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Some information about the
spectrophotometric Thorin method
for determination of sulphur
dioxide in air

av

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FOREWORD

At the first meeting of Working Group 1 of the International Organization for Standardization's Technical Committee 146, it was decided to prepare a document describing a titrimetric Thorin method for determination of sulphur dioxide in air.

I did not agree and therefore submitted this paper to the members of the Working Group 1 before the second meeting in September 1973.

It was at the second meeting decided to prepare a draft method based on the spectrophotometric and not on the titrimetric principle.

SOME INFORMATION ABOUT THE SPECTROPHOTOMETRIC THORIN METHOD, WORKING DOCUMENT NO TC 146/WG1-N3E PRESENTED AT WG1's FIRST MEETING IN GOTHENBURG MARCH 1973

1. The spectrophotometric Thorin method does not require a special instrument. Any spectrophotometer with a light source around 520 nm may be used. The TCM-method has already been recommended by the WG-1, and the spectrophotometric Thorin method can be carried out on the same type of instrument.
- Two different makes of spectrophotometers have been compared at our laboratory. The results from seven air samples are listed in Table I.

The titration method needs a spectrophotometer equipped with a stirrer, and also a microburette. The titration is performed in an open cell, and the sample is exposed to light during the titration.

The concentration of SO ₂ in 7 samples determined with two different makes of spectrophotometers.		
Sample No.	Hitachi/101	Vitatron
1	2.6 µg SO ₂ /ml	2.7 µg SO ₂ /ml
2	3.9 µg SO ₂ /ml	3.9 µg SO ₂ /ml
3	3.8 µg SO ₂ /ml	3.8 µg SO ₂ /ml
4	3.5 µg SO ₂ /ml	3.5 µg SO ₂ /ml
5	2.6 µg SO ₂ /ml	2.7 µg SO ₂ /ml
6	1.5 µg SO ₂ /ml	1.5 µg SO ₂ /ml
7	4.0 µg SO ₂ /ml	3.9 µg SO ₂ /ml

Table I

2. The titration method is time consuming compared to the spectrophotometric Thorin method. It is possible to run 10 analyses per hour, including sample preparations and calculations, when using the spectrophotometric method. Only three samples per hour can be run with the titration method.
Even if all the samples have to be analysed twice by the spectrophotometric method in order to adjust the concentrations to the range 1 - 8 $\mu\text{g SO}_2/\text{ml}$, the spectrophotometric method will be faster than the titration method.
3. The method is easily adapted to an automatic analyser. Some laboratories, where SO_2 is analyzed as a routine, have years of experience with this automatic system.
4. The spectrophotometric method is sensitive, reproducible and selective. The accuracy is good, as compared to the accuracy of the sampling method. Reproducibility and repeatability are demonstrated in some of the tables below, where standard deviation for each series of analyses is included.
5. The method is recommended in "WMO Operations Manual for Sampling and Analysis Techniques for Chemical Constituents in Air and Precipitation, part II". Unfortunately this document is still in draft form and not available.
6. This method was also recommended to the countries participating in the OECD-programme: Long Range Transport of Air Pollutants (LRTAP). The concentration of sulphur dioxide in air and sulphate in precipitation, are determined in this programme. Ten European countries participate, two of these countries prefer to use the titration method while eight are using the spectrophotometric method.

7. It was essential to obtain comparable results from all the laboratories participating in the LRTAP-programme, and therefore an interlaboratory test programme was run in 1972. The test samples were prepared from $10^{-2}N$ H_2SO_4 , $MgSO_4/7H_2O$ and the absorption solution. A blank containing only the absorption solution was sent together with the samples to all the laboratories. The results from five "air samples" analysed by the spectrophotometric method in eight different countries are shown in Table II. Sample no. 4 had to be diluted for this method.

Table II

Concentration of SO_2 in air samples. Results from an interlaboratory test. The spectrophotometric Thorin method has been used. The results are expressed in $\mu g SO_2/ml$.

Sample No.	Calculated concentration	Results from country no.							
		1	2	3	4	5	6	7	8
1	1.2	1.1	1.2	1.1	1.1	1.2	1.4	1.8	1.2
2	5.6	5.5	5.2	5.6	5.4	5.3	5.5	6.0	5.6
3	3.4	3.4	3.3	3.2	3.4	4.0	3.4	4.0	3.5
4	19.0	17.2	17.9	17.8	18.6	16.8	-	19.2	19.5
5	0.6	0.8	0.7	0.7	0.8	0.4	0.6	1.3	0.6

Precipitation samples (6 - 10) were prepared from $10^{-2}N$ H_2SO_4 , $MgSO_4/7H_2O$ and water (distilled and deionised). An interfering cation was added to these samples, therefore they had to be ion exchanged prior to the analysis. The results are given in Table III.

