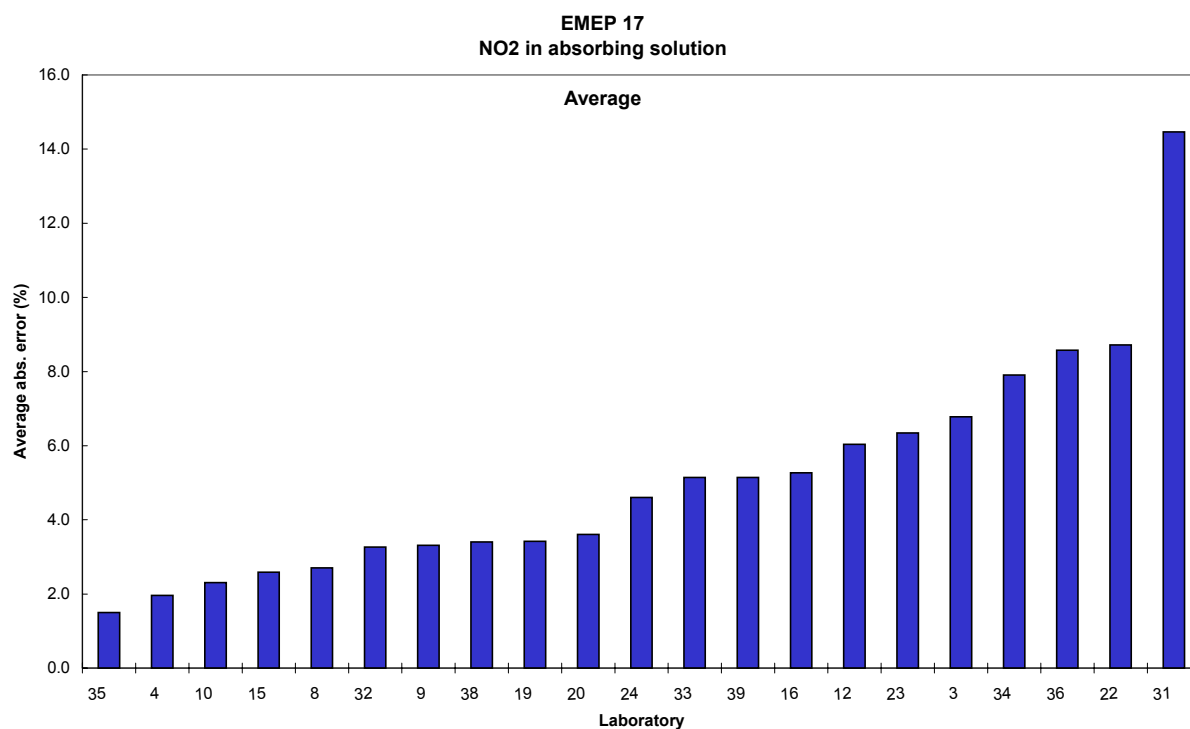


The seventeenth intercomparison of analytical methods within EMEP

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**EMEP Co-operative Programme for Monitoring and Evaluation
of the Long-range Transmission of Air Pollutants
in Europe**

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methods within EMEP**

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The seventeenth intercomparison of analytical methods within EMEP

1. Introduction

29 different laboratories in European countries are performing chemical analysis of air and precipitation samples within EMEP (Co-operative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe). Since the measurement programme is based on individual national networks, the participating laboratories apply different sampling and analytical methods. Most of the methods used are described in the manual for sampling and chemical analysis (EMEP 1977, EMEP 1996, <http://www.nilu.no/projects/ccc/manual/index.html>).

In order to improve the data comparability and to get a picture of the different laboratories' performance, interlaboratory comparisons are organized by the Chemical Co-ordinating Centre (CCC) at the Norwegian Institute for Air Research (NILU). So far sixteen intercomparisons have been arranged (Hanssen, 1988, 1990; Hanssen et al., 1983; Hanssen and Ladegård, 1984, 1985, 1987; Hanssen and Skjelmoen, 1992, 1994, 1995, 1996, 1997; Thrane, 1978, 1980a, 1980b, 1981).

This report gives the results of the seventeenth interlaboratory test.

2. Organization of the intercomparison

The samples for the seventeenth intercomparison (see Table 1) were prepared and distributed to 36 laboratories in July 1999. In addition to the European participants, two laboratories in North America received samples as a part of the co-operation between EMEP and the North American networks for acid deposition. One European laboratory not yet reporting to the CCC also received samples.

All of the laboratories had returned their results to the CCC within 15 days after the deadline given as 1 September 1999. 35 laboratories have returned results.

A preliminary evaluation of the data was given in the EMEP Workshop in Dubrovnik, Croatia in October 1999. The participating laboratories received the theoretical (expected) values 20 November 1999 by e-mail. The laboratories were then asked to compare their results with the expected ones, and give corrected values if obvious mistakes e.g. misprints had occurred. A few corrections were reported. In those cases the corrected values are used in this report. Particularly the instruction for a new way of reporting the results for NO₂ in absorbing solution had been overlooked by many participants.

In accordance with the decision of the Steering Body of EMEP, the results are presented in such a way that the different laboratories are identified. Table 2 gives

the names of the participating laboratories together with the numbers used when presenting the results in tables and figures.

Information received on the analytical methods used is given in Tables 3, 4, 5, 6 and 7.

3. Treatment of the data

The data reported from the participants are presented in Tables 8, 10, 12, 14, 15, and 17-28 and in Figures 1-17.

The method of data analysis is the same as in earlier intercomparisons. The results for the samples are presented in the tables in decreasing order together with the number of the laboratory (see Table 2). The expected (theoretical) value, the number of reported values, the arithmetic mean value, the median, the standard deviation and the relative standard deviation in percent are also given. After the first statistical run with all results included, the calculation was repeated with the "outliers" excluded. The outliers (unused) are defined as the results more than two standard deviations from the mean value in the first run.

Due to changes in NILU's data systems, Youden-plots are not used for the graphical presentations of the data in this report. Instead, the results are plotted to show the deviation in per cent from the expected value or the median value. These plots show the errors in ranked order.

4. Results

4.1 Sulphur dioxide

Six samples and one blank absorbing solution were distributed to the laboratories using the hydrogen peroxide absorption solution method. The reported results for the synthetic samples for sulphur dioxide in hydrogen peroxide absorbing solutions are given in Table 8. The reported value for the blank has been subtracted from all the other reported values. The ratios of the theoretical to the reported values are listed in Table 9. The relative errors based on the expected values are shown in Figure 1.

Only 6 laboratories now use a hydrogen peroxide absorption solution for their SO₂-measurements, but one additional laboratory (No. 15) analysed these samples.

Table 8 shows that the relative standard deviations are quite high, between 54.1 and 7.1% for the six samples when outliers are removed. This is higher than in the previous intercomparisons. The sulphate concentrations in the solutions for these samples correspond to a SO₂-concentration in air of 1.9-8.6 µg S/m³, when 70 ml absorbing solution and 3.6 m³ sample volume are used. The lowest concentrations are lower than in the previous comparisons, and the high relative errors shown in Figure 2 is an indication that the absorbing solution method may give variable results in this concentration range, which is quite common in European rural areas.

Laboratory No. 19 reported values that were more than two standard deviations from the mean value for two of the samples.

The average of the ratios of the expected values to values found by the laboratories presented in Table 9 vary from 0.86 to 1.56. In this case the very high ratio for Sample No. 1 for Laboratory No. 19 has been omitted.

Laboratory No. 19 reported a very high value for the blank (0.196 $\mu\text{g S/ml}$). This may have been a misprint, but no answer was given from the laboratory when they were asked to check these results.

Figure 1 shows that the relative errors often are higher than 30% for some of the laboratories. For the lowest concentration (A1) 4 of 7 laboratories reported values more than 30% from the expected value.

Impregnated filter samples for sulphur dioxide were analysed by sixteen laboratories. Nine samples were distributed including one blank (B2) that was **not** identified as "Blank". The value reported for this sample was subtracted from the other values before using the data.

The results are shown in Table 10 and in Figure 2. The ratios of the theoretical to the reported values are listed in Table 11.

Table 10 shows that the relative standard deviations are between 4.5 and 15.6% when the outliers are excluded. This result is a little worse than in the preceding comparison, but much better than for sulphur dioxide in absorbing solutions. The amount of sulphur in these samples corresponds to air concentrations between 0.32 and 2.4 $\mu\text{g S/m}^3$ if 25 m^3 of air is sampled.

Laboratories Nos. 20 and 38 reported both two values more than two standard deviations from the mean values. Laboratories Nos. 3 and 33 reported one such value.

Figure 2 shows that most of the reported values are less than 20% from the expected values. Only 11 values out of 128 have an error higher than 20%. The plots show that low values occur more often than high values, indicating insufficient extraction from the filter or a negative matrix effect on the analytical method from the impregnation solution.

The average ratios presented in Table 11 are in the range 0.93 to 1.20. Thirteen laboratories out of sixteen had an average ratio between 0.90 and 1.10. This is a quite satisfactory result.

Since as many as eight samples for sulphur dioxide in impregnated filters were used, x-y plots with reported values plotted against expected values could be used to visualize the results. In Figure 17 such plots are shown for each of the laboratories. In the plots the linear regression line (fully drawn) and the 1:1-line (dotted) are also shown. In addition the equation for the regression line and the corresponding R^2 -values are given in the plots.

Most of the plots show good agreement with the expected values, but Laboratories Nos. 20, 33, 38 and 39 obviously have a systematic error since the correlation is quite good but the slope is different from one or the regression line is crossing below the origin. The reason may be wrong calibration solutions or a matrix effect as mentioned above.

4.2 Nitrogen dioxide

The samples corresponding to nitrogen dioxide in absorbing solutions or extracts from iodide-impregnated filters contained known amounts of sodium nitrite diluted in water. In order to have more stable samples and to give the laboratories the opportunity to use their own sample solution matrix, the distributed solutions were to be diluted 1:10. The results should be reported as the diluted concentrations. Twenty-one laboratories reported results.

The results are shown in Table 12 and in Figure 3. The ratios of the theoretical values to the reported values are listed in Table 13.

The relative standard deviations were between 5.0 and 6.4% when outliers were omitted. This was a little better than in the last intercomparison. Laboratory No. 31 reported results more than two standard deviations from the mean values for three of the samples, while Laboratory No. 12 reported one such result.

The average ratios presented in Table 13 are in the range 0.92 to 1.17. Twenty of the twenty-one laboratories have average ratios between 0.90 and 1.10. This is a quite satisfactory result.

The 10 times diluted samples that were analysed correspond to air concentrations from 4.2 to 8.1 $\mu\text{g NO}_2\text{-N/m}^3$ when 70 ml absorbing solution and 1.4 m^3 of air is sampled. This is a little higher than the annual mean concentrations in remote areas of Central Europe, but much higher than the mean values in the northern part of Europe. When the iodide impregnated filter method is used, the given concentrations in the solutions correspond to 0.48 to 0.93 $\mu\text{g NO}_2\text{-N/m}^3$ when 4 ml extraction solution is used and 0.7 m^3 of air is sampled.

4.3 Sulphate on filters

The samples consisted of Whatman 40 filters to which different amounts of a diluted sodium sulphate solution had been added. The amount of sulphur on the filters distributed were divided into two groups called "low" and "high" since some laboratories use low-volume sampling (1-3.5 m^3) and some use medium volume (10-50 m^3).

The results of the analyses are shown in Tables 14 and 15 and in Figures 4 and 5.

Seven of twenty-five sets of filter samples were in the low concentration range. None of the reported values in this range were outliers.

The relative standard deviations were between 1.8 and 6.4%. This is better than in the last intercomparison even though the corresponding air concentrations were a little lower this time. The range was 0.7 to 3.0 $\mu\text{g S/m}^3$ if 3 m^3 of air is sampled.

Figure 4 show that nearly all reported values are less than 5% from the expected value.

Eighteen sets of filters were distributed in the high concentration range. In this range the relative standard deviations were between 4.9 and 6.7% when one outlier was excluded for three of the samples and two outliers for one of the samples. This is about the same as in the last intercomparison. The air concentrations corresponding to the amount of sulphur added to the filters are 0.5 to 2 $\mu\text{g S/m}^3$ when 25 m^3 of air is sampled. Laboratory No. 30 reported too low values for two of the samples and too high value for one of the samples. Laboratories Nos. 33 and 38 reported one too low value each.

Figure 5 shows that most of the reported values are less than 10% from the expected values.

Table 16 shows the ratios of the theoretical to the reported values and the average ratios for the samples. The average ratios vary between 0.97 and 1.06 in the low concentration range and between 0.96 and 1.32 in the high range. Fifteen out of eighteen laboratories had average ratios between 0.9 and 1.10 in the high range. In the low range all of the seven laboratories had an average ratio within this interval.

4.4 Precipitation

Most of the laboratories now perform the full precipitation programme in EMEP. Four precipitation samples were distributed and 1336 single results from 34 laboratories were reported.

4.4.1 Sulphate

The results from the determination of sulphate are given in Table 17 and in Figure 6. Laboratories Nos. 9, 33 and 35 reported two outlying results each, while Laboratories Nos. 18 and 19 each reported one "outlier". The relative standard deviations after excluding the "outliers" were 3.4-6.2%, which is about the same as in the last intercomparison.

Figure 6 shows that only a few laboratories report values more than 20% from the expected ones. It shows that only a few laboratories now have problems with the important parameter sulphate. The laboratories Nos. 18, and 35 still use other methods than ion chromatography, and this seems to be the reason for deviating results. However, Laboratories Nos. 9, 19 and 33 are using ion chromatography, and still seems to have problems with the precision.

4.4.2 Nitrate

Table 18 and Figure 7 present the results of the nitrate determinations. The standard deviations after excluding the outliers are in the range 3.4-4.6%, which are very low, and lower than in the last intercomparisons. Laboratory No. 40 reported outlying low values for all four samples. Laboratories Nos. 33 and 35 reported one outlying result each.

Figure 7 shows that only a few laboratories have reported values more than 10% from the expected ones. In fact, more than 80% of the reported values are less than 5% from the expected value.

4.4.3 Ammonium

Table 19 and Figure 8 give the results of the ammonium analysis. Laboratories Nos. 3 and 24 both reported two results more than two standard deviations from the expected values. Laboratories Nos. 19, 11 and 31 reported each one outlying result. Relative standard deviations were in the range 3.9-6.3% when outliers were excluded. This is a better than in the last intercomparison.

Figure 8 shows that most laboratories report data less than 10% from the expected values.

4.4.4 pH and strong acid

Tables 20-22 and Figures 9-10 show the results of the pH measurements and the determination of strong acids. Thirty-four laboratories reported pH-values, while only two of these reported titrated concentrations of strong acid.

In Table 21 the pH-data in Table 20 have been recalculated to H^+ concentrations to give realistic standard deviation values.

Laboratory No. 34 reported outlying low pH values for all four samples. Laboratories No. 13 reported low values for three of the samples.

This is the fifth succeeding intercomparison that Laboratory No. 13 reports too low pH-values and shows that the intercomparisons have not been used to improve the results. One reason could be a long storage time in room temperature with evaporation before analysis, but this is not the recommended way to store precipitation samples.

The relative standard deviation for the calculated H^+ concentration, varied between 6.8 and 11.6% when outliers were excluded. This is higher than for the other parameters but a little better than in the last intercomparison.

In Figure 9 and 10 the deviation in pH-units and % from the **median** of the reported values are given instead of from the expected value. This is done since the median for this parameter deviates more from the expected values than for the other parameters.

Only two laboratories reported values for titrated acidity. None of the reported values were outliers.

4.4.5 Chloride

Table 23 and Figure 11 give the results of the chloride determinations. Laboratory No. 19 reported outlying high values for all four samples. Laboratory No. 24 also reported high values, and three of them more than two standard deviations from the mean value. Five other laboratories, Nos. 22, 23, 33, 37 and 39 reported one outlier each.

The relative standard deviations for the reported values when the outliers were removed were between 7.7 and 20.3%, which is higher than for most of the other parameters, but a little better than in the last intercomparison.

Figure 11 shows that relative many reported values more than 20% from the expected values.

4.4.6 Sodium

Table 24 and Figure 12 show the results of the sodium determinations. Laboratory No. 40 reported too low values for all four samples, while Laboratories Nos. 9, 17 and 38 reported outlying values for one of the samples each.

The relative standard deviations were between 3.3 and 8.3% when the outliers were excluded, which is better than in the last intercomparison.

Only a few reported values were more than 10% from the expected values for the highest sample pair (Sample Nos. 2 and 3), but for the samples with the lowest concentration there were more laboratories with larger errors.

4.4.7 Magnesium

The results of the magnesium determinations are presented in Table 25 and Figure 13. Laboratory No. 40 reported too low values for all four samples while Laboratory No. 38 reported too high values for three of the samples and Laboratory No. 23 too high values for two of the samples.

The relative standard deviations after excluding the outliers were in the range 6-9.5%, which is approximately the same as in the preceding intercomparison.

Relative many values have an error larger than 10% as seen in Figure 13.

4.4.8 Calcium

Table 26 and Figure 14 show the results of the calcium determinations. Laboratories Nos. 23, 32 and 37 reported outlying values for two of the samples, while Laboratories Nos. 30, 35 and 40 reported outliers for one sample each.

The relative standard deviation after omitting the outliers was in the range 7.3-14.1%. This is better than in the last intercomparison.

Figure 14 show that many of the reported values are more than 20% from the expected ones. It should be noted that the Ca concentrations given in the samples are lower than the usual concentration in the precipitation samples in some countries.

4.4.9 Potassium

In Table 27 and Figure 15 the results of the potassium determinations are shown. Laboratory No. 18 reported all four values too high, while Laboratories Nos. 11 and 40 reported two outliers each.

The standard deviations after omitting the outlying results were between 10.1 and 21.5%, which is about the same as in the last intercomparison.

Many reported values are more than 20% from the expected values, as can be seen in Figure 15. The potassium concentrations in the samples are relatively low, but this is usually also the case for the real samples at EMEP sites.

4.4.10 Conductivity and ion balance

The results of the conductivity measurements are given in Table 28 and Figure 16. Laboratory No. 17 reported three of the values too high, while Laboratory No. 40 reported one high and one low value. Laboratories Nos. 20, 22 and 33 reported one low “outlier” each.

The relative standard deviations were in the range 3.9-9.2%, which is a little higher than in the last intercomparison.

Only a few laboratories reported values more than 20% from the expected values. The shape of the plots for Samples G2 and G4 in Figure 16 is a little unusual, with nearly all of the reported values lower than the expected ones. However, many of the reported values are only a few % from the expected values, and the median of the reported values is only 3% lower than the expected values. If the median of the reported pH-values had been used for calculation of the expected values for conductivity, the shape had been more normal.

Conductivity measurements are mainly used in EMEP for quality control reasons by comparing measured with calculated values when all main ions in the precipitation have been measured. In Table 29 the ratio of the measured to the calculated conductivities (from the reported results) are given. By inspecting these values, it is seen that at least Laboratories Nos. 17 and 18 should have looked closer into the reported results, since the ratios between measured and calculated conductivity is far from 1. Also Laboratory No. 38 has two of the ratios deviating much from 1, but as last time it seems that the conductivity measurement for these samples having a low conductivity is the reason. Laboratory No. 23, which in this intercomparison reported more outlying results than earlier, should have got a warning when looking into these ratios.

