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REMARKS ON THE QUALITY OF THE LRTAP GROUND SAMPLING DATA

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CONTENTS

INTRODUCTION

In addition to the collection and edition of the results from the ground sampling network, the CCU has been responsible for the distribution of standard procedures for sampling and chemical analysis (1-6), and for testing of the methods through distribution of standards and exchange of samples. Results of the intercalibration and other tests giving information on the precision and accuracy of the methods, as well as more general remarks on the data quality are given in the following.

ANALYSIS OF STANDARD SAMPLES AND EXCHANGE OF SAMPLES

A serie of synthetic standard samples have been circulated to the participating countries for testing of the precision of the methods. Results from the collaborative testing are presented in Table I, also presented in the table are the mean values and the dispersion of the results expressed by the root mean square deviation.

While the dispersions of the sulphate data (- "in precipitation") are nearly constant and independent of the added amount of sulphate, the dispersions of the sulphur dioxide and the strong acid results are more variable. The analyses were run in the preparatory phase of the project and several of the laboratories had limited practical experiences in the application of these particular methods.

Table II gives results of a comparative test using several different methods. These were: X-ray fluorescence (7), isotope dilution (IDA)(8), Wickbold nephelometric method (9), and the results are given with the added amount of sulphur as sulphate. The results from five precipitation samples using the same three methods and in addition the Thorin method are also included.

Several filters from air samples have been distributed among the participants and analysed by the XRF-method at different laboratories. Table III gives the XRF results of filters from 1974 exposed at the Austrian stations and analysed at Bundesstaatliche Bakteriologisch-serologische Untersuchungsanstalt in Austria by XRF and at the Norwegian Institute for Air Research (NILU) by the Thorin method. Table IV gives corresponding results analysed by XRF at Warren Spring Laboratory and at the Norwegian Institute for Atomic Energy (IFA).

Warren Spring Laboratory has found out that plots of chemically determined sulphate concentrations versus the X-ray count follows a straight line when I_B/I_F exceeds 0.2. When the I_B/I_F ratio is lower than 0.2 the slope of the curve is no longer independent of I_B/I_F and if a linear relation is assumed an error may be introduced. However, the errors introduced by this assumption are probably of little practical importance as Figure 1 shows.

A number of precipitation samples have been exhanged between the participating laboratories. Table V gives the results of Dutch samples analysed at RIV and NILU and British samples analysed at WSL and NILU. Some of the discrepancies may be due to storage effects, as these samples were analysed the second time about 4-6 weeks after the sampling.

COMPARISON WITH OTHER SAMPLING AND ANALYSIS METHODS

The Rijksinstitut vor de Volksgesundheit (RIV) in the Netherlands ran a comparison of the tetrachloromercurate and the Thorin method at the three stations Wageningen, Witteven and den Helder in 1972-1973. Table VI compares the TCM method which is specific for sulphur dioxide and the Thorin method which gives the total gaseous sulphur, which can be oxidized to sulphate in an hydrogenperoxide solution at pH 5. The Thorin method gives, as may be expected, generally higher mean concentrations and maximum values. The slope of the regression lines are probably not significantly different from 1.0, indicating that the methods give nearly identical results when considering possible interferences (e.g. by ozone in the TCM method).

The advanced sampling programme sulphate aerosol concentrations are determined using a wet chemical method. Figure 1 presents corresponding results from the NORDFORSK project in 1973. The results are in very good agreement, it might seem as if the wet chemical method has a tendency to give slightly higher results. This may be due to a more efficient collection of larger particles by the high volume sampler.

CORRELATION BETWEEN NEIGHBOURING STATIONS

The correlations obtained between observed and predicted values are limited by several noise factors.

For sulphur dioxide the measurements are probably no better than ± 3-5 μg SO_2/m^3. Also the observations are log-normally distributed, so that the correlation is determined by a few observations (episodes). The correlation coefficients therefore depend on the number of observations and the observation period. Contamination errors and spurious influence from local sources may reduce the correlation seriously.

