.

The rate of sulphation of cylinders 13 and 14, which were provided with louvered box shield, was some 12% lower than the average rate of sulphation of the Group 2 cylinders but the precision was slightly better (Table 3). The DSIR investigators have observed <sup>(1, 2)</sup> that the original cowl cover does not adequately shield the cylinders from driving rain and, since they determined that a wet lead peroxide surface was appreciably more reactive than a dry one, they then adopted the use of a louvered box to shield their cylinders. The difference between cylinders 13 and 14 and the average of the Group 2 cylinders was compared with the hours of rainfall for each period but no significant correlation was found. Presumably the Trail site is not subject to driving rains as are the sites in the United Kingdom. Some seasonal cyclic variation in the difference between cylinders 13 and 14 and the average of the Group 2 cylinders was noted but it was not possible to correlate this difference with any observed meteorological data. The use of a louvered box shield has the effect of reducing the reactivity of the lead peroxide, but this in no way affects the correlation of the instrument with the Thomas autometer, except that a different value of  $b$  is required. If a wet lead peroxide surface is more reactive than a dry one then presumably improved shielding is an advantage and a properly shielded instrument will more truly reflect actual changes in SO<sub>2</sub> concentration. For the Trail site the error incurred through the use of cowl protectors is negligible. However, this point would be worthy of further study.

The rate of sulphation of lead peroxide cylinders 11 and 12, supplied and analysed by the Division of Building Research, of the National



TABLE 4

Results of Atmospheric Sulphur Dioxide Determinations made at a number of Locations in Canada with the Lead Peroxide Instrument (reported as mg SO<sub>2</sub>/dm<sup>3</sup>/day)

	Month	Ottawa	Montreal	Saskatoon		Halifax			Fisheries Exp. Stn.	Rocky Point	Norman Wells	Trail
				Exposure Station	Residential Area	Federal Building	York Redoubt	Atlantic Reg. Stn.				
1954	January	0.83										
	February	0.86										
	March	0.92										
	April	0.48										
	May	0.40										
	June	0.31										
	July	0.37										
	August	0.38										
	September	0.27	1.35									
	October	0.33	1.97	0.38								
	November	0.52	2.00	0.44						0.24		
	December	0.54	2.76	0.60		18.20	0.70			0.06		
1955	January	0.55	3.60	0.45		22.68	1.50			0.07		
	February	0.68	3.49	0.52		18.40	1.47			0.03		
	March	0.50	2.64	0.48		21.86	0.29			0.03		
	April	0.34	1.94	0.29		14.85	0.52			0.03		
	May	0.47	1.79	0.22		14.82	0.63			0.01		
	June	0.28	1.68	0.20		4.45	0.25			0.02		
	July	0.22	1.27	0.18		1.55	0.13			0.04	0.01	
	August	0.21	1.16	0.26		1.49	0.09			0.03	0.02	
	September	0.44	1.38	0.23		10.52	0.11			0.02		
	October	0.39	1.82	0.12		15.44	0.47			0.05		
	November	0.76	2.73	0.27	0.34	18.74	0.17			0.10		
	December	0.70	3.45	0.32	0.28	27.65	0.36			0.06		1.15
1956	January	0.57	3.90	0.27	0.32	19.87	0.89			0.08		1.52
	February	0.85	3.14	0.38	0.43	21.87	0.40	0.45	3.60	0.05		1.42
	March	0.69	2.83	0.19	0.31	21.90	0.74	0.88	3.37	0.08		0.27
	April	0.47	1.93	0.11	0.12	15.32	0.68	0.89	3.26	0.04	0.004	0.20
	May	0.46	1.87	0.11	0.13	4.18	0.61	0.51	2.66	0.05	0.008	0.38
	June	0.25	1.87	0.12	0.08	5.95	0.19	0.40	1.44	0.04	0.002	0.24
	July	0.24	—	0.05	0.03	1.62	0.08	0.18	1.20	0.003	—	0.44
	August	0.24	1.37	0.13	0.09	2.09	0.12	0.36	1.34	0.003	0.006	0.59
	September	0.27	1.54	0.04	0.09	5.35	0.36	0.46	1.38	0.003	0.01	1.01
	October	0.45	1.91	0.10	0.11	9.55	0.61	0.67	2.84	0.03	—	1.16
	November	0.50	2.50	0.31	0.33	9.68	0.42	0.91	2.44	0.09	—	1.23
	December	0.69	2.78	0.41	0.36	10.66	0.52	1.41	3.59	0.05	—	2.85