However, looking only at the ratio between measured and calculated conductivity values, erroneous results may be overlooked if the concentrations are low, and do not count much in the sum of ionic conductivities.

Some obvious mistakes could have been discovered if the laboratories had used the ion balance control. The ratios for anions/cations (equivalents) are seen in Table 30. Laboratories Nos. 9, 32, 33 and 35 have ratios deviating much from 1 for at least two of the samples.

5. Conclusions

In this seventeenth intercomparison of analytical methods within EMEP, 35 laboratories participated. Nearly all laboratories perform the complete programme for the precipitation samples. Totally 1690 single results from synthetic samples with known content were received.

As can be seen from Table 31, the median values of the reported data were generally not more than $\pm 5\%$ away from the theoretical expected value. However, the mean values for H^+ in precipitation calculated from the pH-measurements were between 10 and 14% lower than the expected ones. The reason for this is not obvious.

Like in earlier intercomparisons, "outliers", have been defined as results more than two standard deviations from the mean value. Outliers occur for almost all samples and parameters.

Of the 1690 reported results, 99 were in this way identified as outliers. This is 5.6% of the data, which is a little more than in earlier intercomparisons. When the reported data are normally distributed, the definition of an outlier will result in percentage outliers in this range.

It should be noted that only four laboratories caused about 40% of the outliers. Laboratories Nos. 40, 19, 33 and 38 had seven or more outlying results. These laboratories **must** strengthen the quality control of the laboratory analyses, but also more precise analytical methods have to be used to reach the desired quality. One of these laboratories also had many outliers in the last intercomparison. One laboratory (No. 40) with 17 outliers has not reported data to EMEP yet, but has unofficially participated in the laboratory intercomparisons in the last years.

Twelve of the laboratories had no outliers. That is less than last year. One laboratory had only one outlier.

The relative standard deviations found in this intercomparison are generally in the same range as in the last intercomparison. For some parameters there are less spread in the results than earlier, for some others more.

Some laboratories took part in the intercomparison, even before they have started regular reporting of data. This means that further improvements could be expected when they get more training and experience.

Some laboratories are using methods which today must be characterized as outdated and not suited for analysing the samples and concentrations experienced in EMEP. The main reason for using old methods is lack of funding for modern equipment in some countries.

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Appendix 1

Tables

Table 1: Samples distributed for the seventeenth interlaboratory test.

A.	6 synthetic samples for determination of SO ₂ , consisting of 0.3% H ₂ O ₂ absorbing solution and containing different concentrations of sulphuric acid. One of the samples was an unidentified blank.
B.	9 KOH-impregnated Whatman 40 filters, comprising 1 blank and 8 filters to which different amounts of sulphuric acid have been added.
C.	4 synthetic samples for determination of NO ₂ consisting of sodium nitrite diluted in water.
E.	5 synthetic filter samples for determination of sulphate by wet chemical methods, comprising 1 Whatman 40 blank and 4 filters to which different amounts of Na ₂ SO ₄ (aq) have been added.
G.	4 synthetic precipitation samples, containing SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , H ⁺ , Na ⁺ , Mg ²⁺ and Cl ⁻ , and Ca ²⁺ and K ⁺ .

Table 2: Participating laboratories in the seventeenth laboratory intercomparison. The number in front of the names are used in tables and figures.

Canada	(26)	Atmospheric Environment Service, Toronto
Croatia	(35)	Meteorological and Hydrological Service, Zagreb
Czech Republic	(3)	Czech Hydrometeorological Institute, Praha
Denmark	(4)	National Environmental Research Institute. Air Pollution Laboratory
Estonia	(38)	Estonian Environmental Research Centre, Tallinn
European Commission	(30)	Joint Research Centre, Ispra, Environment Institute
Finland	(5)	Finnish Meteorological Institute. Air Quality Department
France	(6)	Laboratories Wolff Environnement, Evry
FYROM	(40)	Republic Hydrometeorological Institute of Macedonia, Skopje
Germany	(7)	IfE Leipzig GmbH, Umweltlabor
Germany	(8)	Umweltbundesamt, Messtelle Schauinsland
Greece	(9)	Ministry of Environment. Environmental Division, Athens
Hungary	(10)	Institute for Atmospheric Physics
Iceland	(11)	Íðntæknistofnun Islands (Technological Inst. of Iceland)
Ireland	(12)	Meteorological Service, Dublin
Italy	(13)	Istituto Inquinamento Atmosferico of C.N.R
Latvia	(33)	Latvian Hydrometeorological Institute, Environmental Quality Testing Laboratory
Lithuania	(32)	Institute of Physics, Vilnius
Netherlands	(14)	National Institute of Public Health and Environmental Protection (RIVM)
Norway	(15)	Norwegian Institute for Air Research (NILU)
Poland	(16)	Institute of Meteorology and Water Management, Warsaw
Poland	(39)	Environmental Monitoring Laboratory, Institute of Environmental Protection
Portugal	(17)	Direccao Regional do Ambiente e Recursos Naturais do Alentejo, Sines
Romania	(18)	Research and Engineering Institute for Environment
Russian Federation	(22)	Institute of Global Climate and Ecology
Slovakia	(31)	Slovak Hydrometeorological Institute
Slovenia	(36)	Hydrometeorological Institute of Slovenia
Spain	(19)	Centro Nacional de Sanidad Ambiental
Sweden	(20)	Swedish Environmental Research Institute (IVL), Gothenburg
Switzerland	(21)	Swiss Federal Laboratories for Materials Testing (EMPA)
Turkey	(34)	Refik Saydam Institute, Ankara
United Kingdom	(23)	AEA Technology, National Environmental Technology Centre
United States of America	(27)	Illinois State Water Survey
Yugoslavia	(24)	Federal Hydrometeorological Institute, Belgrade

Table 3: Analytical methods used at the participating laboratories for the determination of sulphur dioxide in absorbing solution.

Method	Laboratory
1. Ion chromatography	6, 9, 15, 17, 19, 21, 23

Table 4: Analytical methods used at the participating laboratories for the determination of sulphur dioxide on impregnated filters.

Method	Laboratory
1. Thorin method	3, 33
2. Ion chromatography	4, 5, 11, 15, 16, 20, 22, 26, 31, 32, 34, 36, 38
3. Capillary Ion Analysis	39

Table 5: Wet chemical methods used at the participating laboratories for the determination of sulphate on filters.

Method	Laboratory
1. Thorin method	33
2. Ion chromatography	4, 5, 6, 10, 11, 13, 14, 15, 16, 17, 19, 20, 21, 22, 23, 26, 30, 31, 32, 34, 38
3. Capillary Ion Analysis	39

Table 6: Analytical method used for NO₂ in absorbing solution.

Method	Laboratory
1. ANSA/Sulphanilamide	9, 12, 24
2. NEDA/Sulphanilamide	3, 4, 10, 15, 16, 19, 20, 22, 23, 31, 32, 33, 34, 35, 36, 38, 39
3. NEDA/Sulphanilic acid	8

Table 7: *Analytical methods used for the determination of chemical constituents in precipitation samples.*

Constituents	Methods	Laboratory
SO ₄	1 Thorin 2 Ion chromatography 3 Turbidimetry 4 Capillary Ion Analysis	18 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16, 17, 19, 20, 21, 22, 23, 26, 27, 30, 31, 32, 33, 34, 36, 37, 38 24, 35 39
NO ₃	1 Griess after Cd-red. 2 Ion chromatography 3 UV-method 4 Capillary Ion Analysis 5 SQ-Merck ?	24 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16, 17, 19, 20, 21, 22, 23, 26, 27, 30, 31, 32, 33, 34, 36, 37, 38 35 39 40
NH ₄	1 Indophenol 2 Berthelot reaction, salycilate 3 Ion chromatography 4 Flow injection analysis (FIA) 5 Chloramin T 6 Nessler 7 SQ-Merck ?	3, 4, 10, 11, 17, 19, 24, 27, 32, 33, 34, 35, 38, 39 14, 26 5, 6, 7, 9, 13, 15, 21, 22, 23, 30, 31, 36 8, 20, 37 16 18 40
H ⁺	1 Acidimetric titration 2 Alkali titration to spec. pH	14 6
Mg	1 Atomic absorption (AAS) 2 Ion chromatography 3 ICP-AES	3, 4, 8, 10, 11, 16, 17, 18, 19, 20, 22, 24, 26, 27, 33, 34, 35, 36, 38, 39, 40 5, 6, 7, 9, 12, 13, 15, 21, 23, 30, 31, 37 14
Na	1 AES 2 AAS 3 ICP-AES 4 Ion chromatography	10, 19, 32, 33, 36, 38, 39 3, 4, 8, 16, 17, 20, 24, 26, 27, 34, 35, 40 14 5, 6, 7, 9, 13, 15, 21, 22, 23, 30, 31, 37
Cl	1 Mercury thiocyanate-iron 2 Ion chromatography 3 Capillary Ion Analysis	18, 24, 32, 35 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16, 17, 19, 20, 21, 22, 23, 26, 27, 30, 31, 33, 34, 36, 37, 38 39
Ca	1 AAS 2 ICP-AES 3 Ion chromatography 4 AES	3, 4, 8, 11, 16, 17, 19, 20, 22, 24, 26, 27, 34, 35, 36, 38, 40 14 5, 6, 7, 9, 13, 15, 21, 23, 30, 31, 37 10, 32, 33, 39
K	1 AAS 2 Ion chromatography 3 AES 4 ICP-AES	3, 4, 8, 11, 16, 17, 18, 19, 20, 24, 26, 27, 34, 35, 40 5, 6, 7, 9, 13, 15, 21, 22, 23, 30, 31, 37 10, 32, 33, 36, 38, 39 14

Table 8: Analytical results of the synthetic samples of SO₂ in absorbing solution (A), listed in decreasing order. The theoretical value, arithmetic mean concentration, median, standard deviation, relative standard deviation, the number of laboratories, and the number of "outliers" are included.

SULPHUR DIOXIDE IN ABSORBING SOL. SAMPLE NO.: 1 THEORETICAL VALUE 0.100 UNIT: UG S/ML RUN 1: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 0.095 MEDIAN: 0.108 STANDARD DEVIATION: 0.052 REL. ST. DEVIATION (%): 54.058 RUN 2: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 0.095 MEDIAN: 0.108 STANDARD DEVIATION: 0.052 REL. ST. DEVIATION (%): 54.058 RESULTS IN DECREASING ORDER: 6 0.142 21 0.108 17 0.139 9 0.050 23 0.119 19 0.001 15 0.108 "UNUSED": DATA UNUSED IN RUN 2	SULPHUR DIOXIDE IN ABSORBING SOL. SAMPLE NO.: 2 THEORETICAL VALUE 0.321 UNIT: UG S/ML RUN 1: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 0.307 MEDIAN: 0.323 STANDARD DEVIATION: 0.052 REL. ST. DEVIATION (%): 16.855 RUN 2: NUMBER OF LABORATORIES: 6 ARITHMETIC MEAN VALUE: 0.324 MEDIAN: 0.326 STANDARD DEVIATION: 0.025 REL. ST. DEVIATION (%): 7.828 RESULTS IN DECREASING ORDER: 17 0.352 15 0.313 23 0.347 6 0.282 21 0.329 19 0.202 UNUSED 9 0.323 "UNUSED": DATA UNUSED IN RUN 2
SULPHUR DIOXIDE IN ABSORBING SOL. SAMPLE NO.: 3 THEORETICAL VALUE 0.401 UNIT: UG S/ML RUN 1: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 0.395 MEDIAN: 0.416 STANDARD DEVIATION: 0.063 REL. ST. DEVIATION (%): 16.053 RUN 2: NUMBER OF LABORATORIES: 6 ARITHMETIC MEAN VALUE: 0.417 MEDIAN: 0.426 STANDARD DEVIATION: 0.030 REL. ST. DEVIATION (%): 7.149 RESULTS IN DECREASING ORDER: 9 0.440 21 0.405 23 0.439 6 0.363 17 0.436 19 0.265 UNUSED 15 0.416 "UNUSED": DATA UNUSED IN RUN 2	SULPHUR DIOXIDE IN ABSORBING SOL. SAMPLE NO.: 4 THEORETICAL VALUE 0.140 UNIT: UG S/ML RUN 1: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 0.143 MEDIAN: 0.146 STANDARD DEVIATION: 0.036 REL. ST. DEVIATION (%): 24.903 RUN 2: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 0.143 MEDIAN: 0.146 STANDARD DEVIATION: 0.036 REL. ST. DEVIATION (%): 24.903 RESULTS IN DECREASING ORDER: 17 0.178 15 0.142 9 0.177 6 0.106 23 0.164 19 0.085 21 0.146 "UNUSED": DATA UNUSED IN RUN 2
SULPHUR DIOXIDE IN ABSORBING SOL. SAMPLE NO.: 6 THEORETICAL VALUE 0.441 UNIT: UG S/ML RUN 1: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 0.444 MEDIAN: 0.448 STANDARD DEVIATION: 0.084 REL. ST. DEVIATION (%): 19.008 RUN 2: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 0.444 MEDIAN: 0.448 STANDARD DEVIATION: 0.084 REL. ST. DEVIATION (%): 19.008 RESULTS IN DECREASING ORDER: 9 0.577 21 0.442 23 0.483 6 0.400 17 0.459 19 0.298 15 0.448 "UNUSED": DATA UNUSED IN RUN 2	SULPHUR DIOXIDE IN ABSORBING SOL. SAMPLE NO.: 7 THEORETICAL VALUE 0.301 UNIT: UG S/ML RUN 1: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 0.306 MEDIAN: 0.303 STANDARD DEVIATION: 0.064 REL. ST. DEVIATION (%): 21.007 RUN 2: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 0.306 MEDIAN: 0.303 STANDARD DEVIATION: 0.064 REL. ST. DEVIATION (%): 21.007 RESULTS IN DECREASING ORDER: 9 0.422 15 0.288 23 0.333 6 0.281 21 0.305 19 0.208 17 0.303 "UNUSED": DATA UNUSED IN RUN 2

Table 9: The ratios of the theoretical values and the results found by the laboratories in the determination of sulphur dioxide in absorbing solutions (samples A1-A6).

Lab. No.	<u>Theoretical value</u> Measured value						Average ratio
	Sample No.						
	A1	A2	A3	A4	A6	A7	
6	0.71	1.14	1.10	1.32	1.10	1.07	1.07
9	2.00	0.99	0.91	0.79	0.76	0.71	1.09
15	0.93	1.02	0.96	0.99	0.98	1.04	0.98
17	0.72	0.91	0.92	0.79	0.96	0.99	0.86
19	(100.2)	1.59	1.51	1.65	1.48	1.45	1.56
21	0.93	0.97	0.99	0.96	1.00	0.99	0.97
23	0.84	0.92	0.91	0.86	0.91	0.90	0.89

Table 10: Analytical results of the synthetic samples of SO₂ on KOH-impregnated filter (B1-4 and B6-9). The results are corrected for the reported value for sample B5 (Blank). For explanation, see Table 8.

SULPHUR DIOXIDE ON IMPREGNATED FILTER SAMPLE NO.: 1 THEORETICAL VALUE 60.100 UNIT: UG S/FIL RUN 1: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 59.062 MEDIAN: 59.500 STANDARD DEVIATION: 3.400 REL. ST. DEVIATION (%): 5.757 RUN 2: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 59.062 MEDIAN: 59.500 STANDARD DEVIATION: 3.400 REL. ST. DEVIATION (%): 5.757 RESULTS IN DECREASING ORDER: 31 64.000 16 59.200 3 62.900 22 59.000 15 62.300 4 58.600 5 62.200 26 58.200 32 61.600 33 55.500 36 60.800 38 54.400 34 60.000 39 53.500 11 59.800 20 53.000 "UNUSED": DATA UNUSED IN RUN 2	SULPHUR DIOXIDE ON IMPREGNATED FILTER SAMPLE NO.: 3 THEORETICAL VALUE 16.000 UNIT: UG S/FIL RUN 1: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 15.631 MEDIAN: 15.850 STANDARD DEVIATION: 1.575 REL. ST. DEVIATION (%): 10.074 RUN 2: NUMBER OF LABORATORIES: 15 ARITHMETIC MEAN VALUE: 15.847 MEDIAN: 15.900 STANDARD DEVIATION: 1.364 REL. ST. DEVIATION (%): 8.609 RESULTS IN DECREASING ORDER: 36 18.600 5 15.800 11 17.400 4 15.600 3 17.100 26 15.200 32 16.800 22 14.700 31 16.500 16 14.500 39 16.200 20 14.000 34 16.000 33 13.400 15 15.900 38 12.400 UNUSED "UNUSED": DATA UNUSED IN RUN 2
SULPHUR DIOXIDE ON IMPREGNATED FILTER SAMPLE NO.: 4 THEORETICAL VALUE 8.020 UNIT: UG S/FIL RUN 1: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 7.336 MEDIAN: 7.485 STANDARD DEVIATION: 0.982 REL. ST. DEVIATION (%): 13.385 RUN 2: NUMBER OF LABORATORIES: 14 ARITHMETIC MEAN VALUE: 7.344 MEDIAN: 7.485 STANDARD DEVIATION: 0.693 REL. ST. DEVIATION (%): 9.442 RESULTS IN DECREASING ORDER: 3 9.300 UNUSED34 7.480 32 8.530 36 7.380 39 8.100 26 7.210 15 7.870 31 7.000 4 7.780 16 6.790 33 7.550 22 6.140 5 7.500 20 6.000 11 7.490 38 5.250 UNUSED "UNUSED": DATA UNUSED IN RUN 2	SULPHUR DIOXIDE ON IMPREGNATED FILTER SAMPLE NO.: 5 THEORETICAL VALUE 40.100 UNIT: UG S/FIL RUN 1: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 39.525 MEDIAN: 39.400 STANDARD DEVIATION: 2.275 REL. ST. DEVIATION (%): 5.756 RUN 2: NUMBER OF LABORATORIES: 15 ARITHMETIC MEAN VALUE: 39.893 MEDIAN: 39.400 STANDARD DEVIATION: 1.795 REL. ST. DEVIATION (%): 4.498 RESULTS IN DECREASING ORDER: 3 43.100 5 39.400 31 42.400 16 39.300 36 42.300 33 39.100 32 41.100 26 38.700 11 40.900 15 38.500 22 39.900 39 38.100 34 39.800 38 36.400 4 39.400 20 34.000 UNUSED "UNUSED": DATA UNUSED IN RUN 2

Table 10 cont.