Two of the stations in Norway are sufficiently close to warrant an investigation of the mutual correlation. The correlation in the daily SO_2 values for the months January-June 1974 was 0.540 : the standard deviation in the same period ± 9.1 μg SO_2/m^3. There was, however, at least two cases of strong deviations: 2nd January with 29 μg SO_2 at N01, 1 μg/m^3 at N03. 17th March N01 had 6 μg/m^3, while N03 reported 80 μg/m^3. 3rd January and 16th March gave high

observations at both stations, but the value 80 μg/m^3 is probably an error. When these two observation pairs are left out, however, the standard deviation becomes ± 5.4 μg/m^3, which compares favourably with the estimated precision of ∿ 3 μg SO_2/m^3 ($3\sqrt{2} = 4.2$).
The correlation is increased to 0.726.

The spacing of the ground sampling stations is not sufficiently dense to allow rejection of similar "accidents" from the data on a general basis.

Because of this, calculated correlation coefficients between observed and estimated, and between neighbouring stations cannot be directly interpreted. Some qualitative information may be obtained from a comparison of space correlation coefficients for SO_2 and SO_4, as for example in Figure 2 and 3. (The values are listed in Tables VII and VIII.) It is seen that the calculated correlation coefficients are highest for neighbouring stations and for the stations where long range transport is expected to contribute most significantly to the observed SO_2 and sulphate concentrations.

It may also be of interest to compare correlations between neighbouring stations with correlations between observed and estimated values, for identical sets of observation data.

CONCLUSIONS

Sulphate in precipitation

The precision of the chemical analysis is believed to be close to 0.2 μg/ml, from the results presented in Table I, and considering the improvement in laboratory performance during the programme.

Strong acid in precipitation

The accuracy in this parameter has earlier been found to be accurate to the nearest 5 μeq/ℓ. It seems that storage in polyethylene bottles seems to increase the strong acid concentration slightly.

pH

The storage effect mentioned above will of course also have an effect on the measured pH-values. These pH-values found at NILU in the Austrian samples are generally lower than the corresponding Austrian results, the difference in the British samples are less and the agreement is better. This corresponds with the measured acid concentrations in the Austrian and British samples. There is generally good agreement between measured pH and strong acid concentrations, when pH < 5.5 (Table IX).

Sulphate collected on filter

Calibration of the XRF-results by wet chemical analysis using filters impregnated with sulphate in aqueous solutions as secondary standards has shown that the absorption of X-rays in the filter material and variations of the penetration depth of the particle samples does not have serious effects on the results. A constant factor may be used to obtain the amount of sulphate on the filters (10, 11).

It has been pointed out that wetting of the filters may introduce errors up to 50%. Subsequent wet chemical determination of sulphate was carried out in connection with the testing of the XRF method in the preparatory phase (10), and has since been repeated for a set of filters from Austria (Table III). The agreement is partly limited by the precision in the wet chemical analysis method.

When XRF has been used to determine sulphate on the same filters at different laboratories, the agreement has generally been good.

The comparison between the wet chemical method during the NORDFORSK 100-day period, and the XRF-method gives a generally 15% lower XRF-result, the difference probably due to different collection efficiency for the large particles.

Sulphur dioxide

The minimum detectable sulphur dioxide concentration is around 2-5 $\mu g/m^3$. The dispersion between the concentration values presented in Table 1 is small, the relative standard error is less than 5% for the sample above the detection limit.

Several frequency distributions of sulphur dioxide concentrations are presented (Figure 4-7).

A quantization effect may appear in the data due to a truncation which will occur in the computation of the air concentrations from the analysis results in the laboratories. This will be up to 2-5 $\mu g/m^3$ (Figure 4).

Because of noise in the analytical signal, and because spurious positive readings near the detection limit are not balanced with corresponding negative readings, the mean values will in general be somewhat positive biased. This error will be a fraction of the detection limit, and will occur only if a significant percentage of the daily concentrations are below the detection limit.

More serious truncation errors are revealed in Figures 6 and 7. These errors have been eliminated through a change in laboratory practices.

There has also been a change in the analytical methods for the German stations. This change occurred in February-March 1974.