Research Council, is apparently some 10% higher than the mean of the Group 2 cylinders and some 22% higher than the Trail louvered box cylinders (No's 13 and 14); the precision is the same as the Trail louvered box cylinders. This difference in rate of sulphation represents an accumulation of errors due to differences in reactivity of the lead peroxide used, method of preparing cylinders, systematic errors in analysis, etc. This difference, though moderately large, is not considered to be serious. As described earlier, the NRC Division of Building Research cylinders are prepared from "standardized" lead peroxide obtained from the DSIR Fuel Research Station. The Trail cylinders are prepared from locally available lead peroxide according to established Cominco practice. The DSIR investigators have reported variations of 10% in the reactivity of different batches of lead peroxide<sup>(5)</sup>. Further work is required and is now in progress, to determine the magnitude

of the error associated with differences in method of preparation, analysis, etc. It is clear, however, that with carefully standardized materials and technique the lead peroxide method is a useful tool for evaluating and comparing the sulphur dioxide content of the atmosphere.

The lead peroxide method of measuring the SO<sub>2</sub> "activity" of the atmosphere, as related to outdoor corrosion and exposure studies, satisfies the basic requirement of simplicity of installation, operation and maintenance, and has been shown to correlate with the SO<sub>2</sub> concentration of the atmosphere as determined volumetrically. It has also been shown that the precision of the method is adequate if a standardized technique is used. The 95% confidence limits of a single determination in the series of tests described above (Table 3), where the mean rate of sulphation was 0.772 mg SO<sub>2</sub>/dm<sup>3</sup>/day, was ±0.09, or approximately 12%. This figure is in agreement with the experience of other investigators<sup>(5, 7)</sup>.

The minimum and maximum rate of sulphation observed during the interval of time over which the test was carried out was 0.14 and 3.17 mg SO<sub>2</sub>/dm<sup>3</sup>/day, respectively.

Outdoor corrosion studies are rarely ever carried out over such a short time interval as one month, the shortest practicable period of time being about one year. During this interval, using the standard procedure, 12 lead peroxide cylinders will have been exposed. Since the standard error is reduced by the square root of the number of determinations, this means that the average SO<sub>2</sub> "activity" at an exposure site over an interval of one or more years may be determined with considerable precision. Using the data derived in the series of tests described above, the 95% confidence limits for intervals of one, five and 10 years would be ±3.4% (±0.02), ±1.5% (+0.012), ±1.1% (±0.008).

These results may be compared with the variations in the weight losses due to corrosion of the stand-



