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Forskningscenter Risø, Roskilde; Palmgren Jensen, F.

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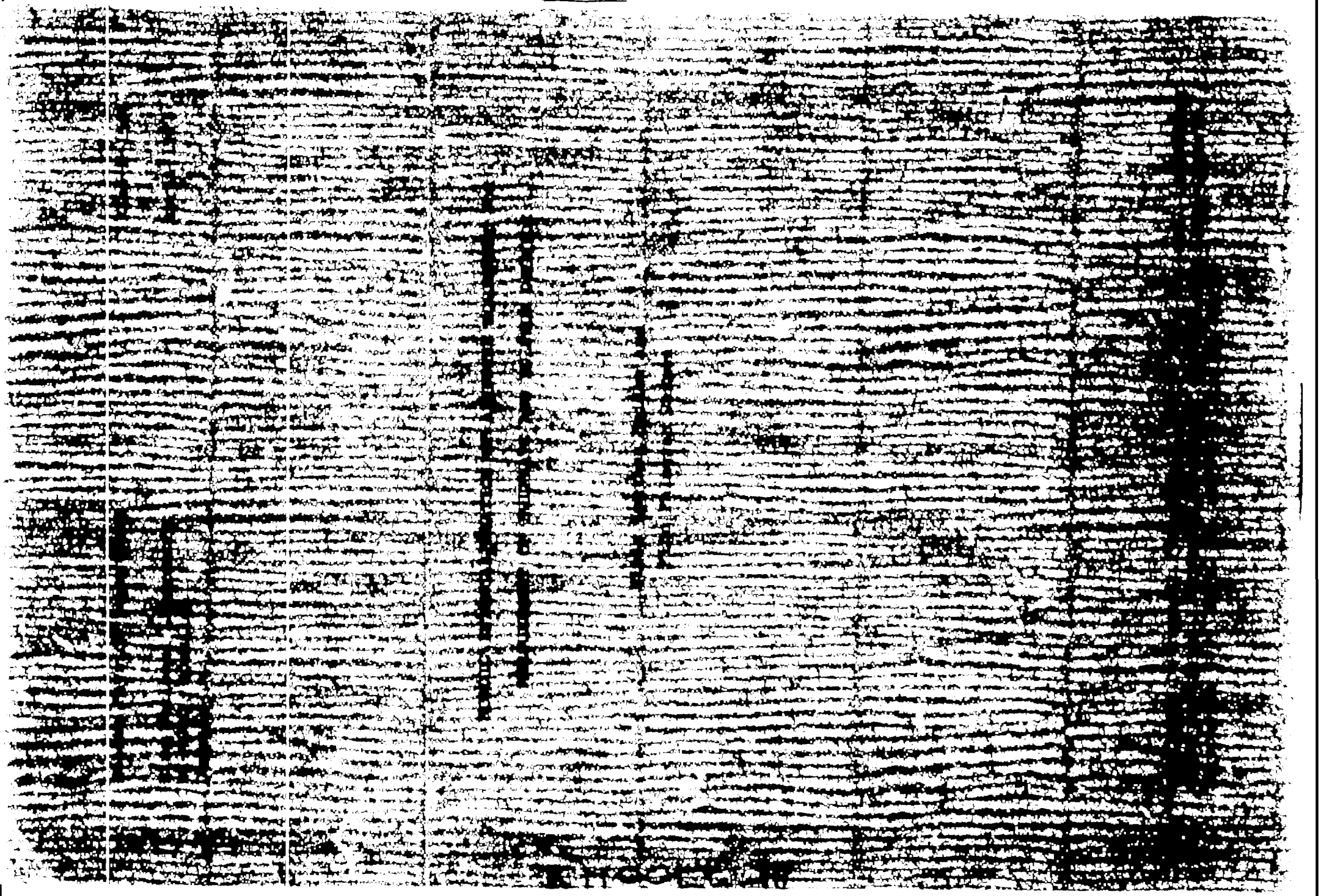

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NORDIC INTERCALIBRATION OF AIRBORNE EQUIPMENT FOR MEASUREMENT OF SULPHATE AND SULPHUR DIOXIDE

Niels Zeuthen Heidam* and
Finn Palmgren Jensen*

* Present adress:
Danish Air Quality Laboratory
Ministry of Environment

Risø National Laboratory, Denmark
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ABSTRACT

Intercalibration experiments with airborne equipment belonging to Nordic laboratories were carried out and the filter samples analyzed by the various methods in use at the laboratories. The results were subjected to statistical analyses of correlation and regression. Intercalibration on the ground comprised Danish, Norwegian, Swedish, and Finnish equipment and an airborne intercalibration was later carried out with Danish and Norwegian equipment installed in two aircraft. Although the sulphate results exhibit good mutual correlation, the results from the samples taken on the ground differ by up to 50%, the main reason being an overestimation by one of the methods used (X-ray fluorescence). Further, the differences between the results from the samples taken in the air are of the same magnitude, except in a single instance where the results differed by a factor of 3; the reason for this is not clear. The sulphur dioxide results exhibit rather poor mutual correlation; the results from the samples taken on the ground differ at most 20%, but in some cases, however, this is the net result of significant loss of material in the apparatus and an overstimation of sulphur dioxide by the analytical methods. The samples taken in the air had too low a content of sulphur dioxide for meaningful comparisons.

CONTENTS

1. INTRODUCTION

In connection with a joint European measuring programme to monitor continental air pollution and its transport across borders, airborne equipment for the determination of the concentration of particulate and gaseous sulphur was constructed and used in the programme by the following four Nordic laboratories: the Aerosol Sciences Laboratory at Risø, Denmark, the Norwegian Institute for Air Research, the Meteorological Institute of the University of Stockholm, Sweden, and the Meteorological Institute of Finland.

The present report describes the results of an intercalibration experiment of this equipment performed on the ground at Risø in December 1975, with participants from all four countries, and of a Danish-Norwegian airborne intercalibration in July 1976. The latter was carried out over Denmark during a formation flight with the Danish and the Norwegian aircraft.

In all the equipment, samples are collected on filter paper and subsequently analyzed in the laboratory. The air passes two filters in series; particles are collected on the first filter, while the second one is specially impregnated (with 0.5N KOH) to sample sulphur dioxide. In the Norwegian, Swedish and Finnish equipment, circular Whatman-40 filters are used, whereas bands of Whatman-41 filters are used in the Danish apparatus; the exposed filter area is subsequently cut out of the band in the laboratory.

Different analytical methods are applied in the laboratories. In Denmark, the isotope dilution analysis (IDA) (Klockow et al. 1974, Flyger et al. 1976) is used for the determination of both sulphate and sulphur dioxide, in Norway both components are determined by the X-ray fluorescence method (XRF) (e.g. Bonnevie-Svendsen and Follo 1972), in Sweden both components are determined by the Thorin method (e.g. Persson 1966), and in Finland sulphate is determined by XRF and sulphur dioxide by the Thorin method. Unexposed filters are also analyzed to determine filter background.

In order to separate the influence on the results of the different analytical methods from the influence of the different sampling instruments, all the samples were analyzed in two laboratories as explained in greater detail below. The results

are listed in the tables in appendices I and II; they were subjected to a statistical analysis of correlation and regression. The regression lines which have been computed and drawn in the figures, are the orthogonal regression lines (Sokal & Rohlf 1969) described in greater detail in appendix III.

In the comparisons presented in the following sections, the following notation is adopted to identify the results: A (B,C) denotes a result obtained from a sample taken with equipment belonging to country A (D: Denmark, N: Norway, S: Sweden, F: Finland), and analyzed in country B, using the method C (IDA, XRF, Th). Examples: D(D, IDA), F(N, XRF).

2. INTERCALIBRATION ON THE GROUND

The experiments took place at Risø from 15 to 18 December 1975. The four sets of equipment were set up outside a laboratory building at Risø (Figure 1) and run synchronously; 20 samples were taken with each apparatus supplemented with 6 sets of blanks.

During the first two days the sky was overcast, the winds were westerly and rather strong (10 m/s) and the temperature was about 5°C. During the latter two days the sky was clear, the winds were north-easterly and wind speeds varied between 3 and 7 m/s; the temperature fell steadily from +2°C to -4°C. There was no precipitation. The experiments were thus performed under a variety of meteorological conditions quite similar to those normally encountered in flight.

All exposed filters were first analyzed by the XRF method in Norway and thereupon returned to the laboratory or origin for subsequent individual chemical analysis by the methods mentioned above. All the results are listed in appendix I.

In section 2.1 the results of the individual analyses for each country are compared to the corresponding results from the common XRF analysis. These comparisons illuminate the influence of the different analytical methods. In section 2.2 the results are compared of the common XRF analysis on all the filters. As the method of analysis is the same for all filters, the differences in the results can be ascribed to the influence of the sampling apparatus. Finally, in section 2.3 the results are