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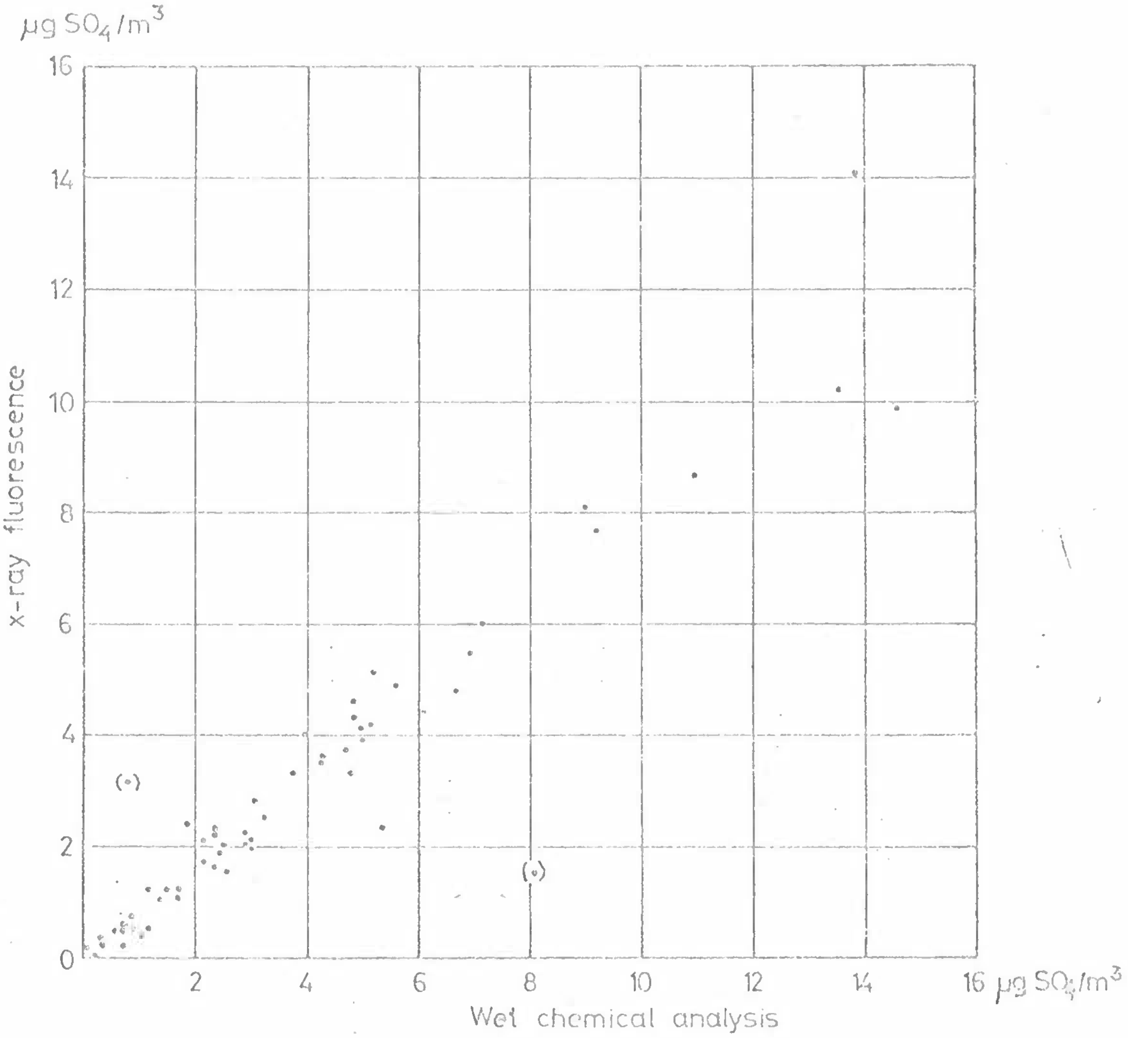

FIGURE 1: Comparison of results by X-ray fluorescence on filters from an OECD-type sampling apparatus with wet chemical analysis of high-volume samples collected on Acropor-5000 filters.
May - June 1973.

FIGURE 2: Correlation between measured daily sulphur dioxide concentrations at neighbouring stations.

FIGURE 3: Correlation between measured daily sulphate aerosol concentrations at neighbouring stations.