SULPHUR DIOXIDE ON IMPREGNATED FILTER SAMPLE NO.: 6 THEORETICAL VALUE 54.100 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 53.050 MEDIAN: 53.650 STANDARD DEVIATION: 3.146 REL. ST. DEVIATION (%): 5.929 RUN 2: NUMBER OF LABORATORIES: 15 ARITHMETIC MEAN VALUE: 53.520 MEDIAN: 53.900 STANDARD DEVIATION: 2.610 REL. ST. DEVIATION (%): 4.877 RESULTS IN DECREASING ORDER: 3 57.100 15 53.400 31 56.300 5 53.000 22 56.100 4 52.600 36 55.300 16 52.500 11 54.900 26 52.300 32 54.800 33 49.200 38 54.100 39 47.300 34 53.900 20 46.000 UNUSED "UNUSED": DATA UNUSED IN RUN 2	SULPHUR DIOXIDE ON IMPREGNATED FILTER SAMPLE NO.: 7 THEORETICAL VALUE 9.020 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 8.764 MEDIAN: 8.645 STANDARD DEVIATION: 1.371 REL. ST. DEVIATION (%): 15.644 RUN 2: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 8.764 MEDIAN: 8.645 STANDARD DEVIATION: 1.371 REL. ST. DEVIATION (%): 15.644 RESULTS IN DECREASING ORDER: 38 11.500 16 8.630 36 11.300 5 8.500 3 10.100 26 8.370 32 9.620 31 7.800 15 9.100 39 7.400 4 9.000 22 7.200 11 9.000 33 7.050 34 8.660 20 7.000 "UNUSED": DATA UNUSED IN RUN 2
SULPHUR DIOXIDE ON IMPREGNATED FILTER SAMPLE NO.: 8 THEORETICAL VALUE 14.000 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 13.131 MEDIAN: 13.150 STANDARD DEVIATION: 1.345 REL. ST. DEVIATION (%): 10.243 RUN 2: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 13.131 MEDIAN: 13.150 STANDARD DEVIATION: 1.345 REL. ST. DEVIATION (%): 10.243 RESULTS IN DECREASING ORDER: 36 15.600 11 13.100 3 14.900 26 13.100 32 14.800 16 12.500 15 14.200 39 12.100 4 13.700 20 12.000 5 13.600 22 11.900 34 13.400 38 11.100 31 13.200 33 10.900 "UNUSED": DATA UNUSED IN RUN 2	SULPHUR DIOXIDE ON IMPREGNATED FILTER SAMPLE NO.: 9 THEORETICAL VALUE 36.100 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 34.906 MEDIAN: 35.050 STANDARD DEVIATION: 2.459 REL. ST. DEVIATION (%): 7.044 RUN 2: NUMBER OF LABORATORIES: 15 ARITHMETIC MEAN VALUE: 35.253 MEDIAN: 35.200 STANDARD DEVIATION: 2.101 REL. ST. DEVIATION (%): 5.958 RESULTS IN DECREASING ORDER: 36 39.000 11 34.900 3 38.100 4 34.600 32 36.700 26 34.600 5 36.600 39 34.400 34 36.100 16 34.100 31 36.000 38 33.300 15 35.200 20 30.000 22 35.200 33 29.700 UNUSED "UNUSED": DATA UNUSED IN RUN 2

Table 11: The ratios of the theoretical values and the results found by the laboratories in the determination of sulphur dioxide on impregnated filters. The reported results are corrected for the value for B2 (Blank).

Lab. No.	Theoretical value Measured value								Average ratio
	Sample No.								
	B1	B3	B4	B5	B6	B7	B8	B9	
3	0.96	0.94	0.86	0.93	0.95	0.89	0.94	0.95	0.93
4	1.03	1.03	1.03	1.02	1.03	1.00	1.02	1.04	1.02
5	0.97	1.01	1.07	1.02	1.02	1.06	1.03	0.99	1.02
11	1.01	0.92	1.07	0.98	0.99	1.00	1.07	1.03	1.01
15	0.97	1.01	1.02	1.04	1.01	0.99	0.99	1.02	1.01
16	1.01	1.11	1.18	1.02	1.03	1.04	1.13	1.06	1.07
20	1.13	1.15	1.34	1.18	1.18	1.29	1.17	1.20	1.20
22	1.02	1.09	1.31	1.00	0.96	1.25	1.18	1.02	1.10
26	1.03	1.05	1.11	1.03	1.03	1.08	1.07	1.04	1.06
31	0.94	0.97	1.15	0.95	0.96	1.16	1.06	1.00	1.02
32	0.98	0.95	0.94	0.97	0.99	0.94	0.95	0.98	0.96
33	1.08	1.19	1.06	1.03	1.10	1.28	1.29	1.21	1.16
34	1.00	1.00	1.07	1.01	1.00	1.04	1.05	1.00	1.02
36	0.99	0.86	1.09	0.95	0.98	0.80	0.90	0.92	0.94
38	1.11	1.29	1.53	1.10	1.00	0.78	1.26	1.08	1.14
39	1.12	0.99	0.99	1.05	1.14	1.22	1.16	1.05	1.09

Table 12: Analytical results of the synthetic samples of NO₂ in absorbing solution (C1-4). For explanation, see Table 8.

NITROGEN DIOXIDE IN ABSORBING SOL. SAMPLE NO.: 1 THEORETICAL VALUE 0.162 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 21 ARITHMETIC MEAN VALUE: 0.161 MEDIAN: 0.160 STANDARD DEVIATION: 0.011 REL. ST. DEVIATION (%): 6.935 RUN 2: NUMBER OF LABORATORIES: 20 ARITHMETIC MEAN VALUE: 0.162 MEDIAN: 0.160 STANDARD DEVIATION: 0.010 REL. ST. DEVIATION (%): 6.133 RESULTS IN DECREASING ORDER: 34 0.181 20 0.160 36 0.181 23 0.160 10 0.174 12 0.158 22 0.173 15 0.155 16 0.172 3 0.153 38 0.170 32 0.152 8 0.166 33 0.150 35 0.163 39 0.150 4 0.161 24 0.149 9 0.160 31 0.137 UNUSED 19 0.160 "UNUSED": DATA UNUSED IN RUN 2	NITROGEN DIOXIDE IN ABSORBING SOL. SAMPLE NO.: 2 THEORETICAL VALUE 0.085 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 21 ARITHMETIC MEAN VALUE: 0.084 MEDIAN: 0.082 STANDARD DEVIATION: 0.005 REL. ST. DEVIATION (%): 6.442 RUN 2: NUMBER OF LABORATORIES: 21 ARITHMETIC MEAN VALUE: 0.084 MEDIAN: 0.082 STANDARD DEVIATION: 0.005 REL. ST. DEVIATION (%): 6.442 RESULTS IN DECREASING ORDER: 36 0.093 4 0.082 22 0.093 9 0.081 34 0.092 19 0.080 12 0.092 20 0.080 38 0.088 23 0.080 8 0.086 33 0.080 10 0.086 39 0.080 32 0.084 16 0.080 15 0.083 3 0.078 35 0.083 31 0.073 24 0.082 "UNUSED": DATA UNUSED IN RUN 2
NITROGEN DIOXIDE IN ABSORBING SOL. SAMPLE NO.: 3 THEORETICAL VALUE 0.149 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 21 ARITHMETIC MEAN VALUE: 0.147 MEDIAN: 0.147 STANDARD DEVIATION: 0.008 REL. ST. DEVIATION (%): 5.791 RUN 2: NUMBER OF LABORATORIES: 20 ARITHMETIC MEAN VALUE: 0.148 MEDIAN: 0.147 STANDARD DEVIATION: 0.007 REL. ST. DEVIATION (%): 5.003 RESULTS IN DECREASING ORDER: 22 0.161 19 0.146 36 0.159 24 0.143 16 0.158 32 0.141 34 0.158 9 0.140 8 0.155 20 0.140 38 0.152 23 0.140 10 0.149 33 0.140 12 0.149 39 0.140 35 0.149 3 0.139 4 0.147 31 0.127 UNUSED 15 0.147 "UNUSED": DATA UNUSED IN RUN 2	NITROGEN DIOXIDE IN ABSORBING SOL. SAMPLE NO.: 4 THEORETICAL VALUE 0.091 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 21 ARITHMETIC MEAN VALUE: 0.091 MEDIAN: 0.090 STANDARD DEVIATION: 0.006 REL. ST. DEVIATION (%): 6.538 RUN 2: NUMBER OF LABORATORIES: 19 ARITHMETIC MEAN VALUE: 0.091 MEDIAN: 0.090 STANDARD DEVIATION: 0.005 REL. ST. DEVIATION (%): 5.204 RESULTS IN DECREASING ORDER: 12 0.103 UNUSED33 0.090 22 0.101 39 0.090 36 0.097 4 0.089 34 0.096 15 0.089 24 0.094 16 0.088 8 0.094 35 0.088 38 0.094 19 0.087 10 0.091 3 0.085 32 0.091 23 0.080 9 0.090 31 0.078 UNUSED 20 0.090 "UNUSED": DATA UNUSED IN RUN 2

Table 13: The ratios of the theoretical values and the results found by the laboratories in the determination of nitrogen dioxide in absorbing solutions.

Lab. No.	<u>Theoretical value</u>				Average ratio
	Measured value				
	Sample No.				
	C1	C2	C3	C4	
3	1.06	1.08	1.07	1.07	1.07
4	1.01	1.03	1.01	1.03	1.02
8	0.98	0.98	0.96	0.97	0.97
9	1.02	1.04	1.06	1.02	1.03
10	0.93	0.98	1.00	1.00	0.98
12	1.03	0.92	1.00	0.89	0.96
15	1.05	1.02	1.01	1.03	1.03
16	0.95	1.06	0.94	1.04	1.00
19	1.02	1.06	1.02	1.05	1.04
20	1.02	1.06	1.06	1.02	1.04
22	0.94	0.91	0.93	0.90	0.92
23	1.02	1.06	1.06	1.14	1.07
24	1.09	1.03	1.04	0.97	1.03
31	1.19	1.15	1.17	1.17	1.17
32	1.07	1.01	1.06	1.01	1.03
33	1.08	1.06	1.06	1.02	1.05
34	0.90	0.92	0.94	0.95	0.93
35	1.00	1.02	1.00	1.04	1.01
36	0.90	0.91	0.94	0.94	0.92
38	0.96	0.96	0.98	0.97	0.97
39	1.08	1.06	1.06	1.02	1.05

Table 14: Analytical results of the wet chemical analysis of sulphate on synthetic filter samples (E1-5). Low concentration range. The results are corrected for the reported value for sample E5. For explanation, see Table 8.

PART. SULPHATE WET CHEMICAL METH. (LOW) SAMPLE NO.: 1 THEORETICAL VALUE 9.800 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 9.673 MEDIAN: 9.660 STANDARD DEVIATION: 0.176 REL. ST. DEVIATION (%): 1.823 RUN 2: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 9.673 MEDIAN: 9.660 STANDARD DEVIATION: 0.176 REL. ST. DEVIATION (%): 1.823 RESULTS IN DECREASING ORDER: 17 9.980 15 9.630 23 9.770 9 9.530 21 9.710 14 9.430 6 9.660 "UNUSED": DATA UNUSED IN RUN 2	PART. SULPHATE WET CHEMICAL METH. (LOW) SAMPLE NO.: 2 THEORETICAL VALUE 2.490 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 2.459 MEDIAN: 2.480 STANDARD DEVIATION: 0.157 REL. ST. DEVIATION (%): 6.403 RUN 2: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 2.459 MEDIAN: 2.480 STANDARD DEVIATION: 0.157 REL. ST. DEVIATION (%): 6.403 RESULTS IN DECREASING ORDER: 17 2.630 21 2.470 23 2.620 15 2.340 14 2.490 9 2.180 6 2.480 "UNUSED": DATA UNUSED IN RUN 2
PART. SULPHATE WET CHEMICAL METH. (LOW) SAMPLE NO.: 3 THEORETICAL VALUE 2.180 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 2.191 MEDIAN: 2.220 STANDARD DEVIATION: 0.100 REL. ST. DEVIATION (%): 4.544 RUN 2: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 2.191 MEDIAN: 2.220 STANDARD DEVIATION: 0.100 REL. ST. DEVIATION (%): 4.544 RESULTS IN DECREASING ORDER: 14 2.330 15 2.130 21 2.270 17 2.120 23 2.230 9 2.040 6 2.220 "UNUSED": DATA UNUSED IN RUN 2	PART. SULPHATE WET CHEMICAL METH. (LOW) SAMPLE NO.: 4 THEORETICAL VALUE 9.020 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 9.007 MEDIAN: 8.980 STANDARD DEVIATION: 0.227 REL. ST. DEVIATION (%): 2.525 RUN 2: NUMBER OF LABORATORIES: 7 ARITHMETIC MEAN VALUE: 9.007 MEDIAN: 8.980 STANDARD DEVIATION: 0.227 REL. ST. DEVIATION (%): 2.525 RESULTS IN DECREASING ORDER: 23 9.430 21 8.900 17 9.150 14 8.790 6 9.020 15 8.780 9 8.980 "UNUSED": DATA UNUSED IN RUN 2

Table 15: Analytical results of the wet chemical analysis of sulphate on synthetic filter samples (E1-5). High concentration range. The results are corrected for the reported value for sample E5. For explanation, see Table 8.

PART. SULPHATE WET CHEMICAL METH. (HIGH) SAMPLE NO.: 1 THEORETICAL VALUE 13.100 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 18 ARITHMETIC MEAN VALUE: 12.691 MEDIAN: 13.050 STANDARD DEVIATION: 1.822 REL. ST. DEVIATION (%): 14.355 RUN 2: NUMBER OF LABORATORIES: 17 ARITHMETIC MEAN VALUE: 13.071 MEDIAN: 13.100 STANDARD DEVIATION: 0.879 REL. ST. DEVIATION (%): 6.723 RESULTS IN DECREASING ORDER: 19 14.900 20 13.000 16 14.700 26 12.800 5 13.600 31 12.600 34 13.500 15 12.500 39 13.500 11 12.300 4 13.400 10 12.200 32 13.300 22 12.200 30 13.200 33 11.400 13 13.100 38 6.240 UNUSED "UNUSED": DATA UNUSED IN RUN 2	PART. SULPHATE WET CHEMICAL METH. (HIGH) SAMPLE NO.: 2 THEORETICAL VALUE 49.800 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 18 ARITHMETIC MEAN VALUE: 47.850 MEDIAN: 48.950 STANDARD DEVIATION: 5.464 REL. ST. DEVIATION (%): 11.419 RUN 2: NUMBER OF LABORATORIES: 17 ARITHMETIC MEAN VALUE: 48.924 MEDIAN: 49.000 STANDARD DEVIATION: 3.111 REL. ST. DEVIATION (%): 6.359 RESULTS IN DECREASING ORDER: 22 55.700 15 48.900 4 51.800 32 48.600 10 51.100 11 48.300 5 51.000 34 48.000 20 51.000 19 47.300 13 50.900 38 44.100 26 49.600 33 43.800 39 49.100 31 43.500 16 49.000 30 29.600 UNUSED "UNUSED": DATA UNUSED IN RUN 2
PART. SULPHATE WET CHEMICAL METH. (HIGH) SAMPLE NO.: 3 THEORETICAL VALUE 11.800 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 18 ARITHMETIC MEAN VALUE: 12.007 MEDIAN: 11.950 STANDARD DEVIATION: 0.917 REL. ST. DEVIATION (%): 7.636 RUN 2: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 12.025 MEDIAN: 11.950 STANDARD DEVIATION: 0.585 REL. ST. DEVIATION (%): 4.863 RESULTS IN DECREASING ORDER: 30 14.000 UNUSED 10 11.900 19 13.600 15 11.800 38 12.800 31 11.800 39 12.500 13 11.700 4 12.300 26 11.700 5 12.100 16 11.500 32 12.100 22 11.500 20 12.000 11 11.100 34 12.000 33 9.730 UNUSED "UNUSED": DATA UNUSED IN RUN 2	PART. SULPHATE WET CHEMICAL METH. (HIGH) SAMPLE NO.: 4 THEORETICAL VALUE 43.600 UNIT: UG S/FIL. RUN 1: NUMBER OF LABORATORIES: 18 ARITHMETIC MEAN VALUE: 42.450 MEDIAN: 43.000 STANDARD DEVIATION: 4.053 REL. ST. DEVIATION (%): 9.548 RUN 2: NUMBER OF LABORATORIES: 17 ARITHMETIC MEAN VALUE: 43.182 MEDIAN: 43.100 STANDARD DEVIATION: 2.682 REL. ST. DEVIATION (%): 6.212 RESULTS IN DECREASING ORDER: 22 49.400 15 42.900 4 46.000 39 42.800 32 45.100 16 42.200 20 45.000 11 42.000 5 44.800 31 41.000 10 44.600 19 40.800 13 44.100 33 38.800 34 43.200 38 38.300 26 43.100 30 30.000 UNUSED "UNUSED": DATA UNUSED IN RUN 2

Table 16: The ratios of the theoretical values to the reported values for the determination of sulphate on synthetic filters (E). The low and high concentration range are given with (L) and (H) respectively.

Lab. no. (range)	<u>Theoretical value</u>				Average ratio
	Measured value				
	Sample no.				
	E1	E2	E3	E4	
4 (H)	0.97	0.96	0.96	0.95	0.96
5 (H)	0.96	0.98	0.98	0.97	0.97
6 (L)	1.01	1.00	0.98	1.00	1.00
9 (L)	1.03	1.14	1.07	1.00	1.06
10 (H)	1.07	0.97	0.99	0.98	1.00
11 (H)	1.07	1.03	1.07	1.04	1.05
13 (H)	1.00	0.98	1.01	0.99	0.99
14 (L)	1.04	1.00	0.93	1.03	1.00
15 (L)	1.02	1.06	1.02	1.03	1.03
15 (H)	1.04	1.02	1.00	1.02	1.02
16 (H)	0.89	1.02	1.03	1.03	0.99
17 (L)	0.98	0.95	1.03	0.99	0.99
19 (H)	0.88	1.05	0.87	1.07	0.97
20 (H)	1.01	0.98	0.99	0.97	0.98
21 (L)	1.01	1.01	0.96	1.01	1.00
22 (H)	1.07	0.89	1.02	0.88	0.97
23 (L)	1.00	0.95	0.98	0.96	0.97
26 (H)	1.02	1.00	1.01	1.01	1.01
30 (H)	0.99	1.68	0.84	1.45	1.24
31 (H)	1.04	1.14	1.01	1.06	1.06
32 (H)	0.98	1.02	0.97	0.97	0.99
33 (H)	1.15	1.14	1.22	1.12	1.16
34 (H)	0.97	1.04	0.99	1.01	1.00
38 (H)	2.09	1.13	0.92	1.14	1.32
39 (H)	0.97	1.01	0.95	1.02	0.99

*Table 17: Analytical results for sulphate in synthetic precipitation samples (G).
For explanation, see Table 8.*