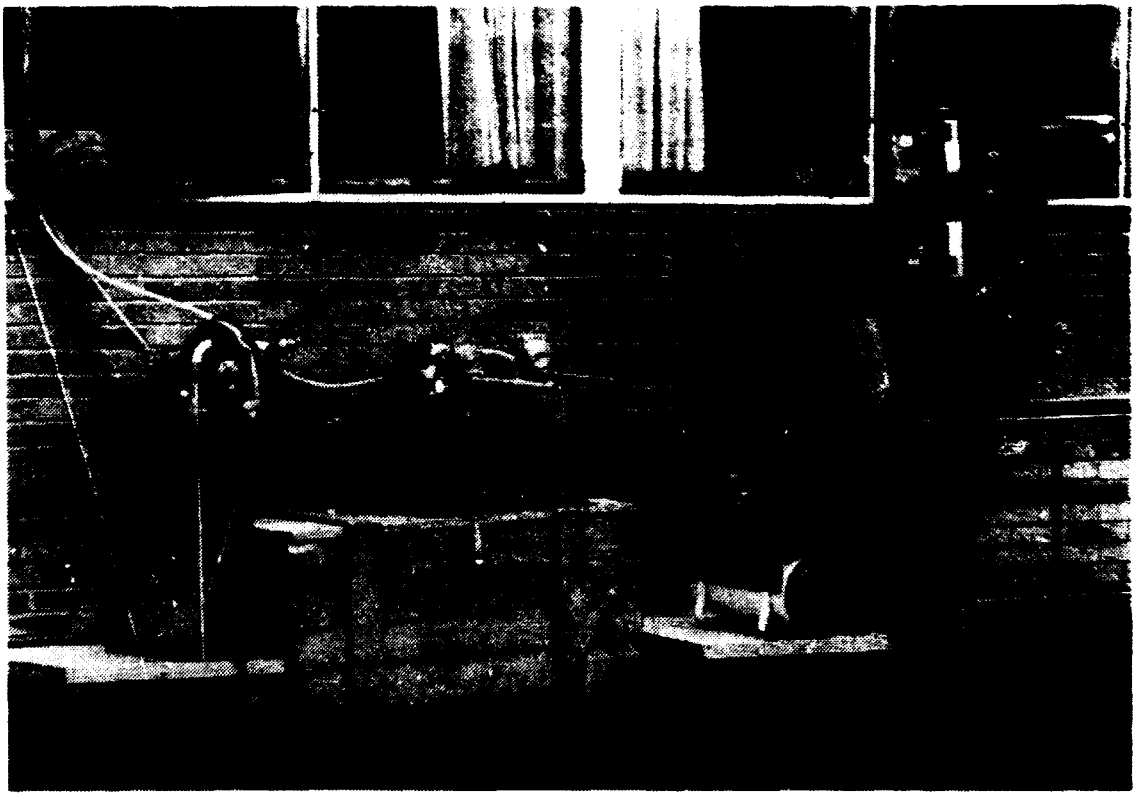

Fig. 1. Intercalibration of airborne equipment at Risø 15-18 December 1975. From left to right: Swedish, Finnish, Norwegian, and Danish equipment.

compared of the individual analyses carried out in the four laboratories; these comparisons include both the effects of the analytical methods and of the sampling procedures.

Due to a mishap the Danish samples Nos. 6 and 7 were taken on the same filter; in all comparisons with Danish results the two samples are treated as one and indicated by a square in the figures. The air volume taken in the Swedish sample No. 9 was not noted, and this sample has therefore been excluded from all comparisons with Swedish results.

2.1. Comparison between individual analyses and the common XRF-analysis

The sulphate results

The results are plotted in figs. 2a-c and the statistical parameters are summarized in table 1. All results are characterized by good mutual correlations; the correlation coefficients r fall in the range 0.86-0.99. The latter value refers to the Finnish and the Norwegian XRF analysis; here also the best (i.e. closest to 1) regression coefficient c appears. Thus the mutual agreement between the XRF methods is very good.

The Danish and Swedish chemical analyses lead, however, to somewhat lower c-values, which may indicate that the XRF-analysis entails a certain overestimation of the sulphate content in the filters. The regression coefficient c pertaining to the analyses of the Danish filters is significantly less than 1, which may be due to the fact that the type of filter is not that for which the XRF analysis was calibrated. This point is presently being separately investigated.

The sulphur dioxide results

The results are plotted in figs. 2d-f and the statistical parameters are summarized in table 2. The results of the chemical analysis at the Swedish laboratory were received together with information to the effect that inefficient ion-exchange during the analyses was suspected; this seems confirmed by the very small values compared to the results of the XRF-analysis. The remaining results are characterized by rather poor correlations and the regression lines reveal an unacceptably large difference between the results of the various analytical methods. The XRF analysis of the Danish filters seems to be impaired by a zero-point error, and the Finnish method (Thorin) leads to a rather large overestimation of the SO_2 content of the filters.

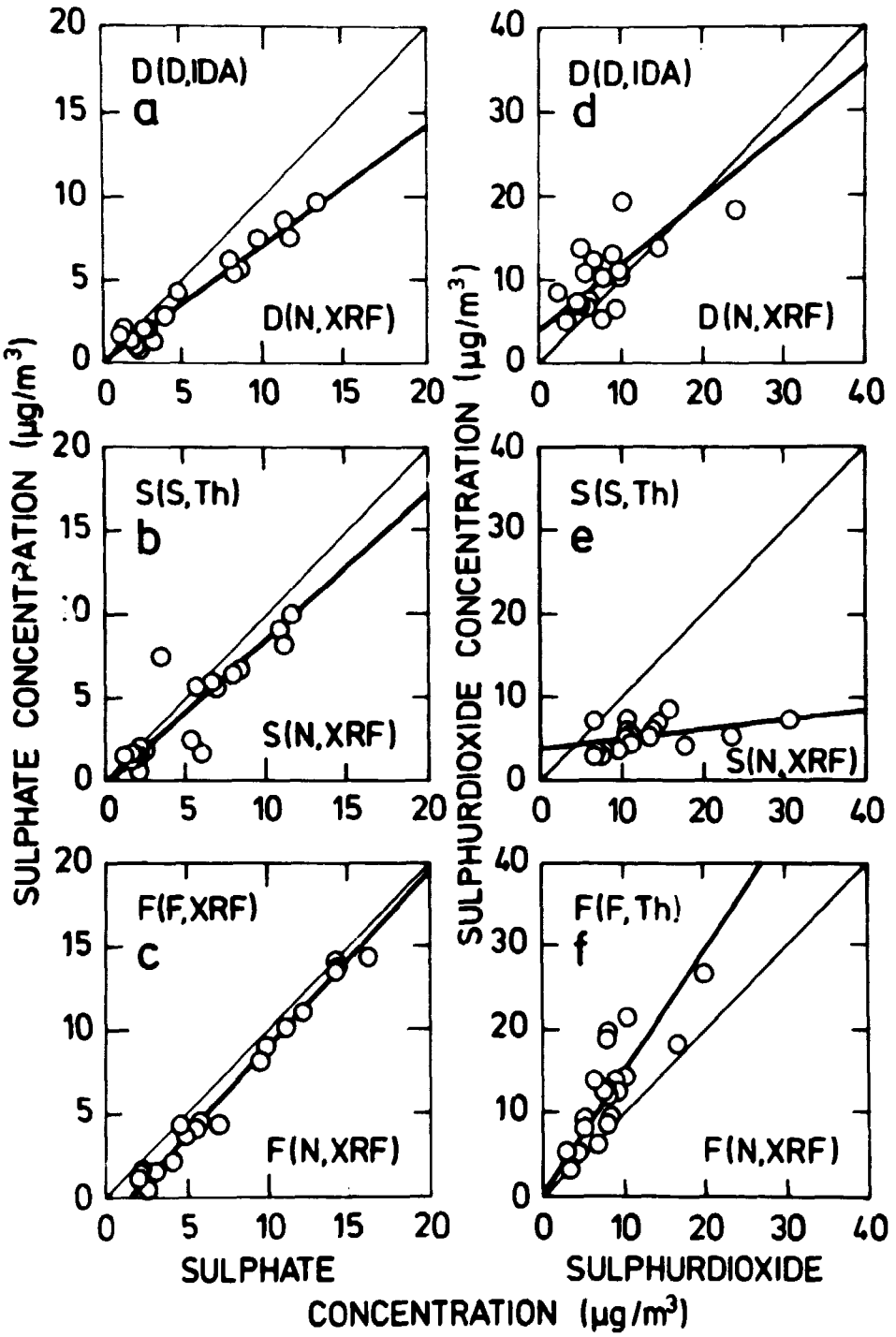

Fig. 2. Intercomparison of analytical methods applied to samples taken on the ground. The heavy lines are the calculated, orthogonal regression lines and the thinner lines depict the ideal relationships, Y = X.
Figs. 2a-c: Sulphate results. Figs. 2d-f: Sulphur dioxide results.

Table 1. Orthogonal regression lines and correlation coefficients for the sulphate results found by individual analyses and by common XRF analysis, respectively. Samples taken on the ground.

Fig. No.	Regression line $Y = cX+Y_{oo}$	95% confidence limits for c lower	upper	Correlation-coefficient r	Number of samples n
2a	D(D,IDA) = 0.70·D(N,XRF) + 0.18	0.62	0.78	0.97	19
2b	S(S,Th) = 0.87·S(N,XRF) - 0.37	0.65	1.14	0.869	18
2c	F(F,XRF) = 1.05·F(N,XRF) - 1.63	0.99	1.12	0.99	20

Table 2. Orthogonal regression lines and correlation coefficients for the sulphur dioxide results found by individual analyses and by common XRF analysis, respectively. Samples taken on the ground.

Fig. No.	Regression line $Y = cX+Y_{oo}$	95% confidence limits for c lower	upper	Correlation-coefficient r	Number of samples n
2d	D(D,IDA) = 0.78·D(N,XRF) + 3.98	0.52	1.12	0.77	19
2e	S(S,Th) = 0.12·S(N,XRF) + 3.87	0.004	0.24	0.42	19
2f	F(F,Th) = 1.45·F(N,XRF) + 0.06	1.08	2.02	0.82	20

2.2. Comparison between the results of the common XRF-analysis

The sulphate results

The results are plotted in figs. 3a-f and the statistical parameters are summarized in table 3. All results are characterized by good mutual correlations; the correlation coefficients fall in the range 0.93-0.96. The results from the Norwegian samples are generally larger than the results from the samples collected with equipment belonging to the other countries; this points to small losses in the Norwegian sampler. The results from the Swedish samples are generally smaller than from the other samples, which indicates a certain loss of sulphate in the Swedish sampler. However, the values of the regression coefficients do not deviate significantly from the ideal value of 1, with the exception of the c = 0.72 of the Swedish and Finnish samples. The Norwegian and Finnish samples yield c = 1.01. The residual constants Y_{oo} are all quite small, but in comparisons involving Danish samples (on the Y axis) and Swedish samples (on the X axis) they are all negative.