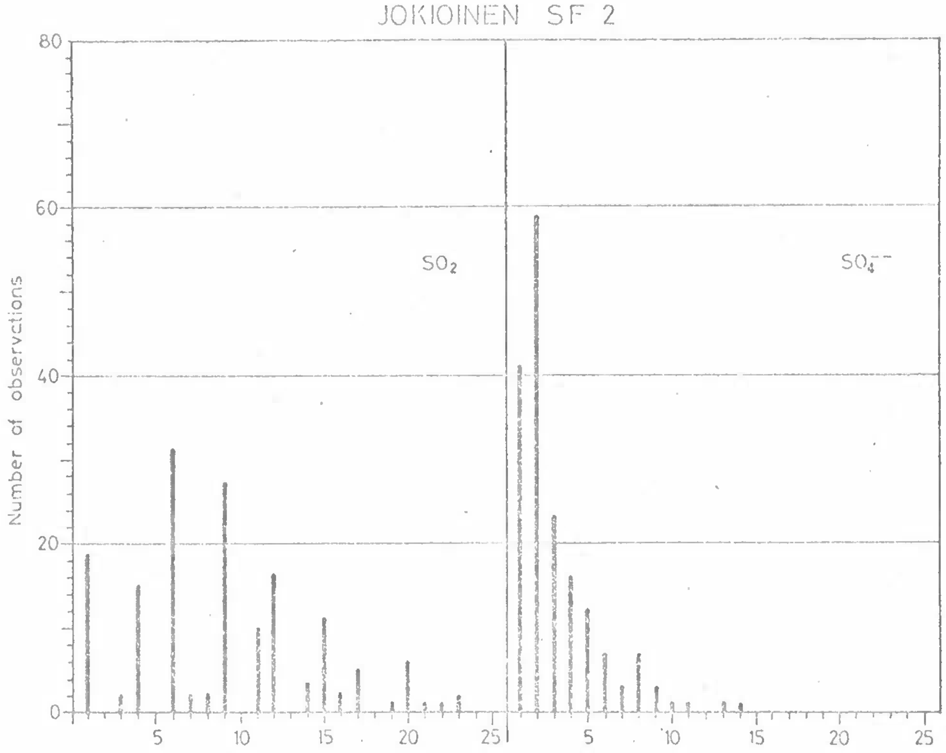

FIGURE 4: Frequency distributions of sulphur dioxide and sulphate aerosol concentrations.

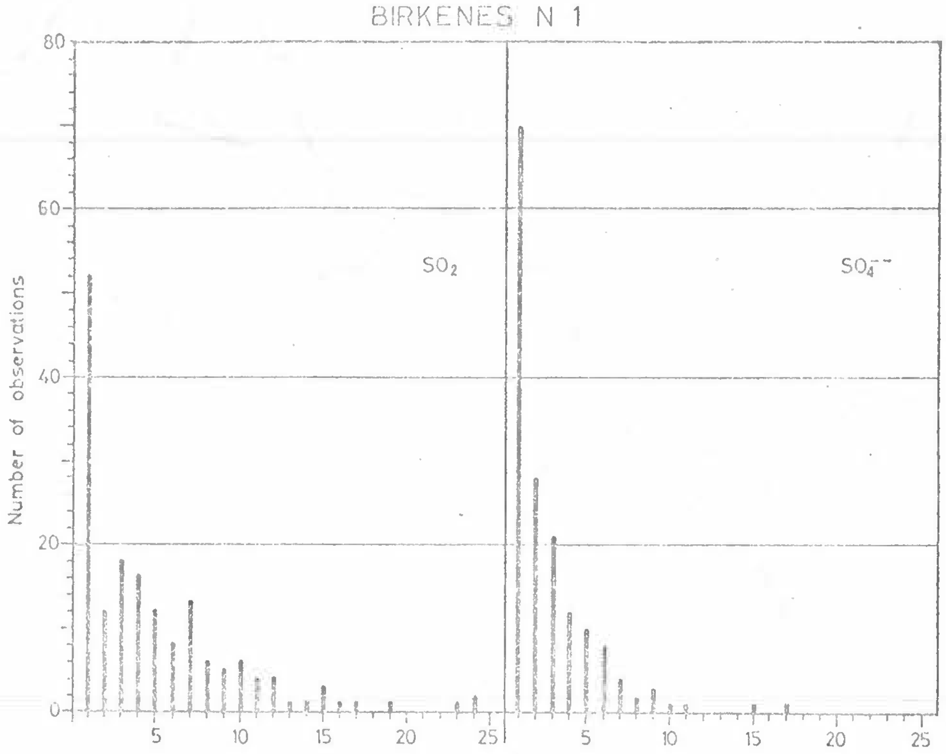

FIGURE 5: Frequency distributions of sulphur dioxide and sulphate aerosol concentrations.