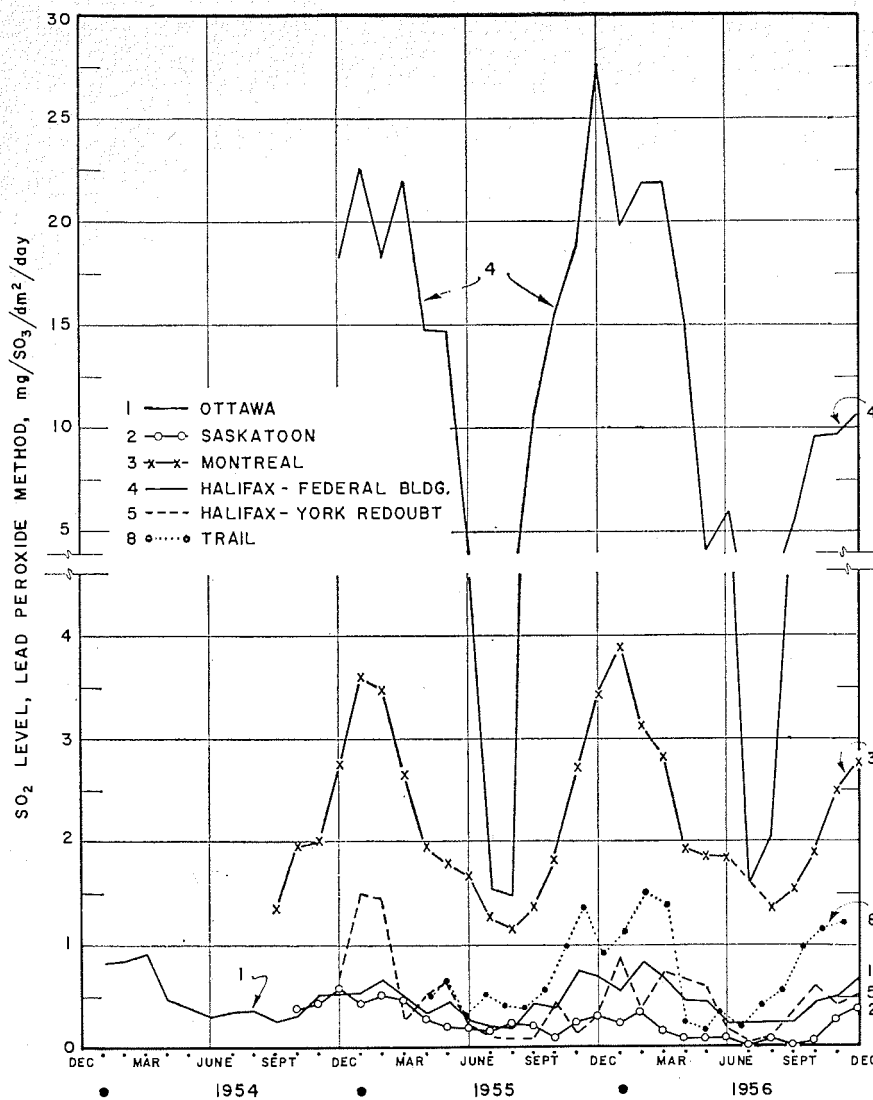


Figure 5— Monthly level of SO<sub>2</sub>—1954 to 1956 at Canadian exposure sites. Lead peroxide method.

TABLE 5  
ANALYSIS OF RUST SAMPLES

Sample	Chloride (ppm)	Sulphur (%)
Site No. 1 — Ottawa.....	161	0.53
Site No. 2 — Saskatoon.....	359	0.47
Site No. 3 — Montreal.....	230	0.97
Site No. 4 — Halifax City.....	796	1.02
Site No. 5 — Halifax-York.....	216	0.49
Redoubt		
Site No. 6 — Norman Wells.....	568	0.31
Site No. 7 — Rocky Point.....	307	0.11
Site No. 8 — Trail.....	146	0.70

ard steel and zinc specimens being exposed by the American Society for Testing Materials <sup>(9)</sup> and referred to later in this report. Four test panels are exposed at each site for each exposure period. The 95% confidence limits of the observed yearly

corrosion rates, expressed as a percentage of the mean, range from approximately 1 to 20%. The average values are 3.1% for the standard steel specimens, and 6.9% for the standard zinc specimens. Since sulphur dioxide is only one cause of variation in cor-

rosion rate (although, as will be shown later, it is a significant factor) a measure of the SO<sub>2</sub> "activity" with a precision of 1 to 2% should be adequate for studies of this type. It is concluded, therefore, that the standard lead peroxide method of measuring the sulphur dioxide content of the atmosphere is particularly well suited to determining the relative SO<sub>2</sub> "activity" at outdoor exposure sites when test specimens are exposed or under study.