The sulphur dioxide results

The results are plotted in figs. 4a-f and the statistical parameters are summarized in table 4. All results are characterized by good mutual correlations; the correlation coefficients fall in the range 0.84-0.98. The analyses of the Swedish filters generally give larger SO_2-concentrations than found from the other samples. This is in contrast to the sulphate concentrations found from Swedish samples, but the results are not sufficiently accurate to reveal an inefficient collection of particles on the Swedish sulphate filter. The results from the analysis of Finnish samples are generally the smallest, the corresponding regression coefficients ($.35 \leq c \leq 1.49$) deviate significantly from 1 (95% confidence) and they are distinctly different from the other c-values (0.94-1.03). A rather large loss of SO_2 in the Finnish apparatus is therefore indicated. The results of the Danish samples are characterized by the lowest correlation coefficients, which may possibly be due to the fact that the filter-type differs from that usually used in the Norwegian XRF analy-

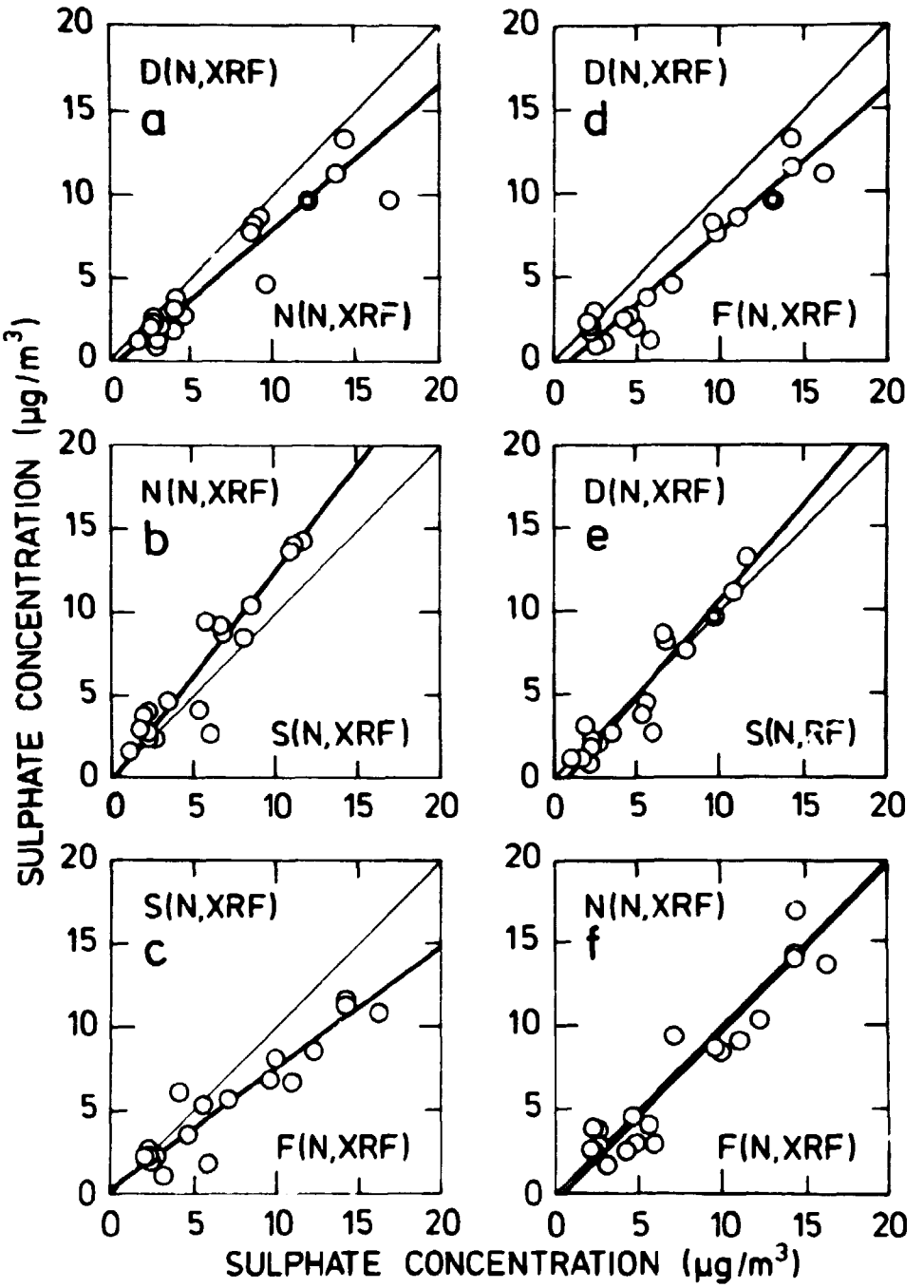

Fig. 3. Intercomparison of sulphate determinations on the samples taken on the ground by a common analytical method to elucidate the influence of the sampling methods. The heavy lines are the calculated, orthogonal regression lines and the thinner lines depict the ideal relationships, Y = X.

Table 3. Orthogonal regression lines and correlation coefficients for the sulphate results found by common XRF analysis applied to all samples taken on the ground.

Fig. No.	Regression line $Y = cX+Y_{oo}$	95% confidence limits for c lower	upper	Correlation-coefficient r	Number of samples n
3a	D(N,XRF) = 0.84·N(N,XRF) - 0.45	0.74	0.96	0.96	19
3b	N(N,XRF) = 1.27·S(N,XRF) - 0.24	1.05	1.54	0.93	18
3c	S(N,XRF) = 0.72·F(N,XRF) + 0.27	0.61	0.85	0.94	18
3d	D(N,XRF) = 0.85·F(N,XRF) - 0.84	0.73	0.98	0.95	19
3e	D(N,XRF) = 1.16·S(N,XRF) - 0.97	1.00	1.36	0.95	17
3f	N(N,XRF) = 1.01·F(N,XRF) - 0.49	0.86	1.19	0.94	20

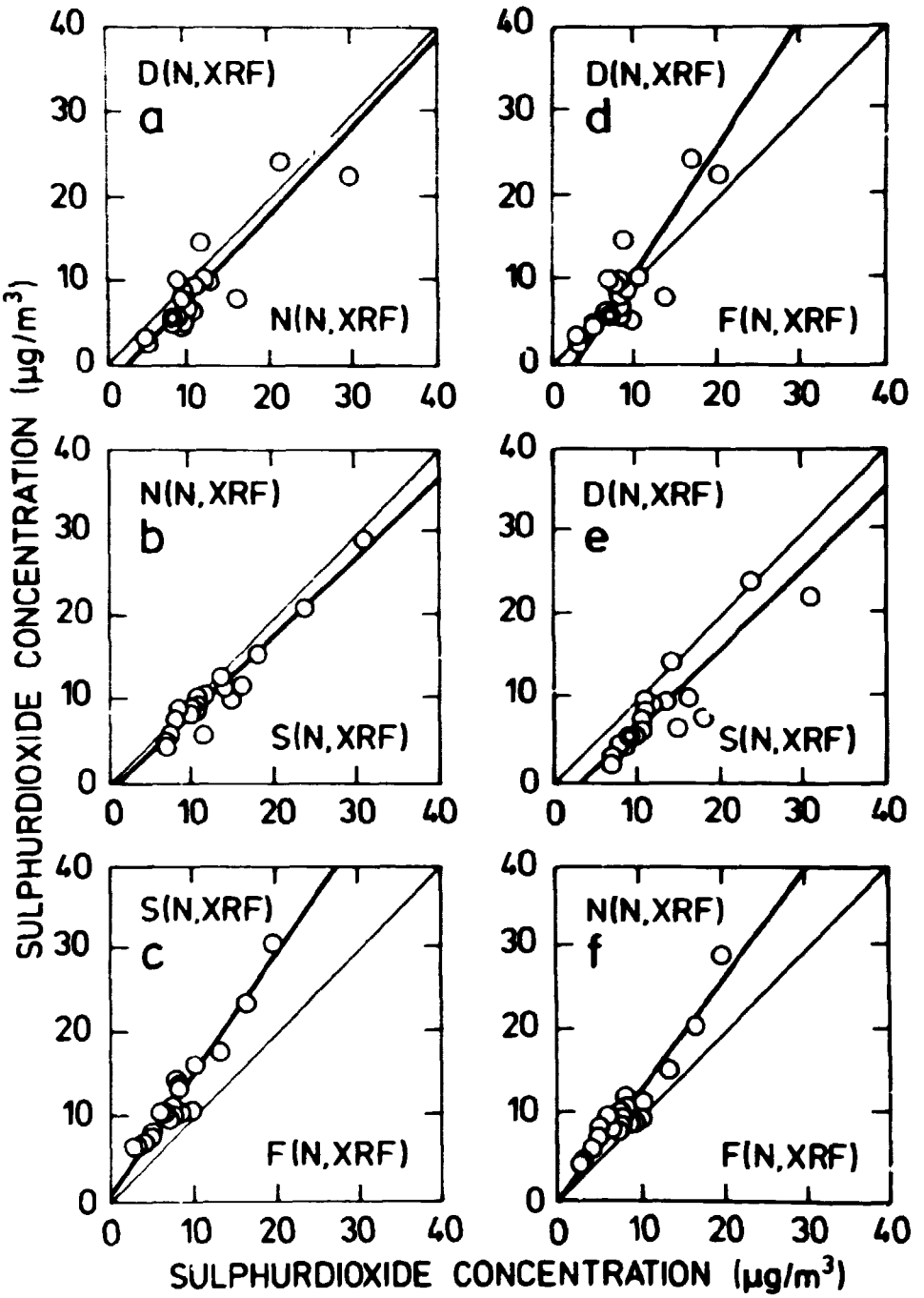

Fig. 4. Intercomparison of sulphur dioxide determinations on the samples taken on the ground by a common analytical method to elucidate the influence of the sampling methods. The heavy lines are the calculated, orthogonal regression lines and the thinner lines depict the ideal relationships, Y = X.