SULPHATE SAMPLE NO.: 1 THEORETICAL VALUE 0.936 UNIT: UG S/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.935 MEDIAN: 0.931 STANDARD DEVIATION: 0.071 REL. ST. DEVIATION (%): 7.547 RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 0.930 MEDIAN: 0.931 STANDARD DEVIATION: 0.032 REL. ST. DEVIATION (%): 3.437 RESULTS IN DECREASING ORDER: 9 1.158 UNUSED13 0.930 33 1.100 UNUSED37 0.930 32 0.996 3 0.925 7 0.977 36 0.925 39 0.971 14 0.922 38 0.970 19 0.922 30 0.960 15 0.921 6 0.950 17 0.919 21 0.949 26 0.919 23 0.945 11 0.910 5 0.941 16 0.908 27 0.940 35 0.904 10 0.938 20 0.892 34 0.937 24 0.865 4 0.933 22 0.831 31 0.933 18 0.707 UNUSED 8 0.931 "UNUSED": DATA UNUSED IN RUN 2	SULPHATE SAMPLE NO.: 2 THEORETICAL VALUE 1.930 UNIT: UG S/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 1.947 MEDIAN: 1.940 STANDARD DEVIATION: 0.097 REL. ST. DEVIATION (%): 4.998 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 1.944 MEDIAN: 1.940 STANDARD DEVIATION: 0.076 REL. ST. DEVIATION (%): 3.886 RESULTS IN DECREASING ORDER: 9 2.244 UNUSED13 1.930 24 2.114 3 1.928 38 2.090 4 1.923 20 2.062 17 1.922 32 2.042 5 1.914 7 2.027 8 1.913 33 2.000 36 1.911 34 2.000 14 1.909 21 1.992 26 1.899 22 1.977 16 1.873 6 1.970 37 1.870 35 1.959 10 1.866 27 1.950 11 1.850 31 1.950 15 1.830 39 1.950 18 1.760 23 1.940 19 1.739 UNUSED 30 1.940 "UNUSED": DATA UNUSED IN RUN 2
SULPHATE SAMPLE NO.: 3 THEORETICAL VALUE 1.000 UNIT: UG S/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 1.033 MEDIAN: 1.010 STANDARD DEVIATION: 0.098 REL. ST. DEVIATION (%): 9.514 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 1.014 MEDIAN: 1.007 STANDARD DEVIATION: 0.063 REL. ST. DEVIATION (%): 6.205 RESULTS IN DECREASING ORDER: 35 1.334 UNUSED19 1.007 33 1.330 UNUSED 4 1.004 9 1.227 8 1.001 24 1.165 13 1.000 38 1.070 39 0.995 32 1.059 26 0.993 7 1.057 14 0.992 27 1.030 15 0.989 31 1.030 16 0.981 37 1.030 11 0.980 21 1.024 22 0.978 5 1.023 36 0.972 6 1.020 20 0.967 30 1.020 17 0.965 10 1.015 3 0.963 23 1.010 18 0.848 34 1.010 "UNUSED": DATA UNUSED IN RUN 2	SULPHATE SAMPLE NO.: 4 THEORETICAL VALUE 1.730 UNIT: UG S/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 1.774 MEDIAN: 1.740 STANDARD DEVIATION: 0.173 REL. ST. DEVIATION (%): 9.748 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 1.749 MEDIAN: 1.740 STANDARD DEVIATION: 0.097 REL. ST. DEVIATION (%): 5.557 RESULTS IN DECREASING ORDER: 35 2.576 UNUSED23 1.739 9 2.046 3 1.729 11 1.890 4 1.720 20 1.876 13 1.720 24 1.868 8 1.716 7 1.842 14 1.713 38 1.840 26 1.707 32 1.832 22 1.703 34 1.800 16 1.689 39 1.800 36 1.685 21 1.792 17 1.675 6 1.760 33 1.670 30 1.760 15 1.640 27 1.750 10 1.638 37 1.750 19 1.572 5 1.741 18 1.550 31 1.740 "UNUSED": DATA UNUSED IN RUN 2

*Table 18: Analytical results for nitrate in synthetic precipitation samples (G).
For explanation, see Table 8.*

NITRATE SAMPLE NO.: 1 THEORETICAL VALUE 0.401 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.393 MEDIAN: 0.398 STANDARD DEVIATION: 0.034 REL. ST. DEVIATION (%): 8.773 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 0.398 MEDIAN: 0.398 STANDARD DEVIATION: 0.019 REL. ST. DEVIATION (%): 4.668 RESULTS IN DECREASING ORDER: 37 0.440 14 0.397 38 0.420 20 0.397 8 0.416 34 0.397 15 0.415 17 0.394 23 0.415 21 0.394 19 0.414 31 0.393 39 0.413 9 0.391 35 0.412 13 0.388 30 0.410 3 0.387 32 0.409 16 0.387 5 0.404 36 0.385 4 0.402 24 0.384 6 0.400 22 0.366 11 0.400 33 0.360 27 0.400 7 0.341 26 0.399 40 0.230 UNUSED 10 0.398 "UNUSED": DATA UNUSED IN RUN 2	NITRATE SAMPLE NO.: 2 THEORETICAL VALUE 0.858 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.849 MEDIAN: 0.858 STANDARD DEVIATION: 0.059 REL. ST. DEVIATION (%): 7.000 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.852 MEDIAN: 0.858 STANDARD DEVIATION: 0.029 REL. ST. DEVIATION (%): 3.420 RESULTS IN DECREASING ORDER: 35 1.008 UNUSED 3 0.850 38 0.920 11 0.850 4 0.886 9 0.849 23 0.875 26 0.849 8 0.872 22 0.848 34 0.872 14 0.847 6 0.870 13 0.844 27 0.870 15 0.842 37 0.870 17 0.839 21 0.868 7 0.822 39 0.868 10 0.822 32 0.867 16 0.816 20 0.866 19 0.804 5 0.865 24 0.793 31 0.865 33 0.770 30 0.860 40 0.600 UNUSED 36 0.858 "UNUSED": DATA UNUSED IN RUN 2
NITRATE SAMPLE NO.: 3 THEORETICAL VALUE 0.747 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.734 MEDIAN: 0.744 STANDARD DEVIATION: 0.048 REL. ST. DEVIATION (%): 6.564 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.744 MEDIAN: 0.746 STANDARD DEVIATION: 0.026 REL. ST. DEVIATION (%): 3.504 RESULTS IN DECREASING ORDER: 35 0.814 39 0.744 38 0.790 26 0.738 22 0.786 14 0.734 37 0.770 3 0.733 4 0.765 10 0.733 27 0.760 9 0.732 32 0.758 36 0.730 8 0.757 13 0.729 23 0.756 15 0.728 34 0.754 16 0.720 21 0.751 17 0.719 6 0.750 19 0.708 11 0.750 7 0.696 30 0.750 24 0.685 20 0.746 33 0.620 UNUSED 31 0.746 40 0.540 UNUSED 5 0.744 "UNUSED": DATA UNUSED IN RUN 2	NITRATE SAMPLE NO.: 4 THEORETICAL VALUE 0.441 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.436 MEDIAN: 0.442 STANDARD DEVIATION: 0.038 REL. ST. DEVIATION (%): 8.698 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 0.442 MEDIAN: 0.442 STANDARD DEVIATION: 0.018 REL. ST. DEVIATION (%): 4.142 RESULTS IN DECREASING ORDER: 10 0.472 26 0.442 37 0.470 6 0.440 38 0.470 7 0.440 11 0.460 27 0.440 8 0.456 31 0.438 20 0.456 21 0.436 39 0.456 15 0.434 19 0.451 3 0.432 22 0.450 9 0.431 23 0.450 17 0.428 30 0.450 13 0.427 4 0.448 36 0.424 32 0.448 16 0.422 34 0.445 24 0.406 35 0.445 33 0.380 5 0.443 40 0.250 UNUSED 14 0.442 "UNUSED": DATA UNUSED IN RUN 2

*Table 19: Analytical results for ammonium in synthetic precipitation samples (G).
For explanation, see Table 8.*

AMMONIUM SAMPLE NO.: 1 THEORETICAL VALUE 0.281 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 0.277 MEDIAN: 0.280 STANDARD DEVIATION: 0.022 REL. ST. DEVIATION (%): 8.105 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.279 MEDIAN: 0.280 STANDARD DEVIATION: 0.015 REL. ST. DEVIATION (%): 5.469 RESULTS IN DECREASING ORDER: 11 0.330 UNUSED 6 0.280 31 0.319 7 0.276 32 0.310 8 0.275 10 0.306 16 0.274 30 0.290 39 0.274 38 0.290 4 0.273 36 0.289 27 0.270 15 0.288 37 0.270 17 0.288 20 0.269 21 0.286 23 0.269 26 0.284 14 0.268 19 0.282 9 0.264 35 0.282 33 0.260 13 0.281 22 0.259 18 0.281 40 0.240 34 0.281 24 0.226 UNUSED 5 0.280 3 0.213 UNUSED "UNUSED": DATA UNUSED IN RUN 2	AMMONIUM SAMPLE NO.: 2 THEORETICAL VALUE 0.561 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 0.563 MEDIAN: 0.568 STANDARD DEVIATION: 0.027 REL. ST. DEVIATION (%): 4.743 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 0.564 MEDIAN: 0.568 STANDARD DEVIATION: 0.022 REL. ST. DEVIATION (%): 3.944 RESULTS IN DECREASING ORDER: 10 0.618 UNUSED 4 0.567 31 0.609 18 0.566 32 0.606 13 0.562 6 0.590 34 0.560 19 0.583 37 0.560 24 0.583 8 0.558 26 0.582 7 0.551 5 0.580 39 0.549 30 0.580 23 0.547 38 0.580 27 0.540 17 0.579 33 0.540 16 0.577 14 0.534 35 0.572 20 0.534 36 0.572 40 0.530 11 0.570 22 0.526 21 0.570 9 0.518 15 0.569 3 0.491 UNUSED "UNUSED": DATA UNUSED IN RUN 2
AMMONIUM SAMPLE NO.: 3 THEORETICAL VALUE 0.481 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 0.484 MEDIAN: 0.482 STANDARD DEVIATION: 0.028 REL. ST. DEVIATION (%): 5.810 RUN 2: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.481 MEDIAN: 0.480 STANDARD DEVIATION: 0.022 REL. ST. DEVIATION (%): 4.490 RESULTS IN DECREASING ORDER: 31 0.588 UNUSED13 0.480 10 0.527 37 0.480 32 0.521 14 0.479 24 0.513 8 0.478 11 0.510 16 0.477 38 0.500 7 0.473 5 0.497 23 0.469 9 0.493 34 0.468 17 0.493 39 0.468 21 0.492 20 0.467 30 0.490 18 0.466 36 0.490 22 0.466 19 0.489 27 0.460 4 0.487 33 0.460 26 0.487 6 0.450 15 0.486 3 0.433 35 0.484 40 0.430 "UNUSED": DATA UNUSED IN RUN 2	AMMONIUM SAMPLE NO.: 4 THEORETICAL VALUE 0.241 UNIT: UG N/ML RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 0.244 MEDIAN: 0.244 STANDARD DEVIATION: 0.019 REL. ST. DEVIATION (%): 7.641 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 0.245 MEDIAN: 0.244 STANDARD DEVIATION: 0.015 REL. ST. DEVIATION (%): 6.252 RESULTS IN DECREASING ORDER: 31 0.287 UNUSED21 0.243 11 0.270 34 0.243 18 0.268 22 0.240 32 0.267 27 0.240 10 0.264 7 0.239 19 0.264 9 0.237 6 0.260 23 0.237 38 0.260 35 0.237 17 0.258 4 0.236 16 0.257 20 0.231 15 0.254 33 0.230 30 0.250 39 0.230 37 0.250 8 0.225 36 0.248 14 0.221 5 0.247 40 0.220 26 0.247 3 0.208 13 0.245 24 0.195 UNUSED "UNUSED": DATA UNUSED IN RUN 2

*Table 20: Analytical results for pH in synthetic precipitation samples (G).
For explanation, see Table 8.*

PH SAMPLE NO.: 1 THEORETICAL VALUE 4.520 UNIT: PH UNITS RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 4.589 MEDIAN: 4.590 STANDARD DEVIATION: 0.063 REL. ST. DEVIATION (%): 1.376 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 4.590 MEDIAN: 4.590 STANDARD DEVIATION: 0.051 REL. ST. DEVIATION (%): 1.109 RESULTS IN DECREASING ORDER: 19 4.740 UNUSED30 4.590 13 4.690 18 4.580 36 4.680 23 4.580 22 4.660 27 4.580 8 4.650 35 4.580 40 4.650 15 4.550 10 4.640 3 4.547 26 4.640 7 4.540 14 4.630 17 4.540 24 4.620 38 4.540 32 4.620 9 4.530 37 4.620 31 4.530 33 4.610 16 4.520 39 4.610 20 4.520 4 4.600 5 4.519 6 4.600 21 4.510 11 4.590 34 4.420 UNUSED "UNUSED": DATA UNUSED IN RUN 2	PH SAMPLE NO.: 2 THEORETICAL VALUE 4.050 UNIT: PH UNITS RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 4.090 MEDIAN: 4.090 STANDARD DEVIATION: 0.045 REL. ST. DEVIATION (%): 1.110 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 4.098 MEDIAN: 4.095 STANDARD DEVIATION: 0.031 REL. ST. DEVIATION (%): 0.766 RESULTS IN DECREASING ORDER: 19 4.170 17 4.090 10 4.160 24 4.090 8 4.140 32 4.090 11 4.140 38 4.090 30 4.140 3 4.085 6 4.120 7 4.080 23 4.120 9 4.070 37 4.120 16 4.070 4 4.110 26 4.070 22 4.110 39 4.070 27 4.110 18 4.060 33 4.110 31 4.060 35 4.110 5 4.059 40 4.110 20 4.050 15 4.100 21 4.040 36 4.100 13 3.990 UNUSED 14 4.090 34 3.930 UNUSED "UNUSED": DATA UNUSED IN RUN 2
PH SAMPLE NO.: 3 THEORETICAL VALUE 4.590 UNIT: PH UNITS RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 4.624 MEDIAN: 4.630 STANDARD DEVIATION: 0.092 REL. ST. DEVIATION (%): 1.985 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 4.620 MEDIAN: 4.630 STANDARD DEVIATION: 0.054 REL. ST. DEVIATION (%): 1.160 RESULTS IN DECREASING ORDER: 39 4.990 UNUSED15 4.630 19 4.730 27 4.630 40 4.710 33 4.620 10 4.690 11 4.610 24 4.690 35 4.610 22 4.680 9 4.600 30 4.660 5 4.590 14 4.650 38 4.590 17 4.650 18 4.570 4 4.640 26 4.570 6 4.640 16 4.560 8 4.640 20 4.560 23 4.640 21 4.560 36 4.640 32 4.560 37 4.640 31 4.550 3 4.630 13 4.470 7 4.630 34 4.390 UNUSED "UNUSED": DATA UNUSED IN RUN 2	PH SAMPLE NO.: 4 THEORETICAL VALUE 4.090 UNIT: PH UNITS RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 4.122 MEDIAN: 4.125 STANDARD DEVIATION: 0.049 REL. ST. DEVIATION (%): 1.199 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 4.132 MEDIAN: 4.130 STANDARD DEVIATION: 0.030 REL. ST. DEVIATION (%): 0.723 RESULTS IN DECREASING ORDER: 19 4.200 7 4.120 24 4.190 9 4.120 10 4.170 11 4.120 36 4.170 17 4.120 8 4.160 40 4.120 22 4.160 3 4.115 23 4.160 14 4.110 4 4.150 18 4.110 27 4.150 32 4.110 30 4.150 16 4.100 37 4.150 5 4.098 38 4.150 20 4.090 6 4.140 26 4.090 33 4.140 31 4.090 15 4.130 21 4.080 35 4.130 13 3.980 UNUSED 39 4.130 34 3.950 UNUSED "UNUSED": DATA UNUSED IN RUN 2

Table 21: Analytical results for strong acid calculated from pH in synthetic precipitation samples (G). For explanation, see Table 8.

STRONG ACID CALCULATED FROM PH SAMPLE NO.: 1 THEORETICAL VALUE 30.000 UNIT: UEQ/L RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 26.032 MEDIAN: 25.700 STANDARD DEVIATION: 3.866 REL. ST. DEVIATION (%): 14.851 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 25.894 MEDIAN: 25.700 STANDARD DEVIATION: 3.010 REL. ST. DEVIATION (%): 11.623 RESULTS IN DECREASING ORDER: 34 38.300 UNUSED30 25.700 21 30.900 4 25.100 5 30.300 6 25.100 16 30.200 33 24.500 20 30.200 39 24.500 9 29.500 24 24.000 31 29.500 32 24.000 7 28.800 37 24.000 17 28.800 14 23.400 38 28.800 10 22.900 3 28.400 26 22.900 15 28.200 8 22.400 18 26.300 40 22.400 23 26.300 22 21.900 27 26.300 36 20.900 35 26.300 13 20.400 11 25.700 19 18.200 UNUSED "UNUSED": DATA UNUSED IN RUN 2	STRONG ACID CALCULATED FROM PH SAMPLE NO.: 2 THEORETICAL VALUE 90.000 UNIT: UEQ/L RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 81.771 MEDIAN: 81.300 STANDARD DEVIATION: 9.133 REL. ST. DEVIATION (%): 11.169 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 80.031 MEDIAN: 80.350 STANDARD DEVIATION: 5.680 REL. ST. DEVIATION (%): 7.097 RESULTS IN DECREASING ORDER: 34 116.900 UNUSED38 81.300 13 102.300 UNUSED15 79.400 21 91.200 36 79.400 20 89.100 4 77.600 5 87.300 22 77.600 18 87.100 27 77.600 31 87.100 33 77.600 9 85.100 35 77.600 16 85.100 40 77.600 26 85.100 6 75.900 39 85.100 23 75.900 7 83.200 37 75.900 3 82.200 8 72.400 14 81.300 11 72.400 17 81.300 30 72.400 24 81.300 10 69.200 32 81.300 19 68.400 "UNUSED": DATA UNUSED IN RUN 2
STRONG ACID CALCULATED FROM PH SAMPLE NO.: 3 THEORETICAL VALUE 26.000 UNIT: UEQ/L RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 24.232 MEDIAN: 23.400 STANDARD DEVIATION: 4.822 REL. ST. DEVIATION (%): 19.901 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 23.835 MEDIAN: 23.400 STANDARD DEVIATION: 2.545 REL. ST. DEVIATION (%): 10.679 RESULTS IN DECREASING ORDER: 34 40.900 UNUSED15 23.400 13 33.900 UNUSED27 23.400 31 28.200 4 22.900 16 27.500 6 22.900 20 27.500 8 22.900 21 27.500 23 22.900 32 27.500 36 22.900 18 26.900 37 22.900 26 26.900 14 22.400 5 25.700 17 22.400 38 25.700 30 21.900 9 25.100 22 20.900 11 24.500 10 20.400 35 24.500 24 20.400 33 24.000 40 19.500 3 23.400 19 18.500 7 23.400 39 10.200 UNUSED "UNUSED": DATA UNUSED IN RUN 2	STRONG ACID CALCULATED FROM PH SAMPLE NO.: 4 THEORETICAL VALUE 82.000 UNIT: UEQ/L RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 76.018 MEDIAN: 75.000 STANDARD DEVIATION: 9.663 REL. ST. DEVIATION (%): 12.712 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 73.975 MEDIAN: 74.100 STANDARD DEVIATION: 5.015 REL. ST. DEVIATION (%): 6.779 RESULTS IN DECREASING ORDER: 34 112.700 UNUSED15 74.100 13 104.700 UNUSED35 74.100 21 83.200 39 74.100 20 81.300 6 72.400 26 81.300 33 72.400 31 81.300 4 70.800 5 79.800 27 70.800 16 79.400 30 70.800 14 77.600 37 70.800 18 77.600 38 70.800 32 77.600 8 69.200 3 76.700 22 69.200 7 75.900 23 69.200 9 75.900 10 67.600 11 75.900 36 67.600 17 75.900 24 64.600 40 75.900 19 63.400 "UNUSED": DATA UNUSED IN RUN 2

Table 22: Analytical results for titrated strong acid in synthetic precipitation samples (G). For explanation, see Table 8.