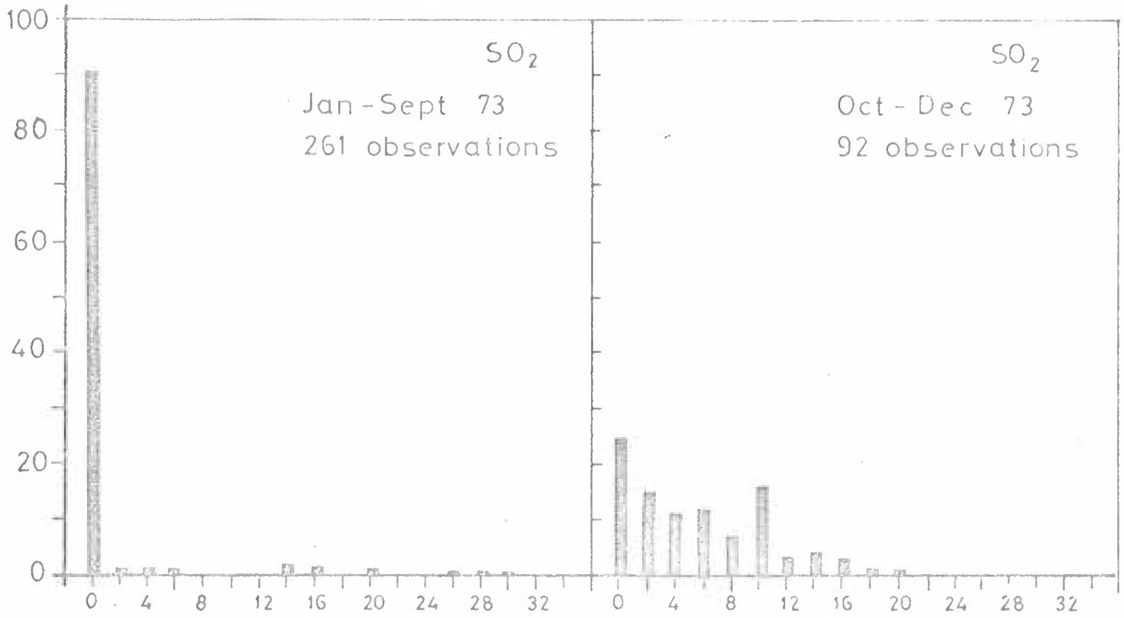

FIGURE 6: Frequency distributions of sulphur dioxide.
Ryda Kungsgård, S04.