Table 4. Orthogonal regression lines and correlation coefficients for the sulphur dioxide results found by common XRF analysis of the samples taken on the ground

Fig. No.	Regression line $Y = cX+Y_{oo}$	95% confidence limits for c lower	upper	Correlation-coefficient r	Number of samples n
4a	D(N,XRF) = 1.03·N(N,XRF) - 2.55	0.81	1.32	0.88	19
4b	N(N,XRF) = 0.94·S(N,XRF) - 0.83	0.86	0.94	0.98	19
4c	S(N,XRF) = 1.43·F(N,XRF) + 0.74	1.25	1.64	0.96	19
4d	D(N,XRF) = 1.49·F(N,XRF) - 3.81	1.12	2.04	0.84	19
4e	D(N,XRF) = 0.96·S(N,XRF) - 3.12	0.75	1.22	0.89	18
4f	N(N,XRF) = 1.35·F(N,XRF) - 0.34	1.18	1.56	0.95	20

sis. Furthermore, as the residual constants connected with the results of the Danish filters are not only the largest, but also of the same magnitude as found above in section 2.1, it is concluded that the Norwegian XRF analysis, which is calibrated on Whatman-40 filters, gives rise to a zero-point error when applied to Whatman-41 filters.

2.3. Comparison between the results of the individual analyses

The sulphate results

The results are plotted in figs. 5a-f and the statistical parameters are summarized in table 5. All results are characterized by good mutual correlation; the correlation coefficients fall in the range 0.89-0.97. The regression coefficients c in table 5, which describe the combined effects of the methods of sampling, sample handling and analysis, and the corresponding 95% confidence limits are not in disagreement with the values of c that can be found from insertion of the regression equations of table 3 into those of table 1.

The results of the Finnish samples are generally the largest, and as the results of the Finnish and the Norwegian samples agree well this again indicates that the XRF analyses lead to an overestimation of the sulphate content of the filters.

The results of the Swedish samples may possibly be influenced by loss of sulphate in the apparatus, but they agree well with the Danish results.

The sulphur dioxide results

The results are plotted in figs. 6a-f and the statistical parameters are summarized in table 6. The results of the Swedish samples are doubtful, but even when ignoring these samples the remaining results are still characterized by rather poor correlation; the correlation coefficients between Danish, Norwegian and Finnish results fall in the range 0.72-0.76.

The regression coefficients c in table 6, which describe the combined effects of the methods of sampling, sample handling and analysis, and the corresponding 95% confidence limits, are consistent with the values of c that can be found from insertion

of the regression equations of table 4 into those of table 2.

The Finnish results are generally the largest, which is probably due to the above-mentioned overestimation of sulphur dioxide by the Finnish Thorin method. As the Norwegian and Finnish analysis results agree well, it seems that the XRF analysis of sulphur dioxide also leads to an overestimation.

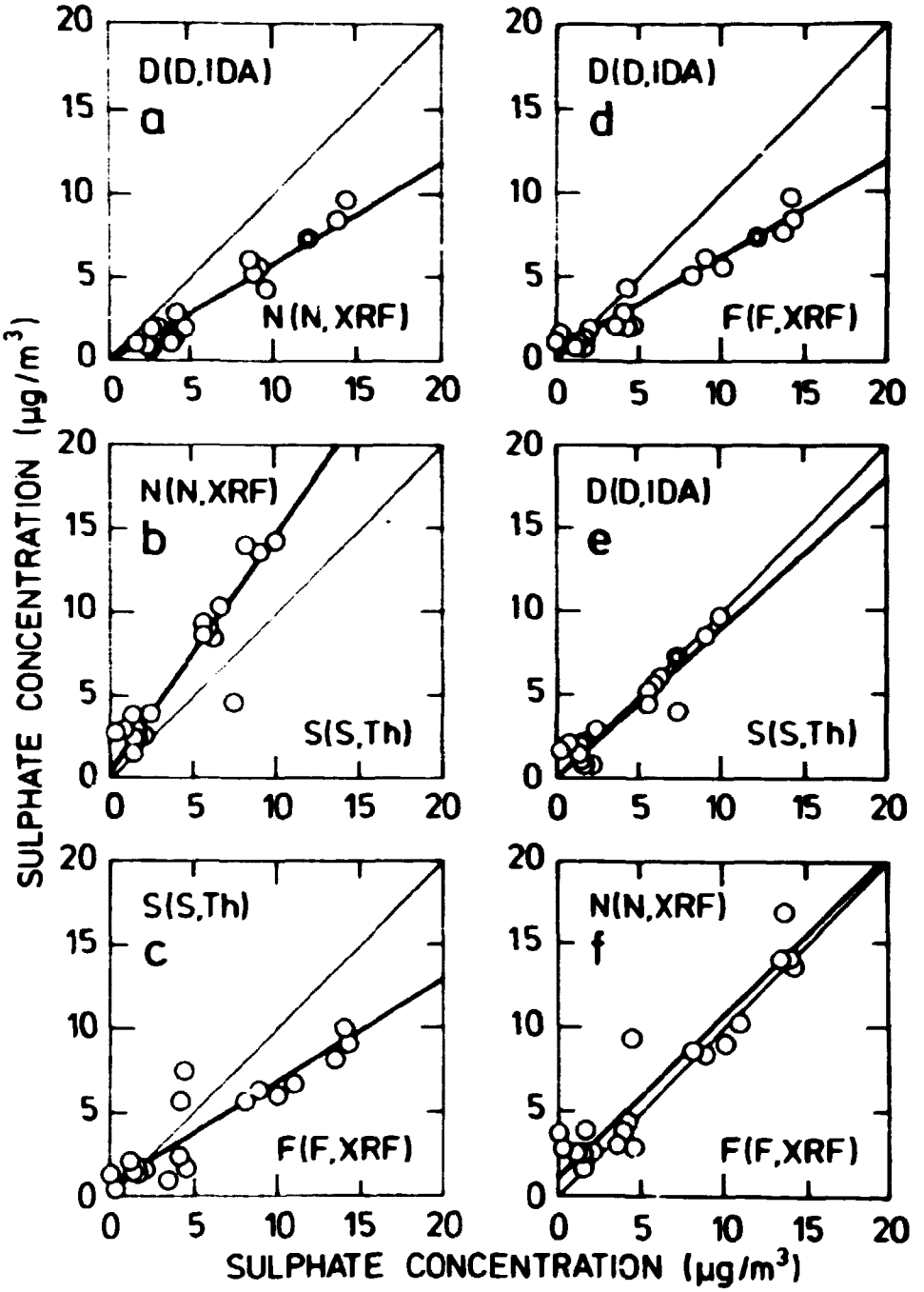

Fig. 5. Intercomparison of the individual analytical results of sulphate samples taken on the ground. The heavy lines are the calculated, orthogonal regression lines and the thinner lines depict the ideal relationships, Y = X.

Table 5. Orthogonal regression lines and correlation coefficients for the sulphate results found by individual analyses of the samples taken on the ground.

Fig. No.	Regression line $Y = cX+Y_{oo}$	95% confidence limits for c lower	upper	Correlation-coefficient r	Number of samples n
5a	D(D,IDA) = 0.59·N(N,XRF) - 0.12	0.51	0.68	0.95	19
5b	N(N,XRF) = 1.43·S(S,Th) + 0.50	1.19	1.75	0.92	19
5c	S(S,Th) = 0.61·F(F,XRF) + 0.61	0.48	0.75	0.90	19
5d	D(D,IDA) = 0.57·F(F,XRF) + 0.50	0.51	0.64	0.97	19
5e	D(D,IDA) = 0.89·S(S,Th) + 0.06	0.70	1.13	0.89	18
5f	N(N,XRF) = 0.96·F(F,XRF) + 1.09	0.82	1.13	0.94	20

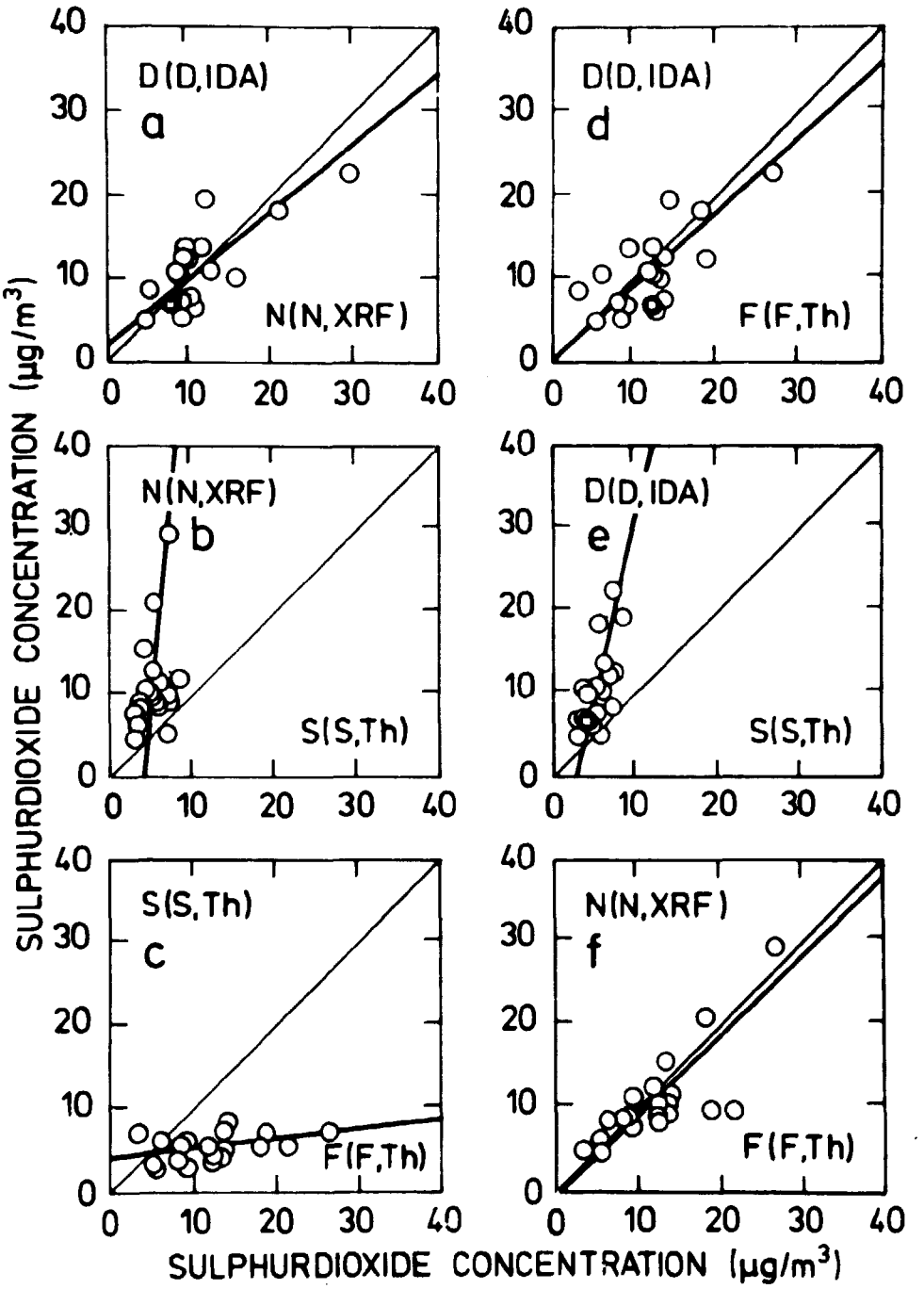

Fig. 6. Intercomparison of the individual analytical results of sulphur dioxide samples taken on the ground. The heavy lines are the calculated, orthogonal regression lines and the thinner lines depict the ideal relationships, Y = X.