STRONG ACIDS SAMPLE NO.: 1 THEORETICAL VALUE 30. UNIT: UEQ RUN 1: NUMBER OF LABORATORIES: 2 ARITHMETIC MEAN VALUE: 31.150 MEDIAN: 31.150 STANDARD DEVIATION: 1.202 REL. ST. DEVIATION (%): 3.859 RUN 2: NUMBER OF LABORATORIES: 2 ARITHMETIC MEAN VALUE: 31.150 MEDIAN: 31.150 STANDARD DEVIATION: 1.202 REL. ST. DEVIATION (%): 3.859 RESULTS IN DECREASING ORDER: 6 32.000 14 30.300 "UNUSED": DATA UNUSED IN RUN 2	STRONG ACIDS SAMPLE NO.: 2 THEORETICAL VALUE 90. UNIT: UEQ RUN 1: NUMBER OF LABORATORIES: 2 ARITHMETIC MEAN VALUE: 90.400 MEDIAN: 90.400 STANDARD DEVIATION: 2.263 REL. ST. DEVIATION (%): 2.503 RUN 2: NUMBER OF LABORATORIES: 2 ARITHMETIC MEAN VALUE: 90.400 MEDIAN: 90.400 STANDARD DEVIATION: 2.263 REL. ST. DEVIATION (%): 2.503 RESULTS IN DECREASING ORDER: 6 92.000 14 88.800 "UNUSED": DATA UNUSED IN RUN 2
STRONG ACIDS SAMPLE NO.: 3 THEORETICAL VALUE 26. UNIT: UEQ RUN 1: NUMBER OF LABORATORIES: 2 ARITHMETIC MEAN VALUE: 25.700 MEDIAN: 25.700 STANDARD DEVIATION: 2.404 REL. ST. DEVIATION (%): 9.355 RUN 2: NUMBER OF LABORATORIES: 2 ARITHMETIC MEAN VALUE: 25.700 MEDIAN: 25.700 STANDARD DEVIATION: 2.404 REL. ST. DEVIATION (%): 9.355 RESULTS IN DECREASING ORDER: 14 27.400 6 24.000 "UNUSED": DATA UNUSED IN RUN 2	STRONG ACIDS SAMPLE NO.: 4 THEORETICAL VALUE 82. UNIT: UEQ RUN 1: NUMBER OF LABORATORIES: 2 ARITHMETIC MEAN VALUE: 81.600 MEDIAN: 81.600 STANDARD DEVIATION: 3.394 REL. ST. DEVIATION (%): 4.160 RUN 2: NUMBER OF LABORATORIES: 2 ARITHMETIC MEAN VALUE: 81.600 MEDIAN: 81.600 STANDARD DEVIATION: 3.394 REL. ST. DEVIATION (%): 4.160 RESULTS IN DECREASING ORDER: 6 84.000 14 79.200 "UNUSED": DATA UNUSED IN RUN 2

*Table 23: Analytical results for chloride in synthetic precipitation samples (G).
For explanation, see Table 8.*

CHLORIDE SAMPLE NO.: 1 THEORETICAL VALUE 0.232 UNIT: UG CL/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.248 MEDIAN: 0.223 STANDARD DEVIATION: 0.083 REL. ST. DEVIATION (%): 33.369 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.231 MEDIAN: 0.221 STANDARD DEVIATION: 0.047 REL. ST. DEVIATION (%): 20.279 RESULTS IN DECREASING ORDER: 19 0.523 UNUSED 4 0.221 33 0.510 UNUSED 7 0.221 23 0.393 8 0.220 24 0.323 10 0.218 22 0.313 14 0.217 35 0.297 15 0.216 11 0.260 20 0.207 16 0.259 3 0.206 31 0.238 6 0.200 34 0.238 9 0.196 13 0.236 17 0.194 32 0.232 39 0.190 21 0.231 18 0.189 27 0.230 37 0.180 5 0.228 38 0.180 26 0.226 30 0.170 36 0.223 "UNUSED": DATA UNUSED IN RUN 2	CHLORIDE SAMPLE NO.: 2 THEORETICAL VALUE 0.579 UNIT: UG CL/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.579 MEDIAN: 0.564 STANDARD DEVIATION: 0.072 REL. ST. DEVIATION (%): 12.396 RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 0.574 MEDIAN: 0.564 STANDARD DEVIATION: 0.047 REL. ST. DEVIATION (%): 8.149 RESULTS IN DECREASING ORDER: 19 0.777 UNUSED16 0.564 24 0.726 UNUSED14 0.562 33 0.700 22 0.560 23 0.668 17 0.559 9 0.650 31 0.556 34 0.619 4 0.552 13 0.609 20 0.551 18 0.603 11 0.550 36 0.599 3 0.547 35 0.593 15 0.547 6 0.590 38 0.540 27 0.590 8 0.530 26 0.587 30 0.530 5 0.574 10 0.523 32 0.573 37 0.450 21 0.572 39 0.380 UNUSED 7 0.564 "UNUSED": DATA UNUSED IN RUN 2
CHLORIDE SAMPLE NO.: 3 THEORETICAL VALUE 0.695 UNIT: UG CL/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.696 MEDIAN: 0.677 STANDARD DEVIATION: 0.078 REL. ST. DEVIATION (%): 11.180 RUN 2: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 0.684 MEDIAN: 0.676 STANDARD DEVIATION: 0.053 REL. ST. DEVIATION (%): 7.715 RESULTS IN DECREASING ORDER: 22 0.871 UNUSED 7 0.676 24 0.862 UNUSED14 0.674 19 0.857 UNUSED18 0.674 33 0.820 36 0.674 11 0.790 30 0.670 35 0.776 16 0.666 23 0.770 31 0.662 34 0.721 4 0.660 27 0.700 20 0.657 13 0.698 6 0.650 26 0.697 10 0.645 5 0.695 9 0.640 15 0.685 17 0.638 32 0.685 8 0.630 21 0.684 39 0.550 38 0.680 37 0.530 UNUSED 3 0.677 "UNUSED": DATA UNUSED IN RUN 2	CHLORIDE SAMPLE NO.: 4 THEORETICAL VALUE 0.290 UNIT: UG CL/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.293 MEDIAN: 0.282 STANDARD DEVIATION: 0.066 REL. ST. DEVIATION (%): 22.547 RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 0.274 MEDIAN: 0.277 STANDARD DEVIATION: 0.023 REL. ST. DEVIATION (%): 8.254 RESULTS IN DECREASING ORDER: 19 0.567 UNUSED 8 0.280 24 0.436 UNUSED35 0.274 23 0.430 UNUSED14 0.272 13 0.315 36 0.268 38 0.310 31 0.265 16 0.308 17 0.262 27 0.300 3 0.261 33 0.300 6 0.260 34 0.300 11 0.260 21 0.290 9 0.259 32 0.288 15 0.259 5 0.287 18 0.250 26 0.286 10 0.247 7 0.284 37 0.240 4 0.283 30 0.230 20 0.282 39 0.230 22 0.282 "UNUSED": DATA UNUSED IN RUN 2

*Table 24: Analytical results for sodium in synthetic precipitation samples (G).
For explanation, see Table 8.*

SODIUM SAMPLE NO.: 1 THEORETICAL VALUE 0.258 UNIT: UG NA/ML RUN 1: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 0.250 MEDIAN: 0.254 STANDARD DEVIATION: 0.029 REL. ST. DEVIATION (%): 11.643 RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 0.255 MEDIAN: 0.257 STANDARD DEVIATION: 0.021 REL. ST. DEVIATION (%): 8.346 RESULTS IN DECREASING ORDER: 19 0.295 26 0.253 24 0.294 3 0.252 20 0.282 31 0.251 22 0.279 6 0.250 36 0.274 8 0.250 4 0.270 10 0.250 34 0.267 32 0.250 27 0.265 7 0.249 39 0.264 23 0.246 5 0.261 33 0.243 13 0.261 16 0.240 30 0.260 17 0.210 15 0.259 37 0.210 14 0.258 38 0.200 21 0.258 9 0.191 UNUSED 35 0.255 40 0.156 UNUSED "UNUSED": DATA UNUSED IN RUN 2	SODIUM SAMPLE NO.: 2 THEORETICAL VALUE 0.698 UNIT: UG NA/ML RUN 1: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 0.693 MEDIAN: 0.696 STANDARD DEVIATION: 0.036 REL. ST. DEVIATION (%): 5.121 RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 0.700 MEDIAN: 0.696 STANDARD DEVIATION: 0.024 REL. ST. DEVIATION (%): 3.357 RESULTS IN DECREASING ORDER: 19 0.757 13 0.695 30 0.750 7 0.694 32 0.750 15 0.694 34 0.724 24 0.694 36 0.721 26 0.694 6 0.710 20 0.693 35 0.710 27 0.691 31 0.709 3 0.687 5 0.706 23 0.680 14 0.706 38 0.680 39 0.704 22 0.678 10 0.702 37 0.670 4 0.700 9 0.657 8 0.700 33 0.657 16 0.696 17 0.610 UNUSED 21 0.696 40 0.572 UNUSED "UNUSED": DATA UNUSED IN RUN 2
SODIUM SAMPLE NO.: 3 THEORETICAL VALUE 0.827 UNIT: UG NA/ML RUN 1: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 0.814 MEDIAN: 0.824 STANDARD DEVIATION: 0.044 REL. ST. DEVIATION (%): 5.420 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.821 MEDIAN: 0.825 STANDARD DEVIATION: 0.027 REL. ST. DEVIATION (%): 3.313 RESULTS IN DECREASING ORDER: 19 0.866 3 0.824 30 0.860 15 0.822 36 0.856 7 0.821 37 0.850 4 0.820 21 0.845 6 0.820 13 0.840 32 0.820 5 0.839 22 0.817 34 0.835 38 0.810 8 0.830 23 0.805 35 0.830 9 0.804 39 0.829 20 0.791 31 0.828 16 0.789 14 0.826 24 0.783 27 0.826 33 0.778 10 0.825 17 0.727 26 0.825 40 0.622 UNUSED "UNUSED": DATA UNUSED IN RUN 2	SODIUM SAMPLE NO.: 4 THEORETICAL VALUE 0.322 UNIT: UG NA/ML RUN 1: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 0.314 MEDIAN: 0.322 STANDARD DEVIATION: 0.027 REL. ST. DEVIATION (%): 8.597 RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 0.319 MEDIAN: 0.324 STANDARD DEVIATION: 0.020 REL. ST. DEVIATION (%): 6.177 RESULTS IN DECREASING ORDER: 19 0.360 14 0.321 34 0.342 21 0.321 4 0.340 37 0.320 30 0.340 31 0.314 24 0.338 7 0.313 36 0.337 23 0.309 27 0.332 16 0.308 6 0.330 10 0.306 13 0.330 8 0.300 20 0.327 33 0.293 39 0.327 17 0.289 5 0.326 22 0.285 15 0.326 32 0.280 3 0.325 9 0.278 26 0.324 38 0.260 UNUSED 35 0.323 40 0.226 UNUSED "UNUSED": DATA UNUSED IN RUN 2

*Table 25: Analytical results for magnesium in synthetic precipitation samples (G).
For explanation, see Table 8.*

MAGNESIUM SAMPLE NO.: 1 THEORETICAL VALUE 0.124 UNIT: UG MG/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.123 MEDIAN: 0.123 STANDARD DEVIATION: 0.015 REL. ST. DEVIATION (%): 12.134 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.123 MEDIAN: 0.123 STANDARD DEVIATION: 0.012 REL. ST. DEVIATION (%): 9.542 RESULTS IN DECREASING ORDER: 23 0.164 UNUSED36 0.123 38 0.150 31 0.122 24 0.145 3 0.121 20 0.138 27 0.120 16 0.136 34 0.119 21 0.132 7 0.118 6 0.130 33 0.118 8 0.130 22 0.117 13 0.130 14 0.116 30 0.130 35 0.115 10 0.129 4 0.110 17 0.129 9 0.110 15 0.126 11 0.100 5 0.125 18 0.100 39 0.124 37 0.100 19 0.123 40 0.087 UNUSED 26 0.123 "UNUSED": DATA UNUSED IN RUN 2	MAGNESIUM SAMPLE NO.: 2 THEORETICAL VALUE 0.217 UNIT: UG MG/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.218 MEDIAN: 0.218 STANDARD DEVIATION: 0.017 REL. ST. DEVIATION (%): 7.631 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.218 MEDIAN: 0.218 STANDARD DEVIATION: 0.013 REL. ST. DEVIATION (%): 5.950 RESULTS IN DECREASING ORDER: 38 0.270 UNUSED22 0.218 24 0.251 39 0.217 18 0.240 10 0.216 23 0.233 16 0.216 9 0.230 19 0.216 30 0.230 3 0.214 31 0.227 26 0.214 34 0.227 36 0.212 17 0.226 7 0.210 20 0.222 27 0.207 21 0.222 35 0.204 5 0.220 4 0.200 6 0.220 11 0.200 8 0.220 33 0.190 14 0.219 37 0.190 13 0.218 40 0.184 UNUSED 15 0.218 "UNUSED": DATA UNUSED IN RUN 2
MAGNESIUM SAMPLE NO.: 3 THEORETICAL VALUE 0.201 UNIT: UG MG/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.204 MEDIAN: 0.202 STANDARD DEVIATION: 0.021 REL. ST. DEVIATION (%): 10.355 RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 0.202 MEDIAN: 0.201 STANDARD DEVIATION: 0.013 REL. ST. DEVIATION (%): 6.611 RESULTS IN DECREASING ORDER: 23 0.272 UNUSED36 0.201 38 0.250 UNUSED 7 0.200 30 0.230 8 0.200 24 0.223 18 0.200 9 0.221 19 0.199 20 0.218 31 0.199 21 0.218 16 0.197 13 0.214 3 0.196 6 0.210 27 0.194 34 0.208 22 0.192 17 0.206 35 0.189 5 0.205 33 0.183 15 0.205 4 0.180 10 0.203 11 0.180 14 0.202 37 0.170 26 0.202 40 0.157 UNUSED 39 0.202 "UNUSED": DATA UNUSED IN RUN 2	MAGNESIUM SAMPLE NO.: 4 THEORETICAL VALUE 0.139 UNIT: UG MG/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.140 MEDIAN: 0.140 STANDARD DEVIATION: 0.011 REL. ST. DEVIATION (%): 8.002 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.140 MEDIAN: 0.140 STANDARD DEVIATION: 0.009 REL. ST. DEVIATION (%): 6.254 RESULTS IN DECREASING ORDER: 38 0.170 UNUSED26 0.140 18 0.160 30 0.140 24 0.160 10 0.139 34 0.157 19 0.138 8 0.150 36 0.137 23 0.149 3 0.136 20 0.146 9 0.135 31 0.146 14 0.135 16 0.144 27 0.135 15 0.143 22 0.132 17 0.143 7 0.131 21 0.143 35 0.131 33 0.142 4 0.130 5 0.141 37 0.130 13 0.141 11 0.120 39 0.141 40 0.111 UNUSED 6 0.140 "UNUSED": DATA UNUSED IN RUN 2

*Table 26: Analytical results for calcium in synthetic precipitation samples (G).
For explanation, see Table 8.*

CALCIUM SAMPLE NO.: 1 THEORETICAL VALUE 0.364 UNIT: UG CA/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.379 MEDIAN: 0.370 STANDARD DEVIATION: 0.067 REL. ST. DEVIATION (%): 17.641 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.368 MEDIAN: 0.370 STANDARD DEVIATION: 0.052 REL. ST. DEVIATION (%): 14.105 RESULTS IN DECREASING ORDER: 23 0.560 UNUSED38 0.370 40 0.538 UNUSED34 0.366 30 0.510 15 0.365 20 0.454 24 0.361 22 0.450 39 0.361 8 0.430 11 0.360 13 0.408 17 0.359 6 0.390 7 0.358 21 0.387 31 0.353 36 0.384 26 0.349 19 0.380 3 0.347 14 0.374 16 0.328 5 0.373 35 0.293 27 0.372 9 0.290 4 0.370 37 0.260 10 0.370 33 0.253 32 0.370 "UNUSED": DATA UNUSED IN RUN 2	CALCIUM SAMPLE NO.: 2 THEORETICAL VALUE 0.249 UNIT: UG CA/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.251 MEDIAN: 0.259 STANDARD DEVIATION: 0.028 REL. ST. DEVIATION (%): 11.302 RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 0.258 MEDIAN: 0.260 STANDARD DEVIATION: 0.019 REL. ST. DEVIATION (%): 7.310 RESULTS IN DECREASING ORDER: 20 0.295 14 0.255 30 0.290 5 0.253 40 0.289 8 0.250 10 0.275 15 0.250 34 0.275 16 0.249 19 0.273 27 0.247 23 0.272 22 0.245 24 0.270 26 0.241 31 0.267 38 0.240 36 0.266 21 0.233 13 0.264 7 0.228 3 0.262 33 0.223 4 0.260 9 0.217 6 0.260 32 0.190 UNUSED 11 0.260 35 0.189 UNUSED 39 0.260 37 0.170 UNUSED 17 0.259 "UNUSED": DATA UNUSED IN RUN 2
CALCIUM SAMPLE NO.: 3 THEORETICAL VALUE 0.402 UNIT: UG CA/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.410 MEDIAN: 0.410 STANDARD DEVIATION: 0.066 REL. ST. DEVIATION (%): 16.100 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.398 MEDIAN: 0.402 STANDARD DEVIATION: 0.047 REL. ST. DEVIATION (%): 11.888 RESULTS IN DECREASING ORDER: 23 0.623 UNUSED27 0.402 30 0.560 UNUSED10 0.401 22 0.490 26 0.401 20 0.485 8 0.400 13 0.461 39 0.396 7 0.451 3 0.393 21 0.433 4 0.390 36 0.429 31 0.389 11 0.420 24 0.388 17 0.420 16 0.358 40 0.420 32 0.350 14 0.419 9 0.345 15 0.417 38 0.330 5 0.413 35 0.321 19 0.413 37 0.310 6 0.410 33 0.280 34 0.410 "UNUSED": DATA UNUSED IN RUN 2	CALCIUM SAMPLE NO.: 4 THEORETICAL VALUE 0.287 UNIT: UG CA/ML RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.284 MEDIAN: 0.290 STANDARD DEVIATION: 0.036 REL. ST. DEVIATION (%): 12.669 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.289 MEDIAN: 0.290 STANDARD DEVIATION: 0.030 REL. ST. DEVIATION (%): 10.247 RESULTS IN DECREASING ORDER: 20 0.355 26 0.288 30 0.330 31 0.288 23 0.328 15 0.287 34 0.321 16 0.287 19 0.312 27 0.286 38 0.310 10 0.285 22 0.307 39 0.285 5 0.305 21 0.273 36 0.305 24 0.267 17 0.304 3 0.263 13 0.303 7 0.263 8 0.300 35 0.231 14 0.294 9 0.219 4 0.290 33 0.218 6 0.290 32 0.200 UNUSED 11 0.290 37 0.200 UNUSED 40 0.290 "UNUSED": DATA UNUSED IN RUN 2

*Table 27: Analytical results for potassium in synthetic precipitation samples (G).
For explanation, see Table 8.*