The measurement of sulphur dioxide at the eight cross-Canada sites used by the Associate Committee was started at the Ottawa site in January of 1954. These measurements were extended to the remaining sites on a monthly basis as they became available for exposure testing. The exception was Norman Wells where monthly determinations can only be made from late spring to early fall with one measurement over the winter period. At the Trail exposure site the monthly measurements were correlated with the special series of tests described previously. The results of the sulphur dioxide determinations made at the sites and at certain other locations, beginning in 1954 for Ottawa, are tabulated in Table 4 and shown graphically in Figure 5.

From this it is seen that the level of sulphur dioxide at the Rocky Point and Norman Wells sites is extremely low in comparison with the other sites. Also, the levels vary considerably from site to site and at each, the level appears to be influenced by the amount of fuel burned for heating. A low level occurs during July and August and the highest level is reached during the winter months of December, January, February and March. This change is approximately three-fold for the populated centres.

The levels obtained at the Halifax Federal Building site are exceptionally high in comparison to those obtained at all the other sites. The true levels may be even higher than indicated, due to saturation of the lead peroxide surface, and consequent failure to register the total SO<sub>2</sub> present, as explained earlier. The results for this roof site are undoubtedly affected by the effluent from the low chimney which serves this building during the heating season. While this may well represent an extreme condition of exposure it also represents conditions to which the roof elements of many other buildings are likewise exposed. An indication of the sulphur dioxide levels at other locations in the city of Halifax

was obtained from measurements made during 1956 on the roof of the Atlantic Regional Station, at Dalhousie University and at the Fisheries Experimental Station. Much lower levels were obtained for these locations than for the Federal Building site.

The York Redoubt marine site has a high sulphur dioxide concentration in comparison to that obtained for the west coast marine site at Rocky Point. York Redoubt is also in a rural area but is only seven miles from the city of Halifax. An increase in the level of sulphur dioxide is noted at this site during the heating season and is no doubt affected by combustion products from Halifax and the nearby heating units.

The standard steel and zinc specimens which were used in measuring the relative corrosivity at the American Society for Testing Materials' exposure sites<sup>(9)</sup> were made available for exposure at the Canadian sites.

The weight of metal lost from the standard zinc and steel specimens after a year of exposure at the Canadian sites is shown in Figure 6. The weight losses obtained after exposure for one-and two-year periods indicate a close relationship between the severity of corrosion and concentration of sulphur dioxide in the atmosphere. The results obtained are similar to those obtained by Hudson and Stanners<sup>(10)</sup>. A very small loss of metal was obtained after exposure at Norman Wells and high losses found with the correspondingly high sulphur dioxide levels at the Halifax Federal Building site. It was noted, however, that steel panels exposed at York Redoubt, a marine atmosphere, had metal losses similar to those of panels exposed at Montreal and Trail where sulphur dioxide levels were found to be considerably higher. The effect which atmospheric chlorides or other climatic conditions have on their performance requires further investigation.

As a first step in such an investigation rust was collected from the steel samples at each corrosion site and analysed for chloride and sulphur. The results are shown in Table 5.

The amount of chloride found in the corrosion products at two inland sites, namely, Saskatoon and Norman Wells, was unexpected, so an attempt was made to find a method for measuring atmospheric chlorides at the eight exposure sites across Canada.