Table 6. Orthogonal regression lines and correlation coefficients for the sulphur dioxide results found by individual analyses of the samples taken on the ground.

Fig. No.	Regression line $Y = cX+Y_{oo}$	95% confidence limits for c lower	upper	Correlation-coefficient r	Number of samples n
6a	D(D,IDA) = 0.81·N(N,XRF) + 1.95	0.54	1.19	0.76	19
6b	N(N,XRF) = 10.0 ·S(S,Th) - 43.3	-25	4.2	0.31	19
6c	S(S,Th) = 0.11·F(F,Th) + 4.03	-0.01	0.23	0.38	19
6d	D(D,IDA) = 0.88·F(F,Th) + 0.29	0.55	1.36	0.72	19
6e	D(D,IDA) = 4.35·S(S,Th) - 12.7	2.78	9.1	0.65	18
6f	N(N,XRF) = 0.96·F(F,Th) - 0.70	0.65	1.41	0.76	20

3. NORWEGIAN-DANISH INTERCOMPARISON FLIGHTS

On 13-14 July 1976 an intercomparison was made between Norwegian and Danish aircraft monitoring of sulphur dioxide and particulate sulphur. The investigation was a continuation of the experiments at Risø, cf. section 2. The samplers used for the intercomparison flights were identical with the Norwegian and Danish samplers used for these experiments, however, the Norwegian aircraft was equipped with an extra sampler. In the following, the original sampler is named BN (Big Norwegian filter, 50 mm$^{\emptyset}$) and the extra sampler SN (Small Norwegian, 28 mm$^{\emptyset}$).

During the experiment the Norwegian aircraft followed the Danish aircraft a few hundred meters behind its left side at the same height. On 13 July the flights were carried out over Zealand and the Great Belt; the weather was sunny, temperature 23^{o}C at ground level and 5^{o}C at 2000 m, relative humidity 50% at ground level and 90% at 2000 m.

On 14 July the flights were carried out over the Kattegat; the weather was hazy, temperature 22^{o}C at ground level and 6^{o}C at 2000 m, relative humidity 64% at ground level, 93% at 600 m, and 40% at 2000 m. More details of the flights are listed in appendix II.

At first all samples were analyzed by XRF in Norway and after that by IDA at Risø in Denmark. The results of the analyses are included in appendix II. The comparisons were made between the following analysis results: 1) Analysis by XRF of samples from the different samplers. 2) Analysis by IDA of samples from the different samplers. 3) Analysis of the same filters by IDA and XRF. 4) Analysis by XRF of the Norwegian filters and analysis by IDA of the Danish filters.

The sulphate results

The comparisons of the sulphate results are summarized in figures 7a-k and table 7. The heavy lines are the orthogonal regression lines as described in appendix III. All the results are strongly correlated. The correlation coefficients, r, are between 0.89 and 0.99; they are greatest for the XRF analyses and smallest for the IDA analyses. The correlation between the results of analyses of the same filters is strongest for the

Danish filters and weakest for the big Norwegian filters.

The regression coefficients are approx. 1 for the Norwegian filters analyzed by XRF. The XRF analysis of the Danish filters shows systematically higher sulphate amounts than XRF analyses of the Norwegian ones, in addition the XRF results are generally greater than the IDA results; consequently, the lowest regression coefficient (0.37) relates to the Danish filters analyzed by XRF (X) and IDA (Y).

The regression lines for the IDA analysis of Danish filters show negative intersections with the IDA axis, which are probably due to overestimated blind values.

Three regression lines obtained for the results from the Norwegian-Danish airborne intercomparison experiment could be compared directly with the regression lines for the ground-based experiments at Risø, because the same samplers and analyses were used. The equations for the three pairs of regression lines are shown in table 8. The deviations between the regression coefficients in 1a and 1b, and also 2a and 2b, are significant (95% level). The insertion of 2a and 2b into 1a and 1b, respectively, results in a good agreement with 3a and 3b, respectively; however, this is not surprising because the correlation coefficients are almost 1 and the regression coefficient of each series of experiments was calculated on the basis of the same results. The discrepancies between the regression coefficients in 1a and 1b, as well as in 2a and 2b, can be explained by the above-mentioned overestimation of the sulphate content by XRF in the Danish filters; these results are without importance for the determination of 3b.

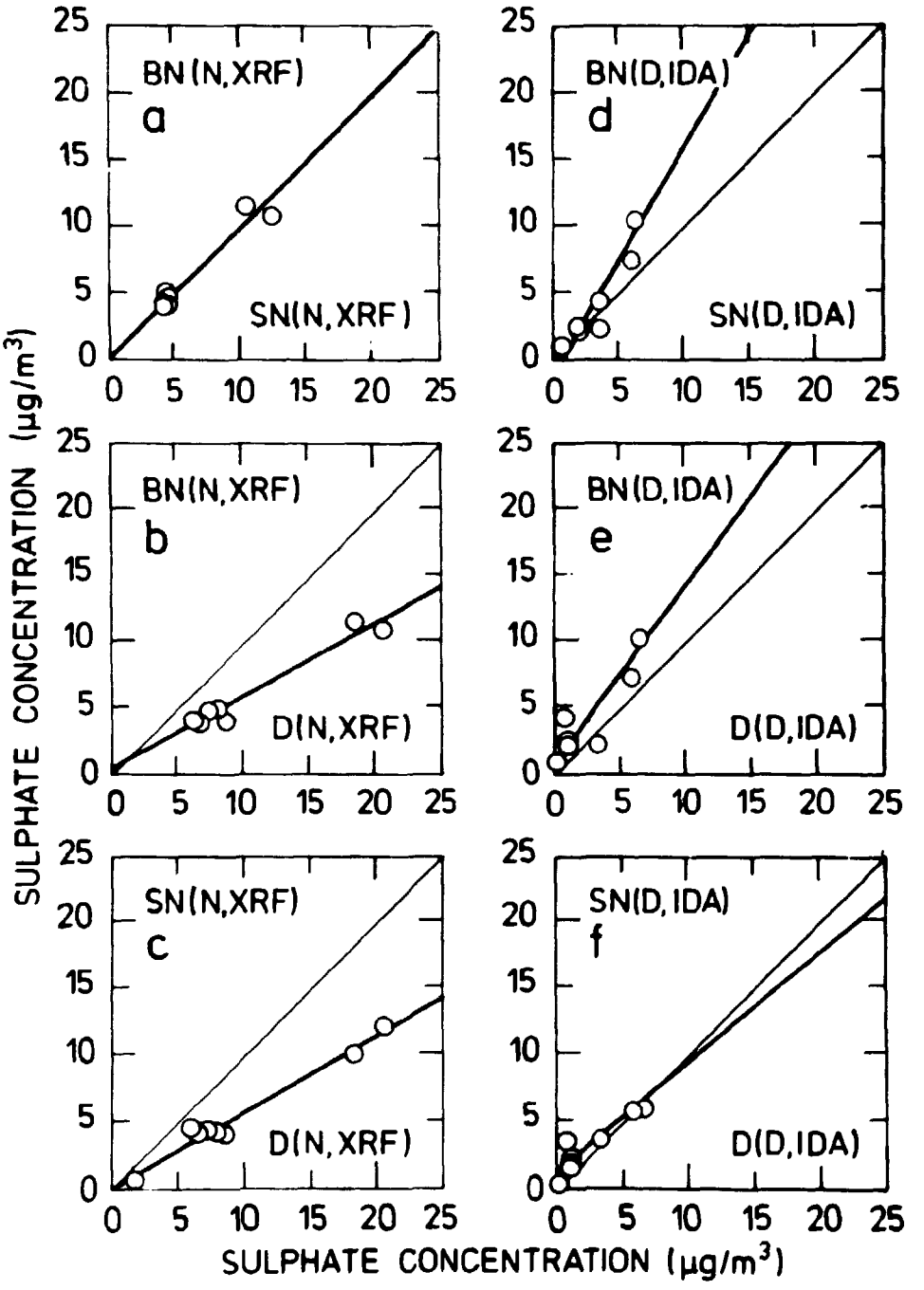

Fig. 7a-f. The airborne intercomparison of sulphate determinations on big Norwegian (BN), small Norwegian (SN) and Danish (D) filters by XRF and IDA analyses. The heavy lines are the calculated, orthogonal regression lines and the thinner lines depict the ideal relationships, Y = X.