POTASSIUM SAMPLE NO.: 1 THEORETICAL VALUE 0.153 UNIT: UG K/ML RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 0.161 MEDIAN: 0.150 STANDARD DEVIATION: 0.048 REL. ST. DEVIATION (%): 29.511 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 0.151 MEDIAN: 0.150 STANDARD DEVIATION: 0.022 REL. ST. DEVIATION (%): 14.435 RESULTS IN DECREASING ORDER: 40 0.350 UNUSED 6 0.150 18 0.306 UNUSED 13 0.150 20 0.227 32 0.150 31 0.210 3 0.148 35 0.168 16 0.146 14 0.164 33 0.144 19 0.164 8 0.140 30 0.160 11 0.140 22 0.159 38 0.140 7 0.158 23 0.139 27 0.155 17 0.137 36 0.155 21 0.137 15 0.154 10 0.132 39 0.153 37 0.130 26 0.152 24 0.128 34 0.152 4 0.120 5 0.150 9 0.115 "UNUSED": DATA UNUSED IN RUN 2	POTASSIUM SAMPLE NO.: 2 THEORETICAL VALUE 0.280 UNIT: UG K/ML RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 0.290 MEDIAN: 0.277 STANDARD DEVIATION: 0.059 REL. ST. DEVIATION (%): 20.471 RUN 2: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 0.281 MEDIAN: 0.277 STANDARD DEVIATION: 0.029 REL. ST. DEVIATION (%): 10.143 RESULTS IN DECREASING ORDER: 18 0.586 UNUSED 34 0.277 31 0.390 36 0.275 40 0.351 3 0.272 20 0.319 7 0.272 35 0.305 11 0.270 22 0.304 23 0.269 19 0.292 33 0.268 30 0.290 9 0.266 32 0.290 5 0.264 37 0.290 16 0.262 14 0.285 24 0.261 6 0.280 8 0.260 27 0.280 17 0.260 15 0.278 38 0.260 39 0.278 10 0.257 13 0.277 21 0.254 26 0.277 4 0.240 "UNUSED": DATA UNUSED IN RUN 2
POTASSIUM SAMPLE NO.: 3 THEORETICAL VALUE 0.102 UNIT: UG K/ML RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 0.106 MEDIAN: 0.101 STANDARD DEVIATION: 0.034 REL. ST. DEVIATION (%): 32.406 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.104 MEDIAN: 0.100 STANDARD DEVIATION: 0.022 REL. ST. DEVIATION (%): 21.513 RESULTS IN DECREASING ORDER: 40 0.196 UNUSED 24 0.100 18 0.187 UNUSED 32 0.100 20 0.171 33 0.100 31 0.168 38 0.100 22 0.143 36 0.097 35 0.123 5 0.096 19 0.111 21 0.096 30 0.110 9 0.094 37 0.110 7 0.093 16 0.106 23 0.091 26 0.105 6 0.090 13 0.104 17 0.084 15 0.103 4 0.080 27 0.103 8 0.080 34 0.103 10 0.075 39 0.103 14 0.071 3 0.102 11 0.010 UNUSED "UNUSED": DATA UNUSED IN RUN 2	POTASSIUM SAMPLE NO.: 4 THEORETICAL VALUE 0.331 UNIT: UG K/ML RUN 1: NUMBER OF LABORATORIES: 34 ARITHMETIC MEAN VALUE: 0.328 MEDIAN: 0.321 STANDARD DEVIATION: 0.089 REL. ST. DEVIATION (%): 27.071 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 0.326 MEDIAN: 0.321 STANDARD DEVIATION: 0.040 REL. ST. DEVIATION (%): 12.113 RESULTS IN DECREASING ORDER: 18 0.681 UNUSED 34 0.321 40 0.495 6 0.320 31 0.377 33 0.318 20 0.371 5 0.317 35 0.356 17 0.316 19 0.343 3 0.312 36 0.343 4 0.310 30 0.340 32 0.310 37 0.340 16 0.305 27 0.335 22 0.305 15 0.331 9 0.300 39 0.330 38 0.300 13 0.329 10 0.293 26 0.327 24 0.289 14 0.325 21 0.285 23 0.323 8 0.250 7 0.321 11 0.033 UNUSED "UNUSED": DATA UNUSED IN RUN 2

Table 28: Analytical results for conductivity in synthetic precipitation samples (G). For explanation, see Table 8.

CONDUCTIVITY SAMPLE NO.: 1 THEORETICAL VALUE 21.600 UNIT: US/CM RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 21.464 MEDIAN: 21.400 STANDARD DEVIATION: 3.636 REL. ST. DEVIATION (%): 16.942 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 20.923 MEDIAN: 21.200 STANDARD DEVIATION: 1.926 REL. ST. DEVIATION (%): 9.204 RESULTS IN DECREASING ORDER: 17 38.750 UNUSED 8 21.000 23 25.000 13 21.000 39 24.000 16 21.000 30 23.130 20 21.000 3 22.510 34 20.900 15 22.300 35 20.840 22 22.200 32 20.800 24 22.000 9 20.700 27 21.900 19 20.520 18 21.870 7 20.100 21 21.790 11 19.200 5 21.700 36 18.780 37 21.700 6 17.600 14 21.500 40 17.300 10 21.410 33 16.800 4 21.400 38 16.200 31 21.400 "UNUSED": DATA UNUSED IN RUN 2	CONDUCTIVITY SAMPLE NO.: 2 THEORETICAL VALUE 53.300 UNIT: US/CM RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 50.204 MEDIAN: 51.900 STANDARD DEVIATION: 6.261 REL. ST. DEVIATION (%): 12.472 RUN 2: NUMBER OF LABORATORIES: 32 ARITHMETIC MEAN VALUE: 51.054 MEDIAN: 51.950 STANDARD DEVIATION: 3.981 REL. ST. DEVIATION (%): 7.798 RESULTS IN DECREASING ORDER: 17 60.000 8 51.800 23 58.000 35 51.700 37 53.300 4 51.500 20 53.200 19 51.500 21 53.100 38 51.500 27 53.100 7 51.300 16 53.000 31 50.800 15 52.700 32 50.400 14 52.600 36 48.850 34 52.500 9 48.100 18 52.300 24 48.000 30 52.140 11 47.100 3 52.050 6 45.800 5 52.000 33 41.000 13 52.000 22 38.500 39 52.000 40 23.000 UNUSED 10 51.900 "UNUSED": DATA UNUSED IN RUN 2
CONDUCTIVITY SAMPLE NO.: 3 THEORETICAL VALUE 26.000 UNIT: US/CM RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 26.501 MEDIAN: 26.000 STANDARD DEVIATION: 3.940 REL. ST. DEVIATION (%): 14.867 RUN 2: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 25.638 MEDIAN: 26.000 STANDARD DEVIATION: 1.793 REL. ST. DEVIATION (%): 6.992 RESULTS IN DECREASING ORDER: 40 43.000 UNUSED37 26.000 17 36.750 UNUSED31 25.900 11 30.800 10 25.860 23 29.000 32 25.700 30 26.850 4 25.600 27 26.800 35 25.590 14 26.400 6 25.400 15 26.300 22 25.400 34 26.300 7 25.300 3 26.230 19 25.260 21 26.230 36 24.100 18 26.160 20 23.900 5 26.000 9 23.800 8 26.000 39 23.000 13 26.000 33 22.200 16 26.000 38 20.700 24 26.000 "UNUSED": DATA UNUSED IN RUN 2	CONDUCTIVITY SAMPLE NO.: 4 THEORETICAL VALUE 44.200 UNIT: US/CM RUN 1: NUMBER OF LABORATORIES: 33 ARITHMETIC MEAN VALUE: 42.339 MEDIAN: 43.000 STANDARD DEVIATION: 3.238 REL. ST. DEVIATION (%): 7.648 RUN 2: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 42.817 MEDIAN: 43.000 STANDARD DEVIATION: 1.689 REL. ST. DEVIATION (%): 3.944 RESULTS IN DECREASING ORDER: 17 51.000 UNUSED39 43.000 23 48.000 34 42.700 21 44.310 7 42.600 27 44.300 31 42.600 3 44.100 38 42.500 10 44.100 32 42.300 14 43.900 24 42.000 15 43.900 30 41.260 37 43.600 11 41.100 8 43.500 9 40.500 18 43.400 36 40.000 35 43.400 6 39.900 5 43.300 40 39.300 19 43.120 20 35.800 UNUSED 4 43.000 22 35.700 UNUSED 13 43.000 33 33.000 UNUSED 16 43.000 "UNUSED": DATA UNUSED IN RUN 2

Table 29: Ratio of the measured to the calculated conductivity in synthetic precipitation samples (G).

Lab. No.	<u>Measured value</u>				Remark
	Calculated value				
	Sample No.				
	G1	G2	G3	G4	
3	1.10	1.04	1.07	1.05	Titrated H ⁺ used
4	1.08	1.05	1.03	1.07	
5	1.00	0.99	1.00	0.99	
6	0.79	0.84	1.01	0.89	
7	0.96	1.00	1.01	1.00	
8	1.10	1.10	1.05	1.10	
9	0.95	0.91	0.90	0.94	
10	1.11	1.13	1.07	1.14	
11	0.98	1.04	1.30	0.99	Missing Na
13	1.14	0.90	0.90	0.82	Titrated H ⁺ used
14	1.00	1.00	1.00	1.02	
15	1.06	1.07	1.05	1.07	
16	0.98	1.04	1.00	1.00	Missing NO ₃ , Na and Ca
17	1.85	1.20	1.52	1.22	
18	-	-	-	-	
19	1.12	1.14	1.07	1.14	
20	0.96	0.99	0.90	0.80	
21	0.99	0.98	0.98	0.99	
22	1.20	0.79	1.02	0.90	
23	1.17	1.19	1.12	1.19	
24	1.15	0.93	1.04	1.09	Missing conductivity
26	-	-	-	-	
27	1.08	1.08	1.07	1.10	
30	1.12	1.10	1.06	1.02	
31	0.99	0.96	0.94	0.96	
32	1.07	1.01	0.99	1.00	
33	0.82	0.84	0.86	0.83	
34	0.85	0.83	0.84	0.77	
35	1.03	1.04	0.94	0.96	Missing Mg
36	1.02	0.98	0.97	1.03	
37	1.14	1.12	1.06	1.09	
38	0.76	1.00	0.78	1.03	
39	1.21	1.01	1.15	1.03	
40	-	-	-	-	Missing SO ₄ and Cl

Table 30: Ratio of equivalent concentration of anions to the equivalent concentration of cations measured in synthetic precipitation samples (G).

Lab. No.	Anions Cations				Remark
	Sample No.				
	G1	G2	G3	G4	
3	1.07	1.06	1.02	1.06	Titrated H+ used
4	1.07	1.08	1.05	1.09	
5	1.00	1.00	0.99	1.01	
6	0.97	0.99	1.03	0.98	
7	1.01	1.07	1.00	1.11	
8	1.06	1.09	1.02	1.12	
9	1.27	1.17	1.10	1.23	
10	1.06	1.04	1.01	1.08	
11	1.17	1.28	1.41	1.32	Missing Na
13	1.07	0.94	0.91	0.86	Titrated H+ used
14	0.99	1.00	0.97	1.02	
15	1.01	1.01	0.99	1.00	
16	1.00	0.99	0.99	0.99	
17	1.01	1.05	1.00	1.01	
18	-	-	-	-	
19	1.21	1.03	1.05	1.10	
20	0.89	1.04	0.93	1.04	
21	0.98	1.02	0.97	1.03	Missing Mg
22	0.98	1.09	1.06	1.10	
23	0.99	1.10	0.94	1.12	
24	1.05	1.08	1.11	1.24	
26	1.08	1.01	0.98	0.99	
27	1.05	1.10	1.06	1.09	
30	0.96	1.06	0.95	1.06	
31	0.97	0.98	0.93	0.97	
32	1.24	1.18	1.16	1.22	
33	1.37	1.12	1.23	1.06	
34	0.92	0.90	0.91	0.84	
35	1.10	1.15	1.26	1.47	
36	1.06	1.04	0.97	1.06	
37	1.23	1.09	1.06	1.13	
38	1.03	1.10	1.05	1.14	
39	1.09	1.01	1.10	1.09	
40	-	-	-	-	

Table 31: The ratio of the median of the reported values to the expected theoretical values for all parameters and samples. The number of reported values are given in parenthesis.

Parameter	Sample No.	Median
		Expected
SO ₂ in abs. solution	1	1.08 (7)
	2	1.01 (7)
	3	1.04 (7)
	4	1.04 (7)
	5	1.02 (7)
	6	1.01 (7)
SO ₂ on imp. filter	1	0.99 (16)
	3	0.99 (16)
	4	0.93 (16)
	5	0.98 (16)
	6	0.99 (16)
	7	0.96 (16)
	8	0.94 (16)
	9	0.97 (16)
NO ₂ in abs. solutions	1	0.99 (21)
	2	0.96 (21)
	3	0.99 (21)
	4	0.99 (21)
SO ₄ on filters low (synthetic)	1	0.99 (7)
	2	1.00 (7)
	3	1.02 (7)
	4	1.00 (7)
SO ₄ on filters high (synthetic)	1	1.00 (18)
	2	0.98 (18)
	3	1.01 (18)
	4	0.99 (18)
SO ₄ in precipitation	1	1.00 (33)
	2	1.01 (33)
	3	1.01 (33)
	4	1.01 (33)
NO ₃ in precipitation	1	0.99 (33)
	2	1.00 (33)
	3	1.00 (33)
	4	1.00 (33)
NH ₄ in precipitation	1	1.00 (34)
	2	1.01 (34)
	3	1.00 (34)
	4	1.01 (34)
pH in prec. (calc. from H ⁺)	1	0.86 (34)
	2	0.90 (34)
	3	0.90 (34)
	4	0.91 (34)
H ⁺ in prec. (titrated)	1	1.04 (2)
	2	1.00 (2)
	3	0.99 (2)
	4	1.00 (2)

Table 31 (contd.)

Parameter	Sample No.	Median
		Expected
Cl in precipitation	1	0.96 (33)
	2	0.97 (33)
	3	0.97 (33)
	4	0.97 (33)
Na in precipitation	1	0.99 (32)
	2	1.00 (32)
	3	1.00 (32)
	4	1.00 (32)
Mg in precipitation	1	0.99 (33)
	2	1.01 (33)
	3	1.00 (33)
	4	1.00 (33)
Ca in precipitation	1	1.02 (33)
	2	1.04 (33)
	3	1.02 (33)
	4	1.01 (33)
K in precipitation	1	0.98 (34)
	2	0.99 (34)
	3	0.99 (34)
	4	0.97 (34)
Cond. in precipitation	1	0.99 (33)
	2	0.97 (33)
	3	1.00 (33)
	4	0.97 (33)

Appendix 2

Figures

Figures 1-16: The figures show the relative error for the reported results for the samples of SO₂ in absorbing solution, synthetic samples of SO₂ in KOH-impregnated filters, NO₂ in absorbing solution, synthetic samples of sulphate on filters, and precipitation samples.

The reported values are plotted in a ranked order from the largest negative error to the largest positive error.

Figure 17: Reported values (corrected for blank) for SO₂ in impregnated filters plotted against the expected values. The linear regression lines and R²-values are also shown.

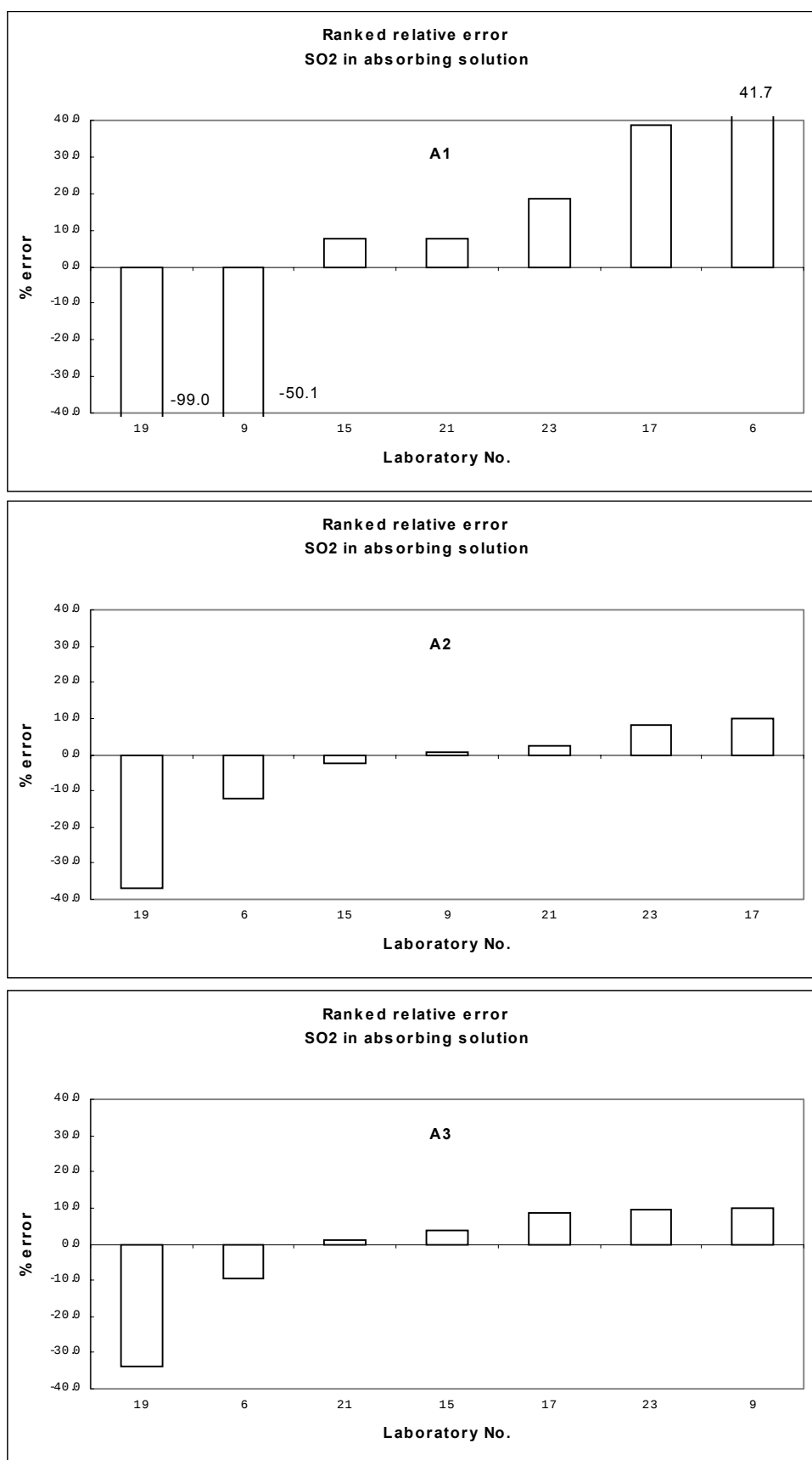


Figure 1.