Four years ago, Moyerman and Shuler<sup>(11)</sup> summarized the results of a literature survey of the published

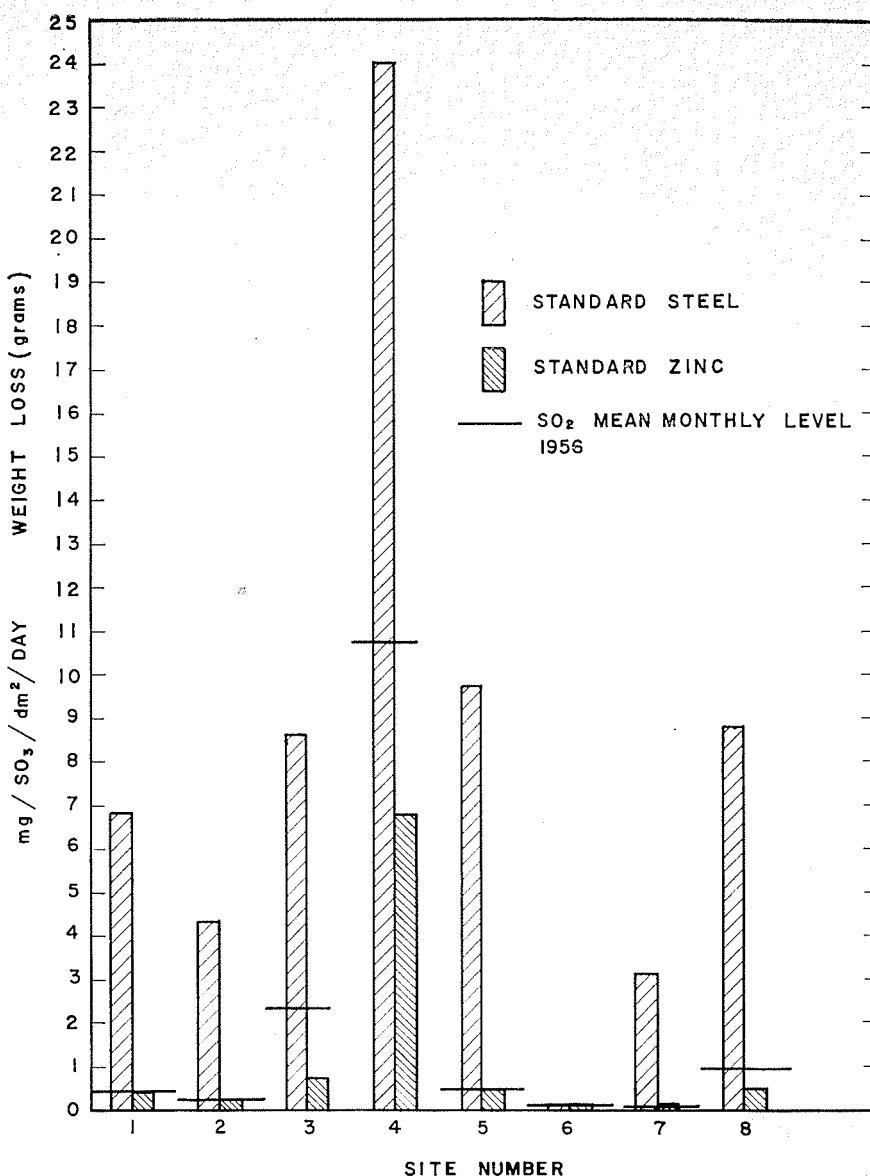


Figure 6—Weight loss of zinc and steel at exposure sites.

Site Numbers	
1. Ottawa	5. Halifax—York Redoubt
2. Saskatoon	6. Norman Wells
3. Montreal	7. Rocky Point
4. Halifax—Federal Building	8. Trail