Table III

Concentration of sulphate in precipitation. Results from an interlaboratory test. The Spectrophotometric Thorin method has been used. The results are given in $\mu\text{g SO}_4^{--}/\text{ml}$.

Sample No.	Calculated concentration	Results from country no.							
		1	2	3	4	5	6	7	8
6	10.76	10.7	10.5	10.1	10.3	-	10.4	11.0	-
7	3.92	3.8	4.1	3.8	4.0	-	3.5	4.7	-
8	5.36	5.0	5.5	6.1	5.2	-	4.8	6.0	-
9	7.9	7.5	7.5	7.5	7.5	-	7.2	8.3	-
10	5.43	5.1	5.4	5.5	5.2	-	5.0	6.2	-

Table IV gives the mean value for each sample, and the standard deviation. This table shows the reproducibility of the method. Some of the laboratories had no previous experience with this method, and the results would probably have been better if the test programme had been repeated now, a year later.

Table IV

The mean value (\bar{x}) and standard deviation (S) for the five test samples for SO_2 in air.

Sample No.	n	calc. conc. $\mu\text{g SO}_2/\text{ml}$	\bar{x} mean $\mu\text{g SO}_2/\text{ml}$	S std.dev	% dev.	n	calc. conc.	\bar{x}	S	%
1	8	1.2	1.26	0.22	17.7	7	1.2	1.19	0.10	8.3
2	8	5.6	5.51	0.23	4.1					
3	8	3.4	3.52	0.29	8.1					
4	7	19.0	18.14	0.93	5.1					
5	8	0.6	0.73	0.24	33.6	7	0.6	0.66	0.13	19.6

The numbers to the right were obtained when the results from country number 7 were excluded (see Table II).

Two of the countries made several independent measurements on each sample and sent us the results. They had no experience with this method, but their results are quite satisfactory, see Table V. The samples were not rerun on the same day. The first column in Table V shows results from country no. 4 for March 23rd, the second for March 27th and the third for May 8th, 1972.

Table V

Results from two different laboratories where the analysis has been repeated on the same sample.

Sample No.	Country no. 4			Country no. 3				
	Air samples $\mu\text{g SO}_2/\text{ml}$							
	3-23	3-27	5 - 8					
1	1.0	1.1	1.1	0.8-1.15-1.2-1.2-1.2-1.15-0.9				
2	5.4	5.7	5.2	5.75-5.2-5.65-6.0-5.9-5.7-5.75-5.3-5.3				
3	3.9	3.2	3.2	2.9	3.1	3.35	3.4	3.25
4	19.6	19.2	17.6	16.8	18.0	17.8	18.8	
5	0.8	0.5	1.0	0.55	0.65	0.7	0.75	0.75
Precipitation samples $\mu\text{g SO}_4^{--}/\text{ml}$								
6	10.5	9.8	10.7	10.2	10.5	9.9	9.75	
7	4.5	3.8	3.6	3.7	4.0	3.8	3.9	
8	5.4	5.1	5.1	5.1	5.2	4.8	5.4	5.2
9	7.2	7.9	7.5	7.8	7.4	7.4	7.5	
10	5.3	5.3	5.0	5.4	5.3	5.4	5.5	

The mean values from each of these two countries are given in Table VI together with the standard deviation and the standard deviation in percent of the mean.

Table VI

The mean values and standard deviation of the numbers given in Table V for country no. 3.

Sample No.	Calculated concentration	n	Country no. 3		
			\bar{x}	S	%
1	1.2 $\mu\text{g SO}_2/\text{ml}$	7	1.09	0.15	14.0
2	5.6 $\mu\text{g SO}_2/\text{ml}$	9	5.62	0.27	4.8
3	3.4 $\mu\text{g SO}_2/\text{ml}$	5	3.20	0.18	5.7
4	19.0 $\mu\text{g SO}_2/\text{ml}$	4	17.85	0.71	4.0
5	0.6 $\mu\text{g SO}_2/\text{ml}$	5	0.68	0.07	11.0
6	10.76 $\mu\text{g SO}_4^{--}/\text{ml}$	4	10.09	0.29	2.9
7	3.92 $\mu\text{g SO}_4^{--}/\text{ml}$	4	3.85	0.11	2.9
8	5.36 $\mu\text{g SO}_4^{--}/\text{ml}$	5	5.14	0.20	3.8
9	7.9 $\mu\text{g SO}_4^{--}/\text{ml}$	4	7.52	0.16	2.2
10	5.43 $\mu\text{g SO}_4^{--}/\text{ml}$	4	5.40	0.07	1.3

The national laboratories participating in the OECD-programme, and the interlaboratory test programme are listed here.