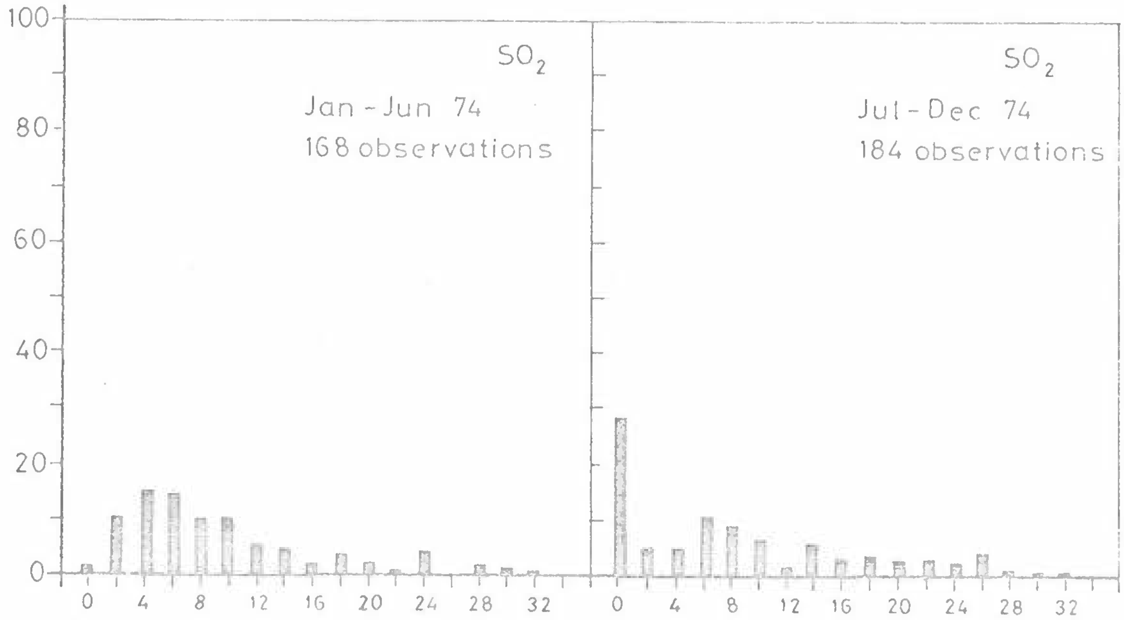

FIGURE 7: Frequency distributions of sulphur dioxide.
Gniben, DK4.

	Sample No	Sollwert	EMPA Switzer-land	IVL Sweden	DKF Denmark	Finland	WSL United Kingdom	Ice-land	Italy	Nether-lands	Austria	Mean value	Dispersion
SO_2 (µg/ml) in air	1	1.2	1.1	1.0	1.2	1.1	1.2	1.1	1.2	1.4	1.8	1.2	0.2
	2	5.6	5.5	5.4	5.2	5.6	5.7	5.4	5.3	5.5	6.0	5.5	0.2
	3	3.4	3.4	3.3	3.3	3.2	3.4	3.4	4.0	3.4	4.0	3.5	0.3
	4	19.0	17.2	17.3	17.9	17.8	18.3	18.6	16.8	(10.0)	19.2	17.9	0.8
	5	0.6	0.8	0.4	0.74	0.7	0.8	0.8	0.4	0.55	1.3	0.7	0.3
SO_4^{--} in pre-cipita-tion (µg/ml)	6	10.76	10.7	11.2	10.5	10.1	10.7	10.3	(6.9)	10.4	11.0	10.6	0.4
	7	3.92	3.8	3.9	4.1	3.8	4.0	4.0	3.4	3.53	4.7	3.9	0.4
	8	5.36	5.0	5.1	5.5	6.1	5.4	5.2	5.3	4.75	6.0	5.4	0.4
	9	(7.9)*	7.5	7.8	7.5	7.5	7.6	7.5	8.2	7.2	8.3	7.68	0.4
	10	5.43	5.1	5.5	5.4	5.5	5.3	5.2	5.9	5.0	6.2	5.46	0.4
Strong acid (µeq/ℓ)	6	120	120	117	-	117	119	-	114	110	65	108.9	19
	7	40	39	41	-	30	41	-	-	34	39	37.3	4
	8	70	71	66	-	60	68	-	61	27	100	64.7	21
	9	142	134	133		133	136	-	128	106	139	129.9	11
	10	9	8	10		6.6	11	-	-	6	14	9.3	3

*Exp. Det. value, NILU.

TABLE I: Collaborative testing.
Analysis of standard samples.

	SO_2					SO_4^{2-}					PRECIPITATION				
Number	I	II	III	IV	V	VI	VII	VIII	XI	X	1	4	6	17	31
Added amount	0.6	2.8	1.7	9.5	0.3	3.6	1.3	1.9	2.6	1.8	-	-	-	-	-
XRF	0.6	2.8	1.8	7.2	0.5	4.0	2.1	1.3	2.3	1.7	1.7	0.7	1.4	0.3	0.7
ID	0.5	2.8	1.8	10.1	0.6	3.6	1.3	1.7	2.6	1.8	1.6	0.7	1.4	0.3	0.8
Wb	0.9	2.6	1.7	6.3	0.7	2.6	1.2	1.1	1.5	0.9	0.9	0.5	0.9	0.6	0.6
Thorin	-	-	-	-	-	-	-	-	-	-	1.6	0.7	1.6	0.3	0.9

TABLE II: Comparison of different methods for determing sulphur.
All figures in mg S/ℓ.