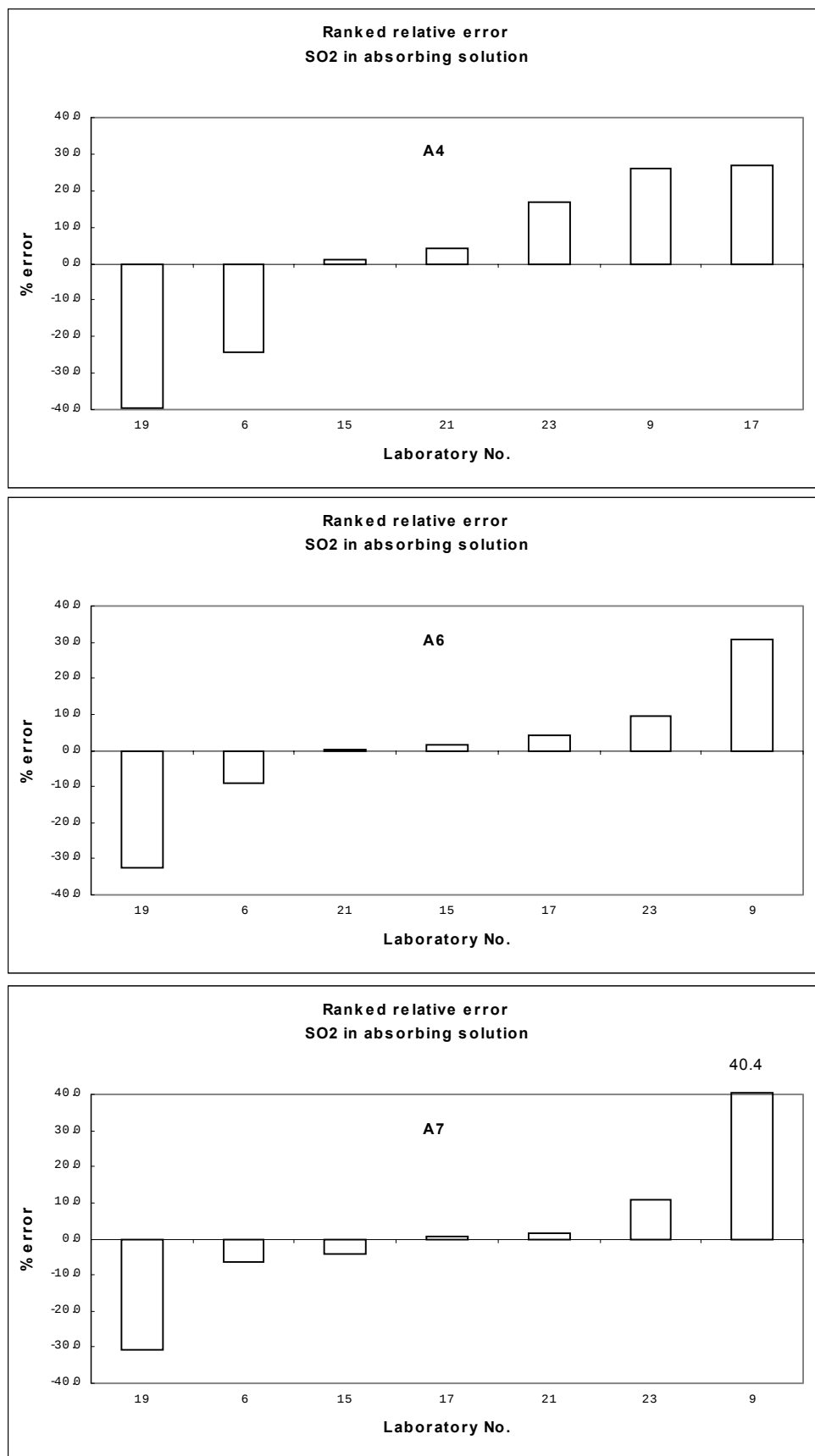


Figure 1, cont.

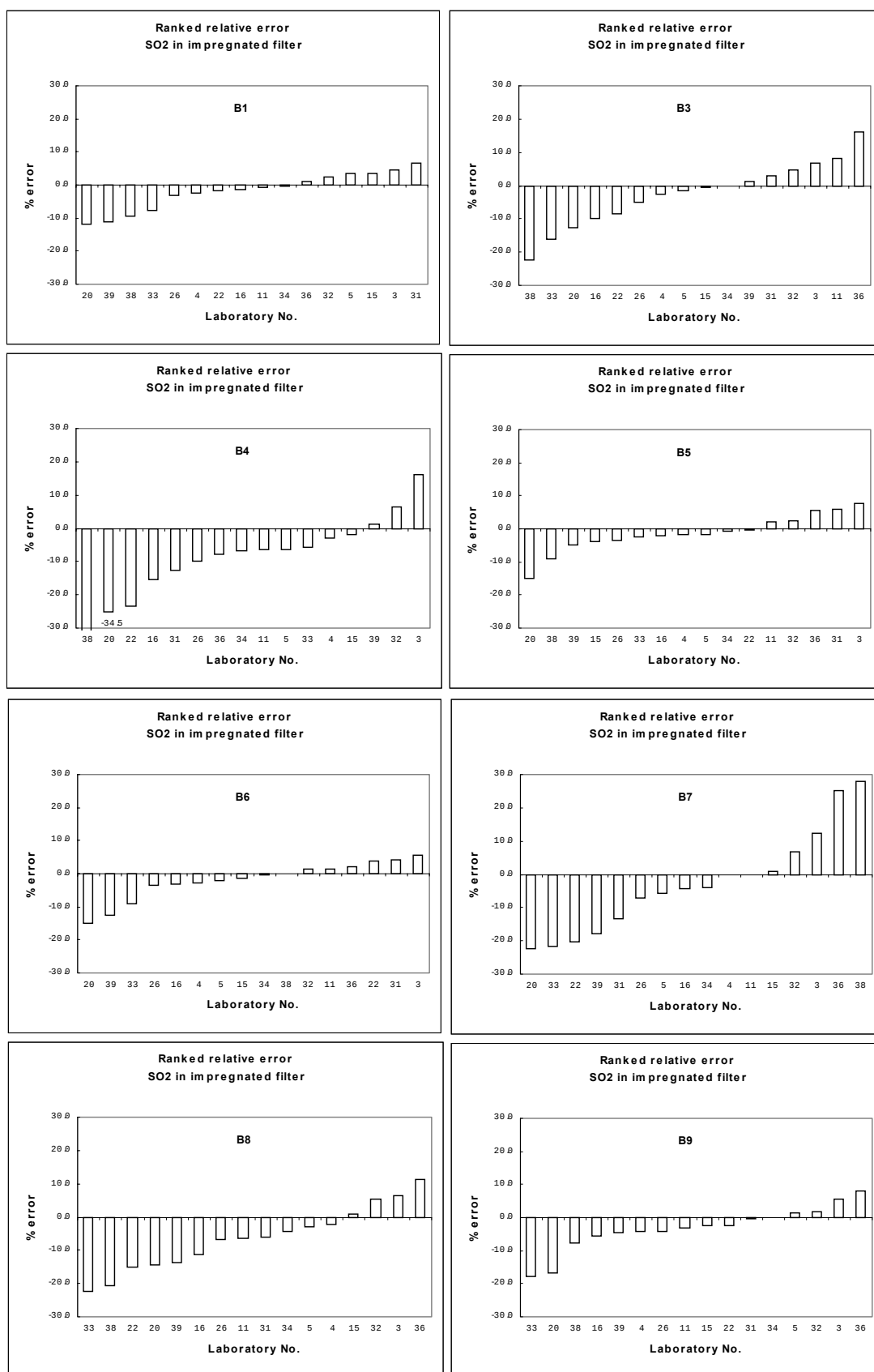


Figure 2.

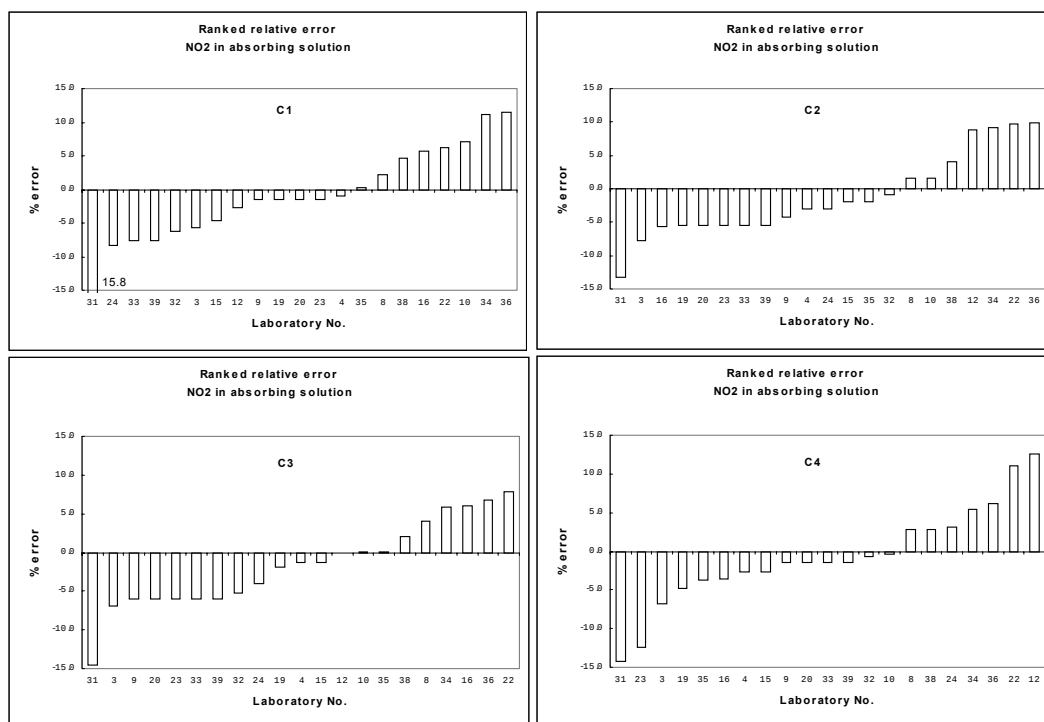


Figure 3.

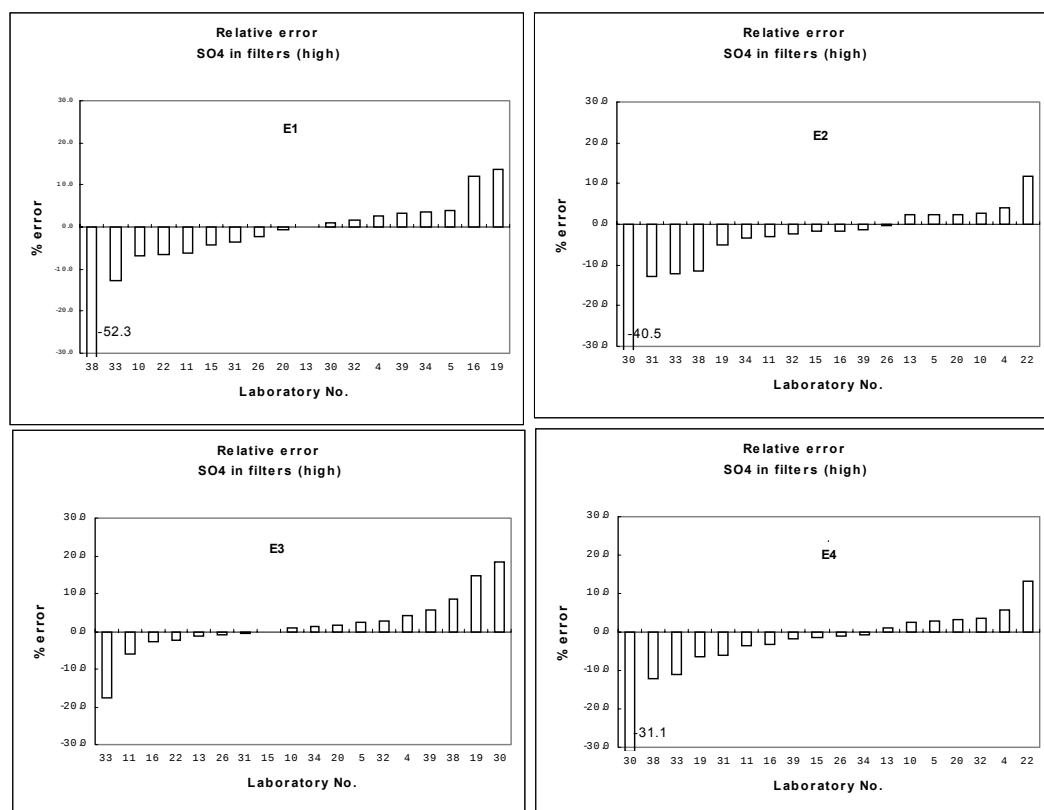


Figure 4.

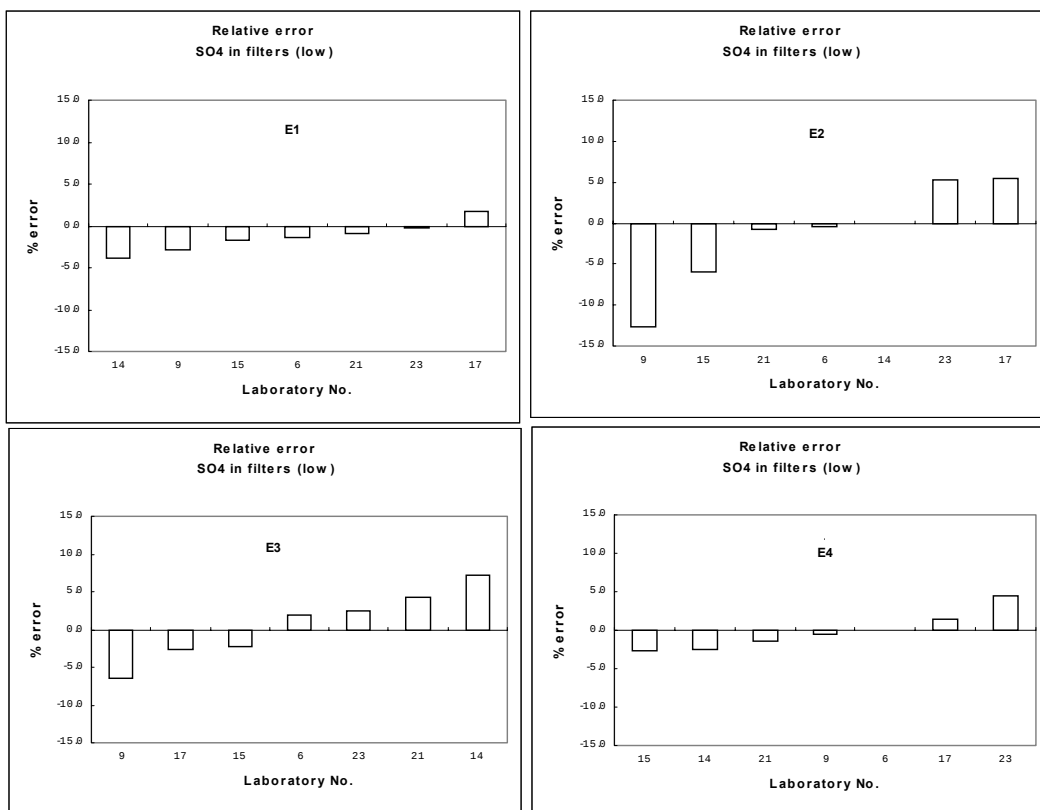


Figure 5.

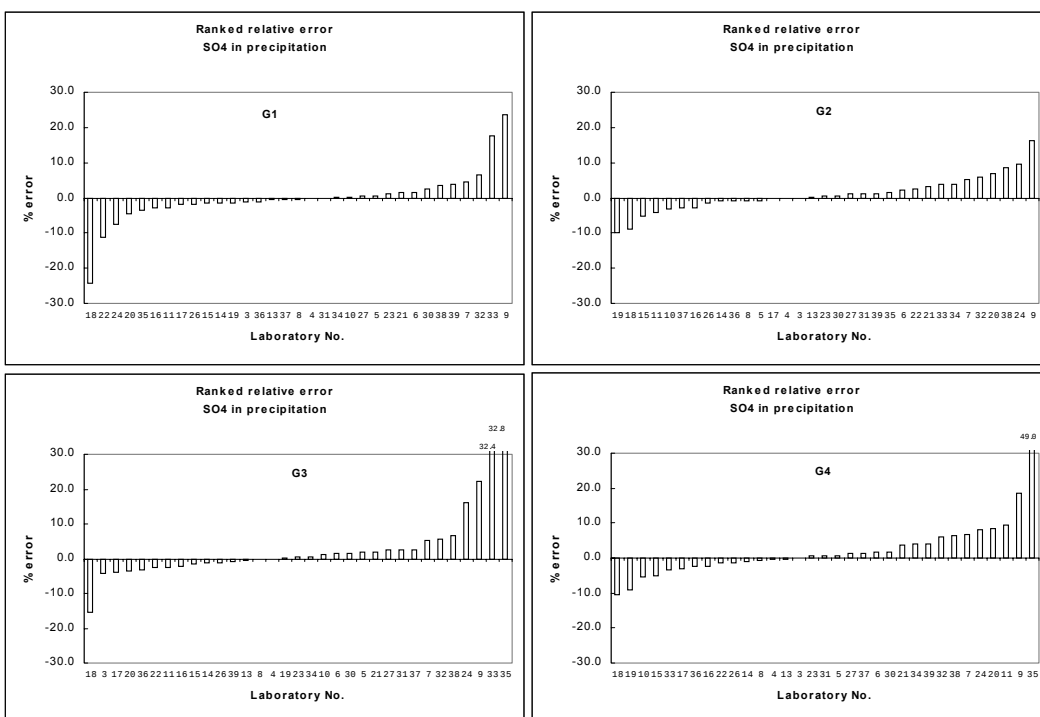


Figure 6.

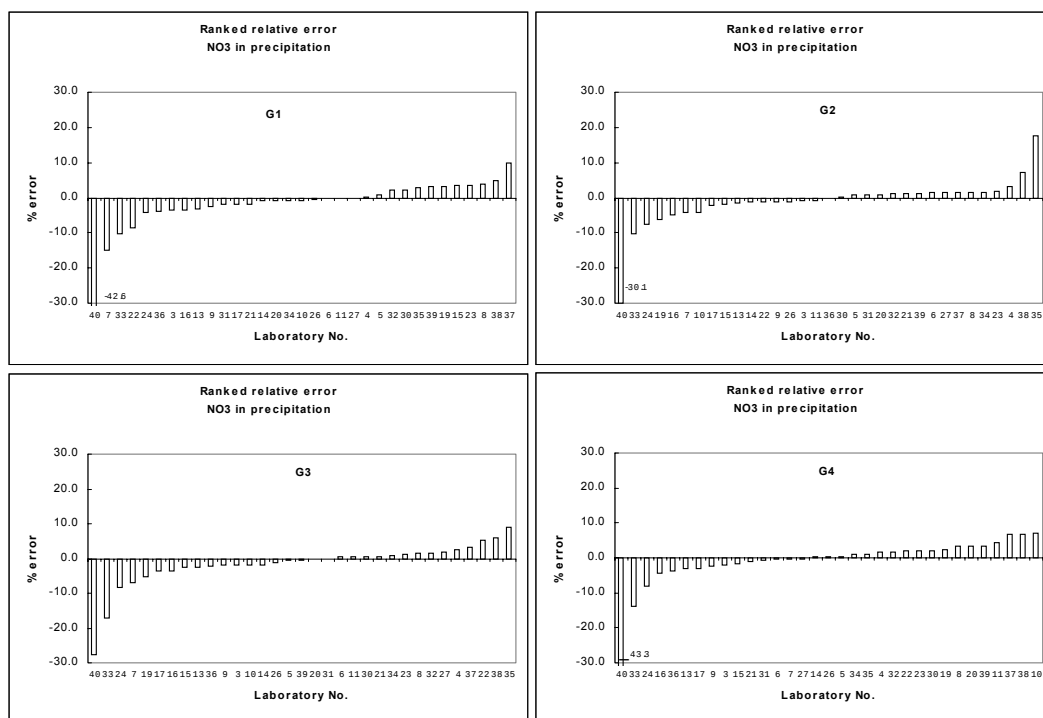


Figure 7.