The British and the Swedish laboratories have been using the Thorin titration method, and their results are therefore not included in the tables above.

The German laboratory was at that time (1972) using the turbidimetric method.

The Italian laboratory took part in the interlaboratory test programme (using the spectrophotometric method), but has not joined the OECD-programme.

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8. An interlaboratory test programme has been run in Norway, and nine laboratories participated. The analytical training and experience was limited, and none of the laboratories had previously been using this method. The results from these laboratories are given in Table VII. The "air" samples were prepared in the way described in 7, and some of the samples are the same as those distributed to the laboratories in the international programme.

Table VII

Results from a Norwegian interlaboratory test programme.
The spectrophotometric Thorin method has been used.

Calculated concentration $\mu\text{g SO}_2/\text{ml}$	Results from laboratory no.									n	\bar{x}	S	$\% = \frac{S \times 100}{\bar{x}}$	
	1	2	3	4	5	6	7	8	9					
0.6														
1.0	0.9	0.7	1.0	1.0	1.1		0.6	1.0		3	0.67	0.05	7.0	
1.2		1.3	1.2	1.2	1.4		0.8			6	0.97	0.09	9.7	
2.0								2.0		5	1.30	0.09	6.8	
2.5	2.5		2.3	2.5	2.5		2.8	2.7		1	2.00			
2.8							2.8			5	2.50	0.13	5.0	
3.0								3.1		1	2.80			
3.4		3.0								2	2.95	0.15	5.1	
4.0							3.8	4.2		1	3.00			
5.0	5.1		4.9	5.0	5.2			5.2		2	4.00	0.20	5.0	
5.6		5.3	5.7	5.5	5.9				5.5	5	5.08	0.12	2.3	
6.0								6.2		6	5.58	0.19	3.3	
7.0	6.7		7.0	6.9	7.1			7.2		1	6.20			
8.0								8.3		5	6.98	0.17	2.5	
9.0								9.2		1	8.30			
9.5							9.8			1	9.20			
10.0								9.9		1	9.80			
19.0			19.6	18.0	18.4	18.7			19.0	5	18.74	0.54	2.9	

Two of the laboratories, number 5 and 8, have analysed the samples several times. The results are given in Table VIII. The same table also contains the mean values and standard deviations.

Table VIII

Repeatability in two of the laboratories analysing test samples in the Norwegian interlaboratory test programme.

Calculated concentration µg SO ₂ /ml	Results from laboratory no. 5				Results from laboratory no. 8					
		n	\bar{x}	S	%		n	\bar{x}	S	%
1.0	1.15-1.05-1.05-1.15-1.15	5	1.11	0.05	4.4	1.0-1.0-0.9-1.0-1.0-0.9	6	0.97	0.05	4.9
2.5	2.55-2.55-2.35-2.50-2.45	5	2.48	0.07	3.0	2.7-2.7-2.7				
5.0	5.6-5.15-5.15-5.15-5.1	5	5.23	0.19	3.6	5.1-5.2-5.4-5.2-5.2-5.2	6	5.21	0.09	1.7
7.0	7.1-7.0-7.2-7.05-7.1	5	7.09	0.07	0.9	7.6-7.0-7.2-7.0-7.6-7.2	6	7.26	0.25	3.4
8.0						8.0-8.5-8.6-8.1	4	8.30	0.25	3.1
9.0						8.9-9.4-9.4-9.2	4	9.22	0.20	2.2
10.0						9.6-9.9-10.0-9.9	4	9.85	0.15	1.5

9. At the National Institute of Public Health in Bilthoven, The Netherlands, SO₂ in air has been determined simultaneously by the TCM method and the spectrophotometric Thorin method for about 1½ year. The air samplers are placed side by side at three different sampling stations. A correlation analysis has now been run on these data from July 1, 1972 through April 30, 1973 (see Table IX).

If another method is to be standardized in addition to the TCM method, it is of course essential that the two methods yield comparable results.

Table IX

Results from a correlation analysis of the spectrophotometric Thorin method versus the TCM method.

station no	n sample size	r coefficient of correlation	Regression line
1	252	0.937	SO ₂ Thorin = 0.937 SO ₂ TCM - 0.187
2	239	0.888	SO ₂ Thorin = 0.897 SO ₂ TCM - 0.200
3	223	0.912	SO ₂ Thorin = 0.946 SO ₂ TCM + 0.511

10. The method has been tested at The Norwegian Institute for Air Research's laboratory for low concentrations of SO₂ in air. The Wøsthof "Dosimat" apparatus giving known amounts of SO₂ was used, and a sampling bottle containing the absorption solution specified by the method. Table X is a list of the amount of SO₂ added per ml solution, and the results after the samples have been analysed. Samples with a concentration lower than 1 µg SO₂/ml were evaporated and rerun.