XRF: X-ray fluorescence analysis
(Deutsche Forschungsgemeinschaft)

ID: Isotopic dilution analysis
(Deutsche Forschungsgemeinschaft)

Wb: Wickbold nephelometric method
(Deutsche Forschungsgemeinschaft)

Thorin: Thorin method (NILU)

Filter	XRF $\mu g\ SO_4$/filter	THORIN $\mu g\ SO_4$/10 ml	THORIN/XRF
1/2-74	61.05	34.50	0.56
2/2	37.80	28.50	0.75
3/2	48.80	33.00	0.67
4/2	18.05	18.00	0.99
5/2	18.71	14.25	0.76
2/3	32.08	18.00	0.56
3/3	32.60	20.70	0.63
4/3	39.55	27.75	0.70
5/3	22.24	19.50	0.87
6/3	47.84	34.20	0.71
1/4	14.4	16.20	1.12
2/4	17.34	16.20	0.93
3/4	13.89	11.25	0.80
4/4	13.93	12.00	0.86
5/4	23.44	17.70	0.75

Mean weighted factor THORIN/XRF: 0.72
Mean factor " : 0.77
Standard deviation : ±0.14 (18%)

(Relative error in THORIN determination: $\lesssim$ 10%)

TABLE III: Comparison of the THORIN and the XRF methods. The filters are exposed at Illmitz.

Date	Station	UK Results		N Results	
		$\mu g\ SO_4/4.9\ cm^2$	I_B/I_F	$\mu g\ SO_4/4.9\ cm^2$	I_B/I_F
721213	Cottered	13	.19	11.5	.22
28	" "	19	.22	16.8	.24
730119	" "	56	.07	75.0	.10
24	" "	30	.07	37.8	.09
17	Eskdalemuir	4	.23	2.4	.04
20	" "	11	.19	9.3	.18
29	Cottered	19	.11	18.9	.15
24	Eskdalemuir	9	.09	10.3	.12
26	" "	7.5	.25	5.9	.20
30	" "	3	.07	3.1	.11

TABLE IV: Sulphate on filters, exposed at Cottered and Eskdalemuir.

SAMPLE	pH			H^+ µeq/ℓ			Na^+ mg/ℓ			Mg^{2+} mg/ℓ			$SO_4{}^{2-}$ mg/ℓ		
	RIV	WSL	NILU	RIV	WSL	NILU	RIV	WSL	NILU	RIV	WSL	NILU	RIV	WSL	NILU
NL1 730212			4.40			47			1.05			0.06			2.78
" "	4.45		4.40	33		40	0.8		0.90	0.05		0.09	3.5		3.08
NL2 730212			4.25			53			0.25			0.01			1.73
" "	4.51		4.40	28		38	1.2		0.20	<0.01		0.01	2.5		2.18
NL3 730212			4.05			87			7.05			0.80			2.40
" "	4.30		4.15	54		71	7.8		7.45	0.53		0.93	2.9		3.08
NL1 730208			4.15			79			-			0.08			7.50
" "	4.31		4.20	53		48	0.2		0.65	0.04		0.06	9.4		8.93
NL2 730208			4.10			66			0.55			0.79			4.35
" "	4.27		4.20	38		68	0.8		0.45	<0.01		0.92	4.7		4.73
NL3 730208			4.15			75			7.55			0.03			4.13
" "	4.53		4.25	39		54	8.1		8.00	0.68		0.04	5.5		5.03
UK2 730114		4.10	4.05		74	92								5.0*	5.48
UK2 730115		4.50	4.60		18	26								2.2*	4.28
UK1 730122		4.20	4.25		38	62								3.0*	3.45
UK2 730121		4.50	4.75		16	16					0.14	0.14		1.0*	0.84*
UK2 730122		4.20	4.45		38	40					0.16	0.16		1.6*	2.21*
UK1 730126		4.50	4.65		22	31					0.1	0.10		3.1*	3.47*

* corrected for sea-spray

TABLE V: Precipitation samples, collected at stations in the Netherlands and the United Kingdom and analysed at RIV, WSL and NILU.