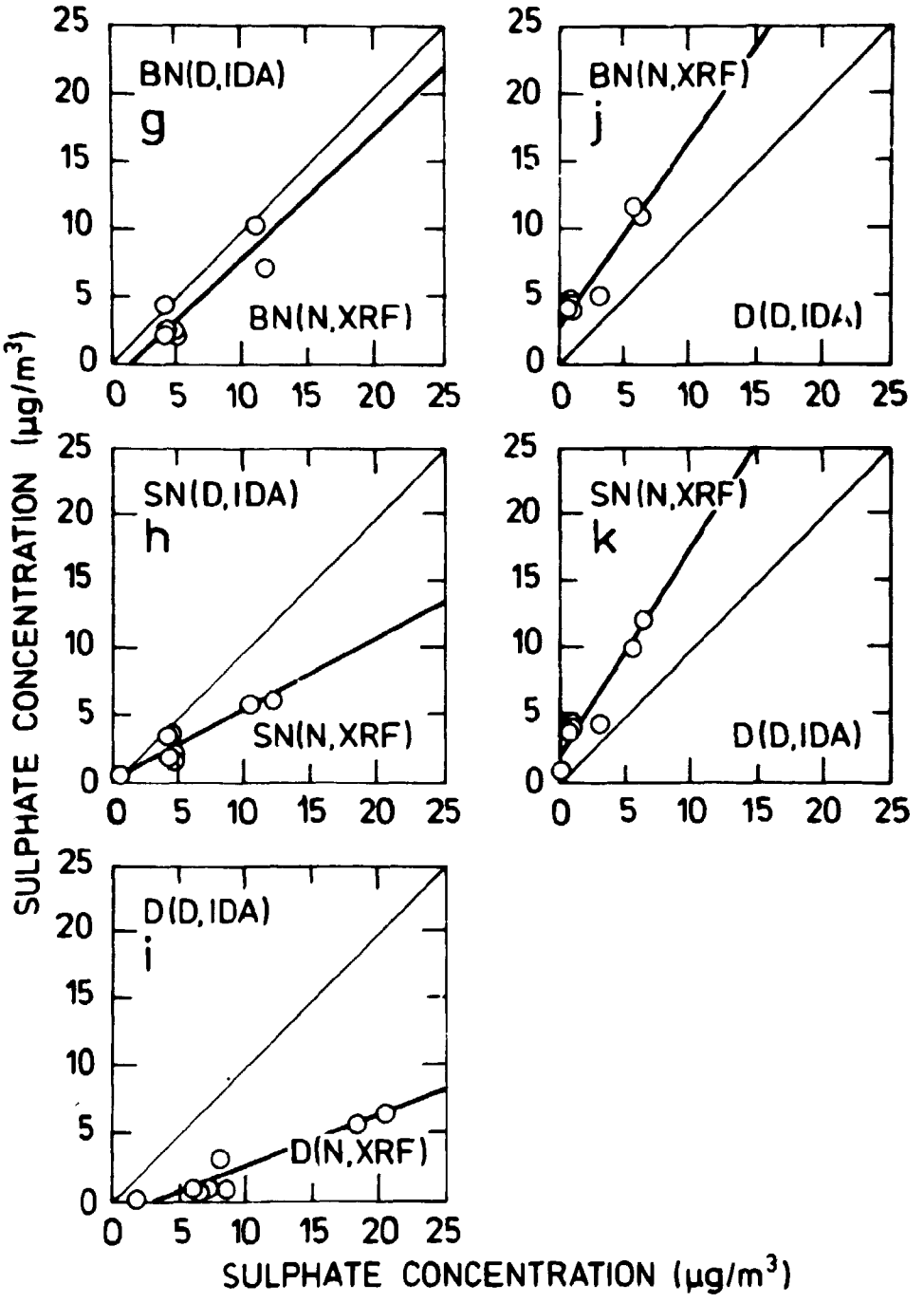

Fig. 7g-k. The airborne intercomparison of sulphate determinations on big Norwegian (BN), small Norwegian (SN) and Danish (D) filters by XRF and IDA analyses. The heavy lines are the calculated, orthogonal regression lines and the thinner lines depict the ideal relationships, Y = X.

Table 7. Correlations coefficients and orthogonal regression lines for the sulphate determinations from the Norwegian-Danish intercomparison flights.

Fig. No.	Regression line $Y = cX+Y_{oo}$	95% confidence limits for c lower	upper	Correlation-coefficient r	Number of samples n
7a	BN(N,XRF) = 0.99·SN(N,XRF)+0.14	0.82	1.20	0.97	7
7b	BN(N,XRF) = 0.55·D(N,XRF) +0.41	0.46	0.65	0.97	7
7c	SN(N,XRF) = 0.57·D(N,XRF) -0.01	0.52	0.64	0.99	8
7d	BN(D,IDA) = 1.61·SN(D,IDA)-0.98	1.20	2.27	0.91	8
7e	BN(D,IDA) = 1.35·D(D,IDA) +1.01	0.96	1.96	0.89	8
7f	SN(D,IDA) = 0.83·D(D,IDA) +1.25	0.63	1.09	0.93	8
7g	BN(D,IDA) = 0.93·BN(N,XRF)-1.36	0.65	1.33	0.90	7
7h	SN(D,IDA) = 0.53·SN(N,XRF)+0.21	0.39	0.69	0.93	8
7i	D(D,IDA) = 0.37·D(N,XRF) -1.27	0.29	0.45	0.96	8
7j	BN(N,XRF) = 1.41·D(D,IDA) +2.70	1.10	1.82	0.95	8
7k	SN(N,XRF) = 1.56·D(D,IDA) +1.97	1.23	2.04	0.95	8

Table 8. Comparable orthogonal regression lines corresponding to the ground-based and the airborne experiments (a and b, respectively). 95% confidence limits of the regression coefficients are given in parenthesis.

1a (Risø): $D(D,IDA) = 0.70 \times D(N,XRF) + 0.18$; $r = 0.97$, $n = 19$

1b (Air): $D(D,IDA) = 0.37\ (^{0.29}_{0.45}) \times D(N,XRF) - 1.27$; $r = 0.96$, $n = 8$

2a (Risø): $N(N,XRF) = 1.19 \times D(N,XRF) + 0.54$; $r = 0.96$, $n = 19$

2b (Air). $BN(N,XRF) = 0.55\ (^{0.46}_{0.65}) \times D(N,XRF) + 0.41$; $r = 0.97$, $n = 7$

3a (Risø): $D(D,IDA) = 0.59 \times N(N,XRF) - 0.12$; $r = 0.95$, $n = 19$

3b (Air): $D(D,IDA) = 0.71\ (^{0.55}_{0.91}) \times BN(N,XRF) - 1.92$; $r = 0.95$, $n = 8$

The sulphur dioxide results

The comparisons of the sulphur dioxide results are summarized in figures 8a-k and table 9. The orthogonal regression lines (cf. appendix III) are drawn for a few cases. All analyses of both the Danish and the Norwegian filters showed low sulphur dioxide concentrations. They were lower than the sulphate-concentrations, which is rather extraordinary. In addition, both the Norwegian and the Danish blind values were comparable with the sulphur content in the samples, especially the blind values of the Danish filters were unusually high.

Consequently, the observed sulphur dioxide concentrations were in most cases within a narrow range and the correlation was weak. The calculated regression lines are therefore without much meaning, and no further analysis of the data was made.

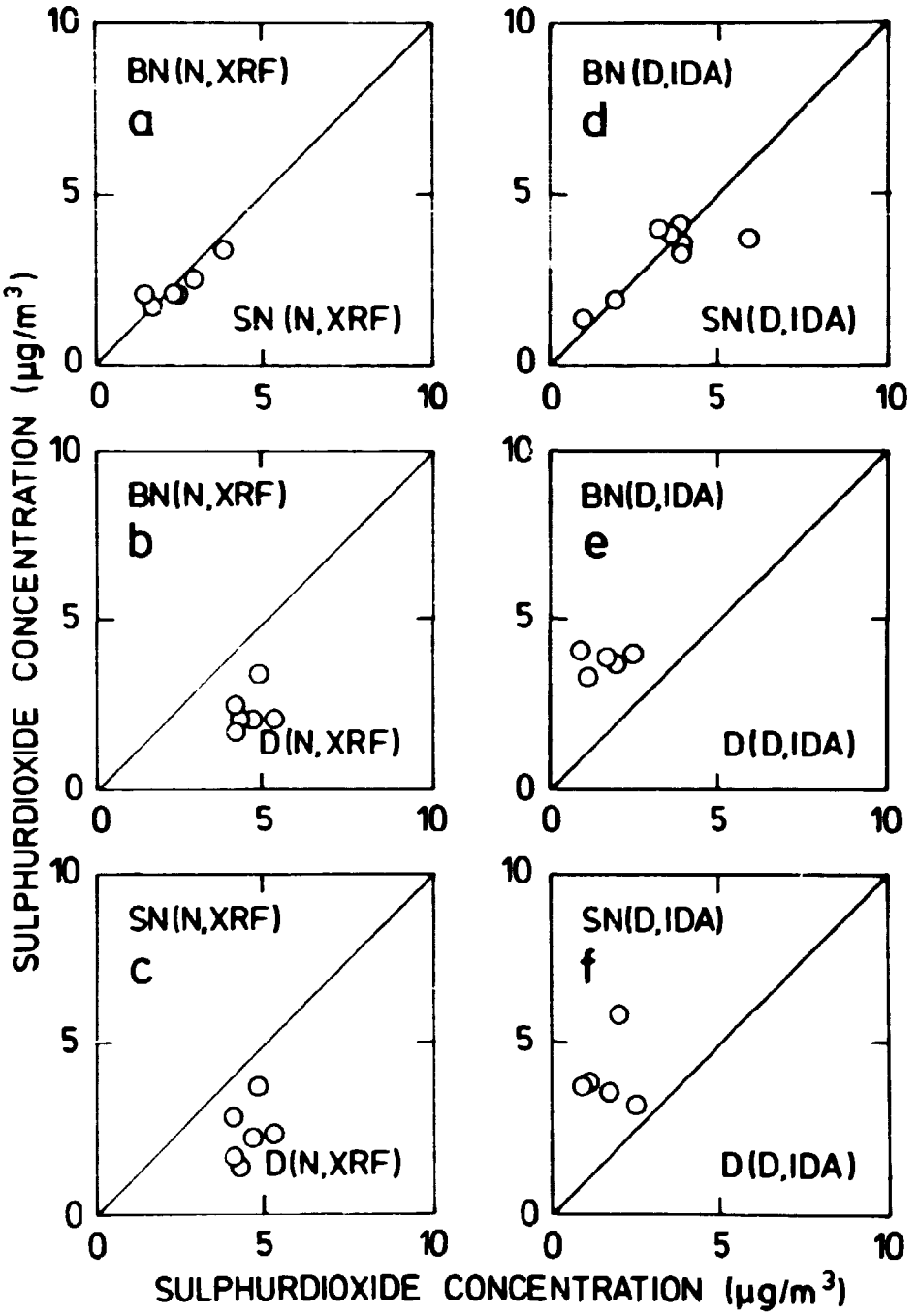

Fig. 8a-f. The airborne intercomparison of sulphur dioxide determinations on big Norwegian (BN), small Norwegian (SN) and Danish (D) filters by XRF and IDA analyses. The thin lines depict the ideal relationships, Y = X.