TABLE 6  
REPORTED METHODS FOR DETERMINING ATMOSPHERIC CHLORIDES

1. Bubbling measured volumes of air through chloride-free water<sup>(14)</sup>.
2. Drawing measured volumes of air through chloride-free filters<sup>(15)</sup>.
3. Drawing measured volumes of air through refrigerated tubes or dew tubes<sup>(12)</sup>.
4. Exposure of wet chloride-free cloths<sup>(12)</sup>.
5. Exposure of wet chloride-free cylinders<sup>(12)</sup>.
6. Measurement of the chloride content of rainwater<sup>(16)</sup>.
7. Collection of chloride in artificial dew on cold flasks<sup>(12)</sup>.
8. Counting salt crystals on exposed slides<sup>(12)</sup>.
9. Collecting salt by impactors or jets<sup>(17)</sup>.
10. Thermal precipitation on glass slides<sup>(12)</sup>.
11. Isopiestic method using glass plates and controlled humidity<sup>(18)</sup>.

data on the concentration of alkali salts in ground level air but only two observations other than volumetric measurements are reported and the manner of correlating these measurements of the amount of salt falling on a surface with the amount per unit volume of air is not stated. The most extensive work reported on the measurement of atmospheric chlorides is that of Ambler and Bain <sup>(12)</sup> as part of a study of the corrosion of metals in Nigeria. Sugawara et al <sup>(13)</sup> showed that the ratio of sodium to chloride ions in various types of moisture varied a great deal and the chloride could not be converted to sodium chloride by assuming a 1:1 ratio as has been done by many workers.

Eleven methods of measuring atmospheric chlorides are listed in Table 6. Seven of these depend upon the accurate determination of relatively small amounts of chloride and the development of a chloride-free technique. The last four are not always specific for chloride because it is difficult to distinguish from other salts—all these methods are tedious.

A suitable method for all Canadian exposure sites must require no electrical power and no attention between monthly visits. It must operate satisfactorily under temperature changes from -70°F. to 100°F. and dust, snow, sleet and freezing rain conditions. It must be continuous in operation and capable of collecting all sizes of chloride particles which have significance in corrosion. A careful consideration of the methods in Table 6 shows that not one of them is entirely satisfactory. Snow and freezing rain have been found to interfere seriously with battery operated instruments which draw air into filtering devices or flasks. Artificial dews cannot be obtained in sub-zero temperatures and the physical methods are not suited to long-term measurements. The most promising methods appeared to be a modification of the "wet candle" method of Ambler and Bain, and the use of rainfall cans.

The "wet candles" were made by wrapping three strips of No. 2 surgical gauze, three inches wide and 28 inches long, around the exposed portion of a 3- by 5½-inch test tube protruding through a rubber or cork stopper (Figure 7). The gauze was freed of chloride by repeated boiling with distilled water. The rubber stopper holding the "candle" was cut away slightly at each side to allow the gauze to reach down into the liquid and act as a wick. The stopper was fitted into a 500 ml wide mouth

Location	Period	Methods of Measurement	No. of Values	Quantity tons NaCl	Quantity mg NaCl
				mi <sup>2</sup> /mo	dm <sup>2</sup> /day
Halifax, Federal Building	Aug. 1956	Wet Candles	5	2.57	.30
Halifax, York Redoubt	Aug. 1956	Wet Candles	5	1.71	.20
Sackville, N.B. (3 mi inland)	Aug. 1956	Wet Candles	5	1.06	.12
Halifax, Technical College	Aug. 1956	Wet Candles	3	1.79	.21
Halifax, Chedabucto Head (135 ft. from sea)	Aug. 1956	Wet Candles	3	31.40	3.67
Halifax, Technical College	Jan. 1957	Wet Candles	4	3.10	.36
Halifax, Technical College	Mar. 1957	Wet Candles	2	3.85	.45
Halifax, Technical College	Apr. 1957	Wet Candles	4	1.45	.17
Halifax, Technical College	Aug. 1956	Rainfall	1	1.49	.17
Halifax-Dartmouth Area	Aug. 1956	Rainfall	12	1.25	.15
Halifax-Dartmouth Area	Aug.—Dec. 1956	Rainfall	44	3.06	.36
Windsor-Detroit* Heavily Polluted Area	Aug.—Dec. 1951	Rainfall	6	2.83	.33
Heavy to Moderate Pollution	Aug.—Dec. 1951	Rainfall	8	1.18	.14
Moderate to Low Pollution	Aug.—Dec. 1951	Rainfall	3	1.23	.14
Low Pollution	Aug.—Dec. 1951	Rainfall	3	1.50	.18

\*Values in reference<sup>(14)</sup> converted from chloride to NaCl.