Method/Station	Observations	Mean concentration	Maximum	Minimum
TCM(1)	120	8.27	52.00	0.00
Th (2)	120	11.66	62.00	0.00
TCM(2)	119	6.31	30.00	0.00
Th (2)	120	7.37	29.00	0.00
TCM(3)	117	6.77	22.00	0.00
Th (3)	118	8.07	35.00	0.00

Linear regression (least squares):

Th(1) = 1.06 TCM(2) + 2.88 R = 0.82
Th(2) = 0.83 TCM(2) + 1.48 R = 0.80
Th(3) = 1.14 TCM(3) + 0.39 R = 0.83

TABLE VI: Comparison of the TCM and the Thorin methods at the three Dutch stations.

TCM(1): Sulphur dioxide concentrations as determined by the TCM or West and Gaeke method (NL1).

Th (3): Total gaseous sulphur compound concentration determined by the Thorin method (NL3).

D04	1.000												
DK3	-.103	1.000											
DK5	.004	.483	1.000										
N01	-.113	.172	.138	1.000									
N03	-.058	.077	.098	.540	1.000								
N09	.108	.023	.198	.221	.136	1.000							
N22	.331	-.011	.008	.152	.173	.200	1.000						
NL1	.244	.028	.051	.206	.068	.131	.346	1.000					
NL2	.216	.009	.265	.190	.163	.180	.368	.664	1.000				
NL3	.113	.011	.157	.154	.046	.151	.174	.600	.630	1.000			
NL4	.246	.119	-.121	.027	.009	.061	.415	.659	.389	.212	1.000		
S02	-.102	.088	.313	.336	.266	.223	.050	-.048	.113	.069	-.069	1.000	
UK1	.030	-.008	.025	.179	.142	.055	.229	.388	.349	.446	.157	.202	1.000
	D04	DK3	DK5	N01	N03	N09	N22	NL1	NL2	NL3	NL4	S02	UK1

TABLE VII: Correlation of daily SO_2-values between stations, January-June 1974.

D04	1.000												
DK3	.099	1.000											
DK5	.135	.803	1.000										
N01	.175	.748	.595	1.000									
N03	.135	.642	.522	.877	1.000								
N09	.182	.485	.425	.548	.554	1.000							
N22	.116	.748	.615	.709	.592	.505	1.000						
NL1	.499	.366	.415	.308	.256	.182	.335	1.000					
NL2	.448	.500	.563	.459	.367	.314	.424	.798	1.000				
NL3	.452	.496	.516	.492	.363	.360	.445	.739	.897	1.000			
NL4	.556	.252	.264	.226	.205	.125	.291	.797	.681	.651	1.000		
S02	-.031	.597	.443	.407	.283	.083	.590	.166	.234	.197	.100	1.000	
UK1	.439	.306	.366	.354	.353	.326	.302	.635	.676	.757	.628	-.008	1.000
	D04	DK3	DK5	N01	N03	N09	N22	NL1	NL2	NL3	NL4	S02	UK1

TABLE VIII: Correlation of daily sulphate in air values between stations, January-June 1974.

Station	"Strong acid" µekv/ℓ	Computed acid µekv/ℓ	Number of stations	pH interval
Birkenes	-1.7	6.8	6	(5.5, 5.0)
"	15.9	17.7	10	(5.0, 4.5)
"	63.6	56.4	33	(4.5, 4.0)
"	143.5	126.0	11	(4.0, 3.5)
Jokioinen	8.8	8.4	5	(5.5, 5.0)
"	20.3	18.3	15	(5.0, 4.5)
"	64.7	55.2	21	(4.5, 4.0)
"	158.8	153.2	4	(4.0, 3.5)
Cottered	-	-	0	(5.5, 5.0)
"	31.5	25.1	2	(5.0, 4.5)
"	57.7	59.6	34	(4.5, 4.0)
"	147.8	146.6	18	(4.0, 3.5)

TABLE IX: Comparison of mean strong acid concentrations and mean computed acid concentrations for different pH intervals.
Period: January-June 1973.