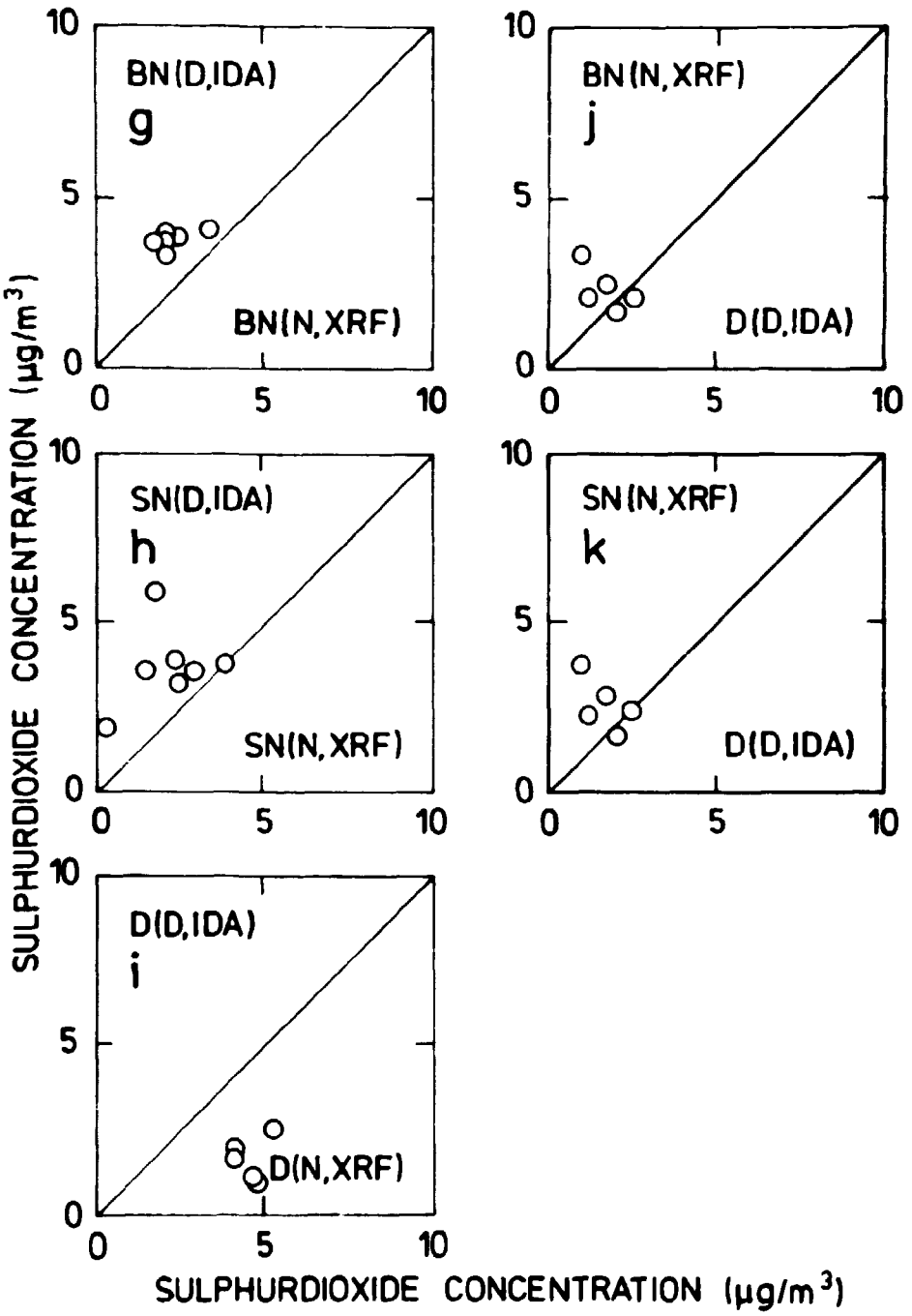

Fig. 8g-k. The airborne intercomparison of sulphur dioxide determinations on big Norwegian (BN), small Norwegian (SN) and Danish (D) filters by XRF and IDA analyses. The thin lines depict the ideal relationships, Y = X.

Table 9. Correlation coefficients for the sulphur dioxide determinations from the Norwegian-Danish intercomparison flights

Fig. No.	Correlation coefficients r	Number of samples n
9a	0.90	6
9b	0.24	6
9c	0.33	6
9d	0.77	8
9e	0.23	5
9f	0.08	5
9g	0.57	6
9h	0.32	7
9i	0.13	5
9j	-0.64	5
9k	-0.59	5

4. CONCLUSION

The sulphate results are characterized by good mutual correlations, but the individual analyses of the samples taken on the ground give results that differ by 5% to 50%. The main reason for this seems to be an overestimation by about 25% for the XRF analyses, whereas loss of material in the samplers is of minor importance. The differences between the results from the samples from the intercomparison flights, which took place half a year later, are of the same magnitude as above, except that the XRF analyses of Danish filters appeared to overestimate the sulphate content by a factor of 3. This point is presently being further investigated.

The sulphur dioxide results are characterized by rather poor mutual correlations. The individual analyses of the samples taken on the ground give results that differ by 5% to 20%, when doubtful Swedish results are ignored. In the case of Finland this is the result of two contradicting tendencies: a strong (40-50%) overestimation of SO_2 by the Thorin method counterbalanced by an SO_2 loss of comparable magnitude in the Finnish apparatus. For the Danish Whatman-41 filters, it was found that the XRF analyses led to a zero-point error and to a rather large scatter of results as compared to the chemical IDA analyses. The results from the intercomparison flights were so poorly correlated, due to extraordinarily low concentrations and relatively large blank-values, that further comparison was abandoned.

In general the experiments showed that the results of the XRF analyses probably depend on the type of filter used, and it is recommended that the standard filters used in the calibration of the method be prepared from the same type of filter as used for the samples proper. Furthermore, over a period of half a year, a very large increase appeared in the systematic deviation between the IDA and the XRF analyses. Taken quite generally, this stresses the importance of recurrent intercalibration between different methods.

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Table IA. Measured concentrations of sulphate

	Denmark			Norway		Sweden			Finland		
Sample No.	Vol. Nm^3	D(D,IDA) $\mu g/m^3$	D(N,XRF) $\mu g/m^3$	Vol. Nm^3	N(N,XRF) $\mu g/m^3$	Vol. Nm^3	S(S,Th) $\mu g/m^3$	S(N,XRF) $\mu g/m^3$	Vol. Nm^3	F(F,XRF) $\mu g/m^3$	F(N,XRF) $\mu g/m^3$
1	1.398	2.1	1.2	0.533	2.9	0.930	1.6	1.7	0.830	4.6	5.9
2	0.690	2.1	2.0	0.275	3.0	0.466	0.84	<2	0.452	3.6	4.9
3	1.398	5.3	8.2	0.502	8.7	0.900	5.6	6.8	0.776	8.2	9.6
4	1.379	5.6	8.6	0.538	9.1	0.882	5.9	6.6	0.852	10.1	11.0
5	4.249	6.1	7.7	1.65	8.5	2.782	6.3	8.0	2.40	9.0	9.9
6	2.516	7.4	9.6	0.561	10.4	0.917	6.6	8.5	0.860	11.0	12.2
7				0.422	14.1	0.711	8.1	11.3	0.657	13.5	14.2
8 blind	-	-	-	-		-	-	-	-	-	-
9	0.779	7.7	11.6	0.223	17.0	?	-	-	0.445	13.7	14.3
10	2.069	9.7	13.2	0.817	14.3	1.407	9.9	11.6	1.33	14.1	14.2
11	3.186	8.5	11.2	1.08	13.7	2.036	9.0	10.8	1.81	14.3	16.2
12	1.048	2.0	2.6	0.406	2.6	0.656	1.5	6.0	0.638	2.1	4.2
13	1.048	1.7	0.95	0.411	2.8	0.668	0.36	2.2	0.660	0.3	2.6
14	2.069	1.4	1.8	0.781	3.9	1.340	1.3	2.2	1.31	1.7	2.2
15	2.124	0.94	2.1	0.772	2.5	1.402	1.6	2.4	1.32	1.6	2.2
16 blind	-	-	-	-		-		-	-	-	-
17	0.708	0.81	2.4	0.282	2.6	0.466	2.1	2.2	0.461	1.1	2.0
18	1.416	1.2	3.1	0.585	3.8	0.915	1.3	1.9	0.971	0	2.4
19	1.381	1.1	1.2	0.557	1.6	0.914	1.4	1.0	0.886	1.5	3.1
20 blind	-	-	-	-	-	-	-	-	-	-	-
21 blind	-	-	-	-	-	-	-	-	-	-	-
22	2.124	2.9	3.8	0.865	4.0	1.391	2.4	5.3	1.35	4.1	5.6
23	1.062	4.4	4.6	0.413	9.4	0.665	5.6	5.6	0.695	4.3	7.1
24	4.036	2.0	2.7	1.32	4.6	1.968	7.4	3.4	2.01	4.3	4.6
25 blind	-	-	-	-	-	-	-	-	-	-	-
26 blind	-	-	-	-	-	-	-	-	-	-	-