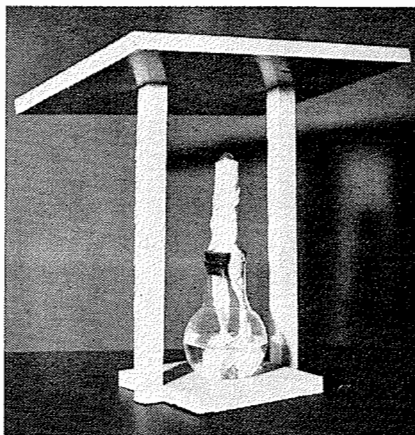


Figure 7—A "wet candle" device.

florence flask containing a mixture of glycerine and water. Concentrations between 0 and 30% by volume were tried but 20% was found to be adequate for Halifax conditions. The apparatus was covered with a sloping roof for protection from rain and sun.

Fibre glass cloth was tried as a substitute for gauze but it did not remain wet. Ice formed in the flasks during freezing weather but it did not break the glass nor cause any noticeable decrease in the pick-up of chloride. Flasks with cork stoppers showed a mold growth during warm weather. The worst hazards were cats and hurricane-force winds.

The "wet candles" collect a considerable amount of soot and grime in industrial atmospheres and these materials increase the difficulty of the analysis for chloride. Both mer-

curimetric and argentimetric methods were tried but the latter appeared to be more reliable. Organic matter and sulphites were removed by excess potassium permanganate which was reduced by hydrogen peroxide. The sequence of operations was: extraction of chlorides from gauze by boiling; filtering oxidation with KMnO<sub>4</sub>; standing; addition of peroxide; boiling if necessary, filtering; evaporation; dilution to 250 ml; and titration of aliquot samples. Sodium nitroprusside was used as the indicator for mercurimetric titrations and potassium chromate for titrations with silver nitrate.

The total area of gauze exposed, on each flask was about 95 cm<sup>2</sup>. Exposure periods of two, three and four weeks were used. The results were calculated to the same basis as those of the rainfall cans exposed at twelve locations in the Halifax area. These cans were of stainless steel and of the design used in the Windsor-Detroit survey <sup>(16)</sup>. The opening was 100 square inches and the period of exposure was one month. The rainfall was evaporated and chloride was determined in the water soluble portion which passed through the filter.

In Table 7, data obtained by two sets of workers in the Halifax area are shown along with data for the Windsor-Detroit area as reported by Katz <sup>(16)</sup>. They appear to indicate that, except for regions very close to where surf breaks on the shore, there is little significant variation in the amount of chloride in the atmosphere. They also indicate that the

"wet candle" measures essentially the same type of chloride deposition as the rainfall cans.

If these conclusions are valid for most areas of Canada then the amounts of chloride found in the rust samples depend upon the degree of leaching by rainfall. Since Norman Wells and Saskatoon are in areas of limited rainfall during the summer and have practically no rainfall in the winter season the chloride results shown in Table 5 might be explained in part by the meteorological conditions which preceded the collection of the samples.

A rare meteorological condition which occurred in Halifax on and after December 30, 1956 throws some light on the mechanism by which sea salt is carried inland. Hurricane force winds without accompanying rain covered the windward side of all objects for several miles inland with a thin layer of salt. This salt layer persisted for some days and noticeably affected the distribution of electricity because the insulators became conductors everytime a slight amount of moisture fell upon them. Sea water was sprayed into the air by intense wave action on the shores

and the moisture evaporated leaving extremely fine crystals of salt to be impinged on suitable vertical surfaces.

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