Table X

Analytical results from samples with air containing a known amount of SO₂. SO₂ has been added to the sample from a Wøsthof "Dosimat" apparatus.

I Concentration added µg SO ₂ /ml	II Concentration analysed µg SO ₂ /ml	III Concentration after evaporation µg SO ₂ /ml
0	0.15	0.26
0	0.05	0.12
0	0.10	0.065
0	0.15	0.094
0.08	0.10	0.105
0.10	0.15	0.155
0.11	0.15	0.160
0.14	0.25	0.265
0.38	0.40	0.405
0.45	0.55	0.562
0.50	0.50	0.480
0.60	0.50	0.690
1.12	1.02	
1.20	1.10	
1.34	1.15	
1.48	1.45	
2.15	1.85	
2.39	2.00	
2.62	2.50	
2.87	2.65	

The correlation coefficient between the calculated concentration (I) and the concentration determined (II) was 0.996, and between I and III it was 0.949.

In a few cases the permeation tube has been used at the laboratory, instead of the Wøsthof "Dosimat" apparatus. The results are given in table XI

Table XI

Analytical results from air samples containing known amounts of SO₂. SO₂ has been added from a permeation tube.

µg SO ₂ added by a permeation tube	µg SO ₂ found in 50 ml absorption solution.
44.0	43.7
50.6	46.2
91.3	92.5
61.6	66.2
101.2	103.2
77.0	80.0
66.0	65.0

11. A new technique for sampling of low SO₂-concentrations has been developed. Air is passed through a filter that has been pretreated with an SO₂-absorbing chemical. SO₂ is oxidized to SO₄²⁻. The filter is leached in water, the solution is ion exchanged and analysed. Several laboratory tests have been run to improve the technique and to look at some of the interferences (such as humidity). Both a permeation tube and the Wøsthof "Dosimat" have been used to prepare air samples with known amounts of SO₂.

The results given in Table XII are from test where the temperature varied from -10°C to +25°C. The relative humidity was kept above 70%.

Another test was run at room temperature, but the relative humidity varied from 20% to 65% (see Table XIII). The reproducibility was poorer in this case. (These two tables are from NILU, Technical Note no 53/73). This work is not finished.

Table XII

A comparison of the amount of SO₂ added to the air samples, of SO₂ determined on the filters, when the spectrophotometric Thorin method is used. The temperature varied from -10°C to +25°C. The relative humidity was above 70%.

µg SO ₂ added	µg SO ₂ found
8.1	7.7
8.6	8.0
7.6	6.2
7.6	8.2
8.1	8.0
8.1	8.2
8.1	8.0
32.5	28.4
5.4	5.4
5.4	5.4
5.4	5.4
5.4	5.5
8.4	9.7
5.4	5.85
5.4	5.9
5.4	5.5
5.4	5.7
7.05	8.15

Correlation coefficient: 0.993.

Repeatability when 5.4 µg SO₂ and 8.1 µg SO₂ are added, is as follows:

added	n	\bar{x}	S
5.4	8	5.58	0.194
8.1	4	7.98	0.178

n = sampling size
 \bar{x} = arithmetic mean
 S = standard deviation

Table XIII

A comparison of the amount of SO₂ added to the air samples and the amount of SO₂ found on the filters, when the spectrophotometric Thorin method is used. The relative humidity varied from 20% to 65%. The tests were run at room temperature.

µg SO ₂ added	µg SO ₂ found	µg SO ₂ humidity %
5.4	4.5	20
8.1	8.0	25
5.4	3.5	26
5.4	6.0	26
8.1	7.7	28
8.1	7.9	28
8.1	8.0	29
8.1	7.0	29
5.4	4.0	30
5.4	4.5	30
5.4	5.5	30
5.4	4.8	30
8.1	8.6	30
8.7	8.0	30
5.4	5.8	33
5.4	5.0	33
24.4	23.5	40
24.4	22.3	47
8.1	8.5	60
8.1	8.7	60
8.1	8.2	60
8.1	8.7	60
0.0	0.0	60
33.6	33.5	65
48.2	45.5	65
24.4	24.5	65
8.1	7.3	65
8.1	8.5	65
8.1	8.7	65
0.0	0.5	-
0.0	0.5	-

Correlation coefficient 0.997.

Repeatability when the dose is 5.4 $\mu\text{g SO}_2$ or 8.1 $\mu\text{g SO}_2$

added	n	\bar{x}	S
5.4	9	4.84	0.779
8.1	13	8.13	0.534

n = sample size

\bar{x} = arithmetic mean

S = standard deviation