Table IB. Measured concentrations of sulphur dioxide

	Denmark			Norway		Sweden			Finland		
Sample No.	Vol. Nm^3	D(D,IDA) $\mu g/m^3$	D(N,XRF) $\mu g/m^3$	Vol. Nm^3	N(N,XRF) $\mu g/m^3$	Vol. Nm^3	S(S,Th) $\mu g/m^3$	S(N,XRF) $\mu g/m^3$	Vol. Nm^3	F(F,Th) $\mu g/m^3$	F(N,XRF) $\mu g/m^3$
1	1.398	7.7	6.4	0.533	10.3	0.930	5.2	10.7	0.830	13.9	6.3
2	0.690	12.4	6.7	0.275	9.7	0.466	7.2	14.6	0.452	18.8	7.9
3	1.398	8.6	2.2	0.502	5.0	0.900	7.2	6.6	0.776	3.2	3.1
4	1.379	5.0	3.2	0.538	4.7	0.882	3.0	6.7	0.852	5.3	2.8
5	4.249	7.1	4.8	1.65	7.7	2.782	2.9	7.8	2.40	9.4	4.9
6	2.516	6.9	5.6	0.581	6.4	0.917	3.3	7.1	0.860	5.2	4.2
7				0.422	9.8	0.711	5.4	10.9	0.657	21.3	10.1
8 blind	-	-	-	-	-	-	-	-	-	-	-
9	0.779	13.7	4.9	0.223	9.4	?	-	-	0.445	12.4	9.3
10	2.069	10.8	5.6	0.817	8.4	1.407	3.8	9.9	1.33	12.4	7.3
11	3.186	7.3	4.6	1.08	8.9	2.036	3.8	8.1	1.81	8.3	4.9
12	1.048	13.8	14.7	0.406	11.5	0.656	6.2	13.7	0.638	9.4	8.2
13	1.048	10.6	10.0	0.411	8.7	0.668	6.2	10.7	0.660	6.1	6.7
14	2.069	6.4	9.4	0.781	10.6	1.340	4.7	11.3	1.31	12.6	7.6
15	2.124	11.1	9.9	0.772	12.5	1.402	5.4	13.3	1.32	11.7	8.2
16 blind	-	-	-	-	-	-	-	-	-	-	-
17	0.708	19.3	10.3	0.282	11.7	0.466	8.7	16.0	0.461	14.1	10.2
18	1.416	12.5	9.0	0.585	9.4	0.915	7.5	10.5	0.971	13.9	8.8
19	1.381	5.2	7.8	0.557	8.9	0.914	5.7	10.2	0.886	8.5	7.8
20 blind	-	-	-	-	-	-	-	-	-	-	-
21 blind	-	-	-	-	-	-	-	-	-	-	-
22	2.124	18.2	24.2	0.865	21.0	1.391	5.3	23.6	1.35	18.2	16.4
23	1.062	22.5	22.4	0.413	29.3	0.665	7.4	30.8	0.695	26.6	19.9
24	4.036	10.1	7.8	1.32	15.6	1.968	4.1	17.8	2.01	13.2	13.4
25 blind	-	-	-	-	-	-	-	-	-	-	-
26 blind	-	-	-	-	-	-	-	-	-	-	-

II. Data from the intercomparison flights

Table IIA. Measured concentrations of sulphate

Sample No.	Big Norwegian			Small Norwegian		
	Vol. Nm^3	BN(N,XRF) $\mu g/m^3$	BN(D,IDA) $\mu g/m^3$	Vol. Nm^3	SN(N,XRF) $\mu g/m^3$	SN(D,IDA) $\mu g/m^3$
1	0.764	4.1	4.3	0.429	4.1	3.5
2	0.768	4.1	2.6	0.412	4.5	2.2
3	0.767	4.0	2.4	0.440	4.2	1.9
4	0.754	4.9	2.7	0.471	4.5	1.6
5	1.321	<0.6	1.0	0.743	0.7	0.46
6	0.764	5.0	2.3	0.414	4.4	3.6
7	0.740	11.6	7.4	0.438	10.2	5.9
8	0.745	10.9	10.4	0.444	12.2	6.2

Table IIB. Measured concentrations of sulphur dioxide

Sample No.	Big Norwegian			Small Norwegian		
	Vol. Nm^3	BN(N,XRF) $\mu g/m^3$	BN(D,IDA) $\mu g/m^3$	Vol. Nm^3	SN(N,XRF) $\mu g/m^3$	SN(D,IDA) $\mu g/m^3$
1	0.764	1.7	3.7	0.429	1.7	5.9
2	0.768	2.1	3.3	0.412	2.3	3.9
3	0.767	2.1	4.0	0.440	2.4	3.2
4	0.754	2.1	3.8	0.471	1.4	3.6
5	1.321	<0.1	1.4	0.743	<0.1	1.01
6	0.764	<0.1	1.9	0.414	0.2	1.9
7	0.740	3.4	4.1	0.438	3.8	3.8
8	0.745	2.5	3.9	0.444	2.9	3.6

Danish			Date	Time	Route	Height
Vol. Nm^3	D(N,XRF) $\mu g/m^3$	D(D,IDA) $\mu g/m^3$		(local)		m
2.01	6.6	0.73	13/7 77	0936-1006	Værløse-Langeland	636
1.95	6.2	0.84	-	1012-1042	Langeland-Samsø	216
1.94	8.6	0.95	-	1045-1115	Samsø-Langeland	330
1.84	7.3	0.88	-	1118-1148	Langeland-Samsø	630
3.34	1.9	0.08	-	1200-1300	Samsø-Langeland-Værløse	1680 -2275
1.95	8.2	3.1	14/7 77	0858-0928	Hesselø-Samsø	630
1.92	18.4	5.6	-	0935-1005	Samsø-Hesselø	330
1.95	20.7	6.4	-	1009-1039	Hesselø-Samsø	210

Danish			Date	Time	Route	Height
Vol. Nm^3	D(N,XRF) $\mu g/m^3$	D(D,IDA) $\mu g/m^3$		(local)		m
2.01	4.1	2.0	13/7 76	0936-1006	Værløse-Langeland	636
1.95	4.7	1.1	-	1012-1042	Langeland-Samsø	216
1.94	5.3	2.5	-	1045-1115	Samsø-Langeland	330
1.84	4.3	-	-	1118-1148	Langeland-Samsø	630
3.34	<0.4	-	-	1200-1300	Samsø-Langeland-Værløse	1680 -2275
1.95	<0.4	-	14/7 76	0858-0928	Hesselø-Samsø	630
1.92	4.8	0.9	-	0935-1005	Samsø-Hesselø	330
1.95	4.1	1.7	-	1009-1039	Hesselø-Samsø	210

III. The orthogonal regression line

A linear analysis of regression of a set of n data points (X_i, Y_i) entails the calculation of the "vertical" regression line

$$Y_v - \bar{Y} = b(X - \bar{X}) \tag{1a}$$

or

$$Y_v = bX + Y_{ov} \tag{1b}$$

where the regression coefficient b is given by

$$b = r \frac{s_y}{s_x} . \tag{2}$$

Here r is the correlation coefficient given by

$$s_x s_y r = \frac{1}{n-1} \sum (X_i - \bar{X})(Y_i - \bar{Y}) \tag{3}$$

and s_x and s_y are the standard deviations of X and Y.

The line given by eq. (1) minimizes the sum of the squares of the vertical distances between the points and the line

$$S_v(b) = \sum (Y_i - Y_{vi})^2 \tag{4}$$

and it is only valid provided that X is an independent variable, so that the values X_i can be reproduced in a repetition of the experiment. If, instead, Y is the independent variable, then it is the sum of the squares of the horizontal distances which should be minimized

$$S_h(b') = \sum (X_i - X_{hi})^2 , \tag{5}$$

and the "horizontal" regression line becomes

$$X_h - \bar{X} = b'(Y - \bar{Y}) \tag{6}$$

where b' is found from (2) by an interchange of subscripts x and y

$$b' = r \frac{s_x}{s_y} = \frac{r^2}{b} \quad . \tag{7}$$

Equations (1) and (6) describe two different lines in the X-Y plane, a simple inversion does not lead from one to the other. Thus inversion of eq. (6) gives

$$Y-\bar{Y} = \frac{b}{r^2} (X-\bar{X})$$

which is not identical to (1), unless $r^2 = 1$.

If X and Y are both dependent variables, the conditions for the validity or eqs. (1) or (6) are not fulfilled; this happens in cases where the parameters measured are not under full control (e.g. pollutant concentrations in ambient air). In such cases, the correct line is the orthogonal regression line

$$Y_o-\bar{Y} = c(X-\bar{X}) \tag{8a}$$

or

$$Y_o = cX+Y_{oo} \tag{8b}$$

which minimizes the sum of the squares of the orthogonal distances between the data points and the line

$$S_o(c) = \sum \frac{(Y_i-Y_{oi})^2}{1+c^2} = \sum \frac{\{Y_i-\bar{Y}-c(X_i-\bar{X})\}^2}{1+c^2} \quad . \tag{9}$$

The regression line c is given (Sokal and Rohlf 1969) by

$$c = \sqrt{1 + \frac{1}{a^2}} - \frac{1}{a} \tag{10a}$$

where

$$a = \frac{2rs_x s_y}{s_x^2-s_y^2} \tag{10b}$$

The regression coefficient c' for the orthogonal regression line which describes X as dependent on Y

$$X_o-\bar{X} = c'(Y-\bar{Y}) \tag{11}$$

is found from (10) by an interchange of subscripts x and y

$$a' = -a \tag{12}$$

and thus

$$c' = \sqrt{1 + \frac{1}{a^2}} + \frac{1}{a} = \left(\sqrt{1 + \frac{1}{a^2}} - \frac{1}{a}\right)^{-1} = \frac{1}{c} \, . \tag{13}$$

Equations (8) and (11) therefore describe the same line in the X-Y plane and eq. (11) is simply the inverted version of eq. (8) and vice versa. It can be shown that

$$b \leq c \leq \frac{b}{r^2} \tag{14}$$

so that the three lines are coincident for $r^2 = 1$ only.