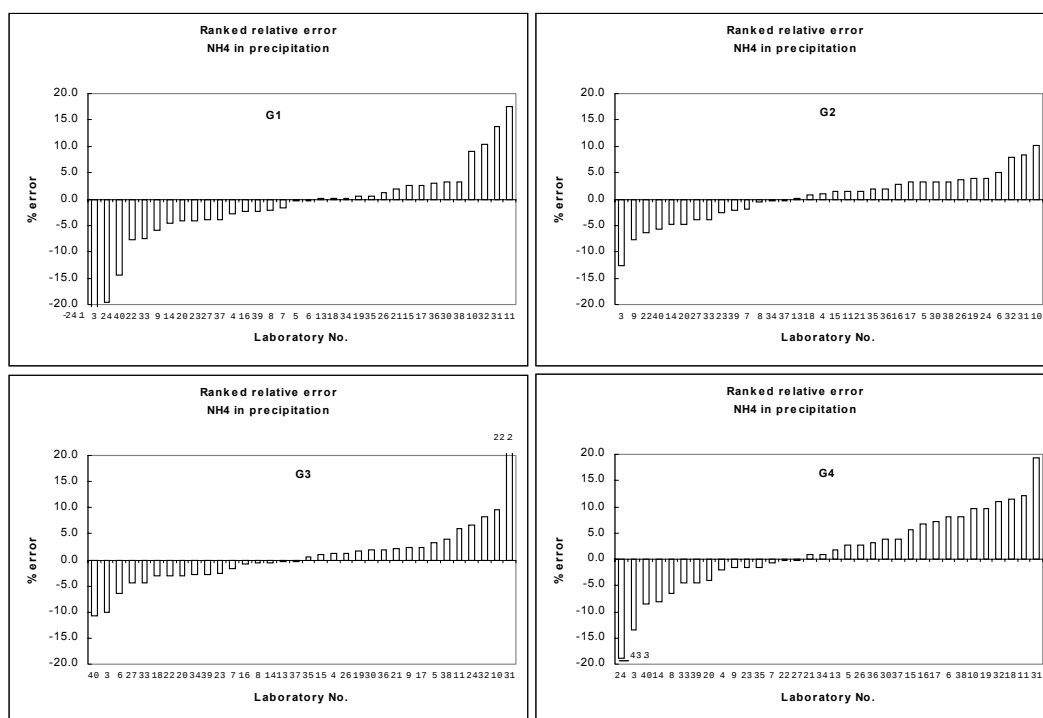


Figure 8.

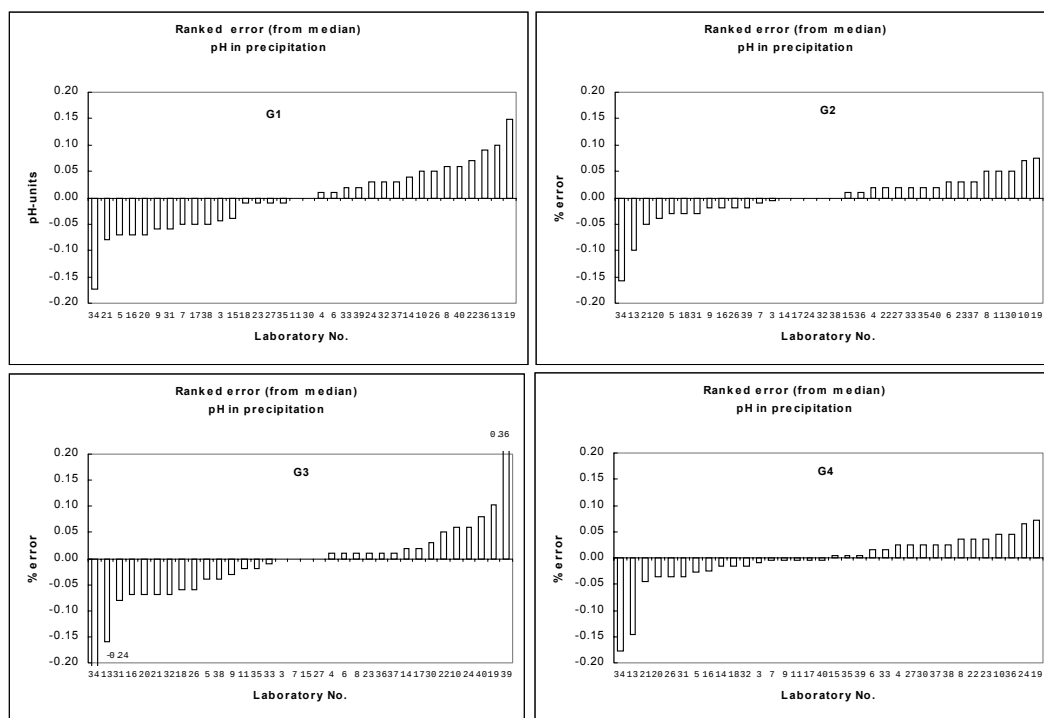


Figure 9.

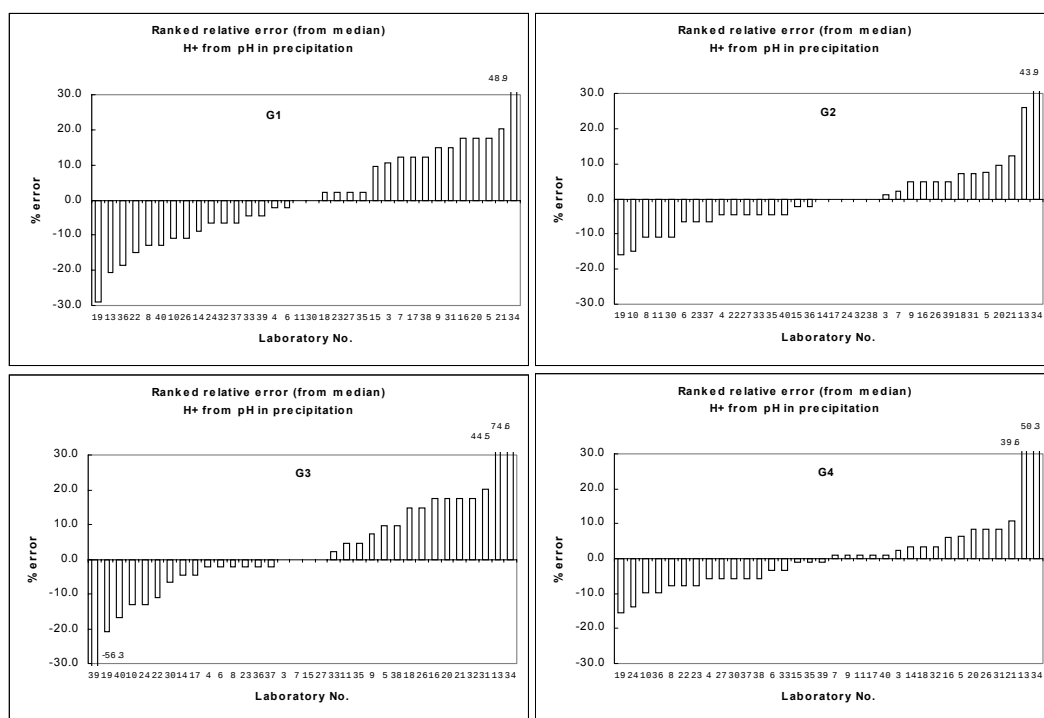


Figure 10.

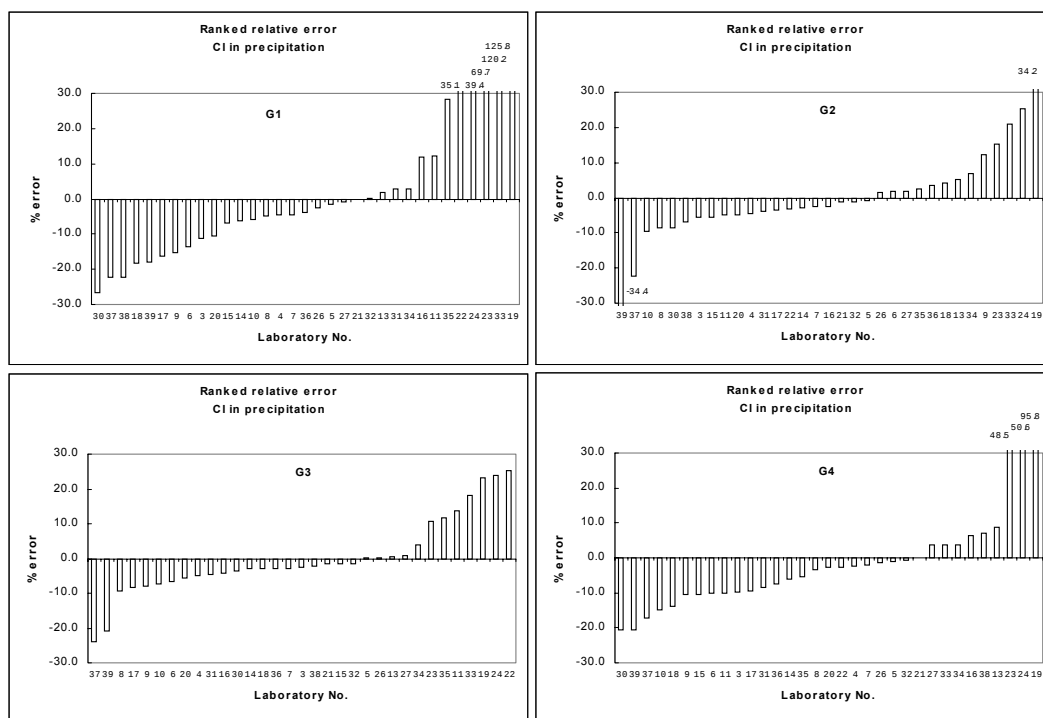


Figure 11.

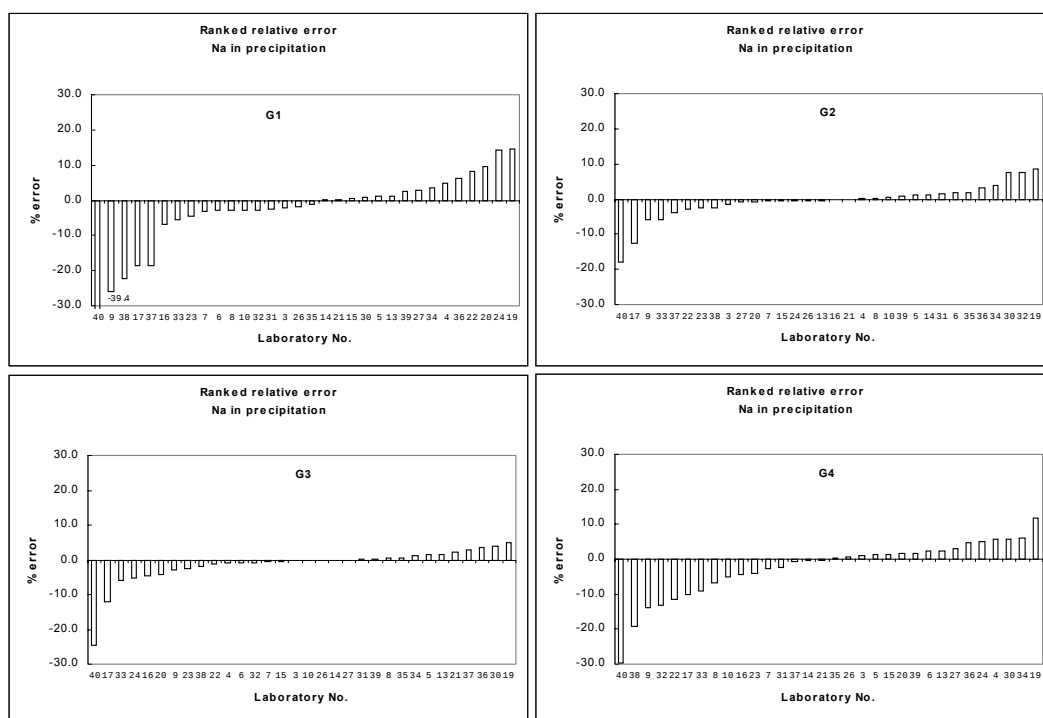


Figure 12.

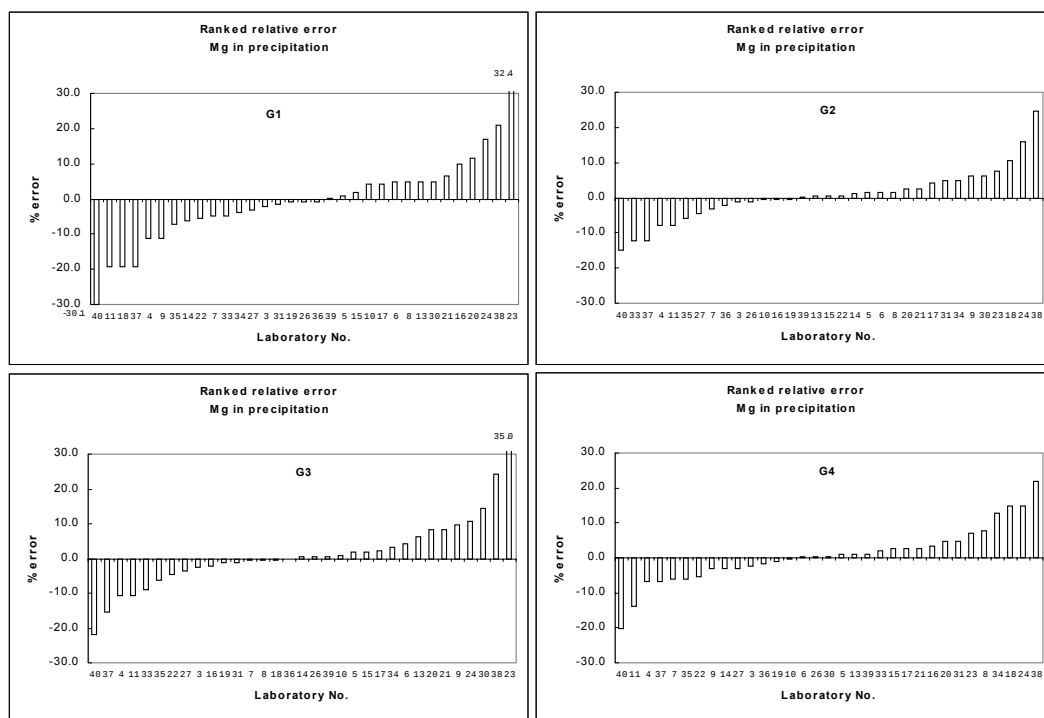


Figure 13.

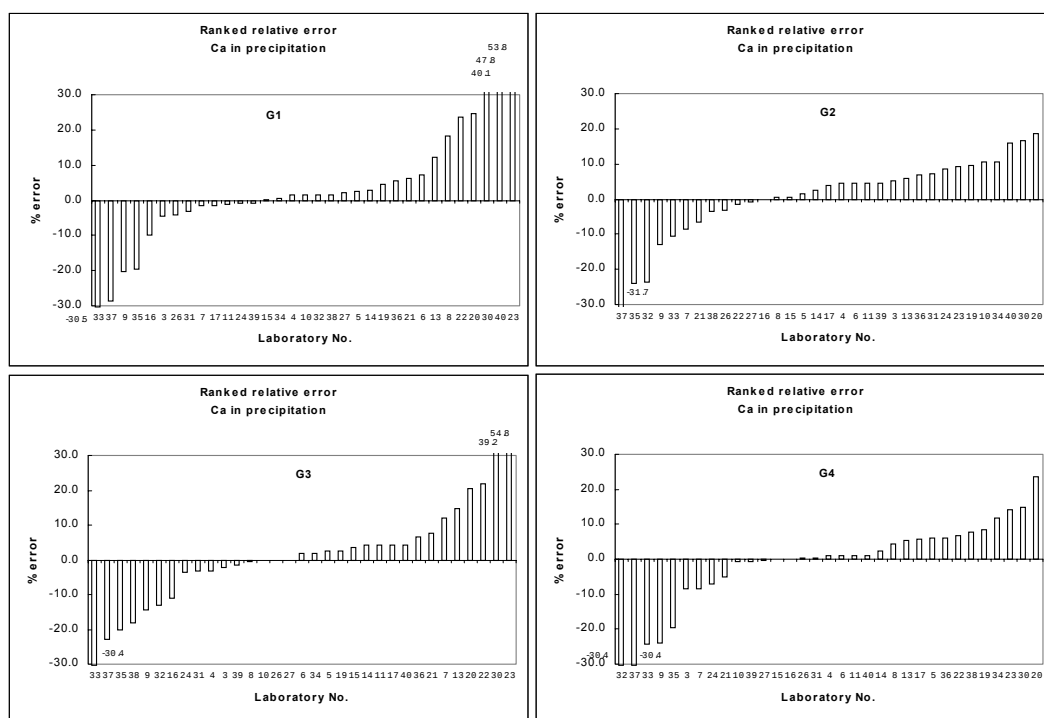


Figure 14.

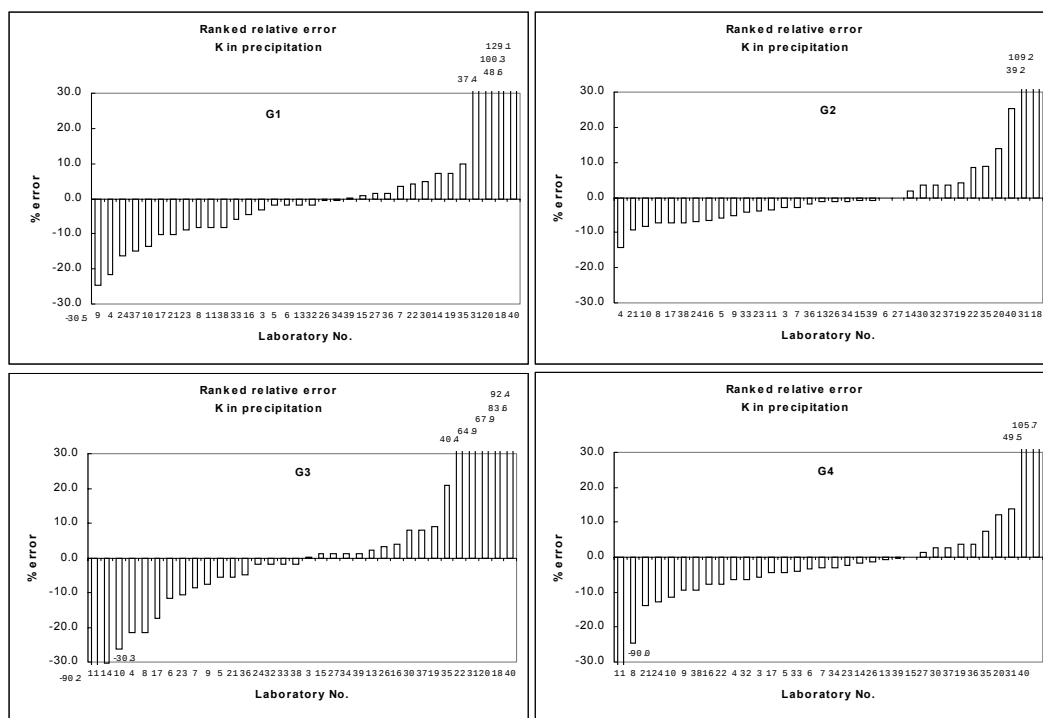


Figure 15.

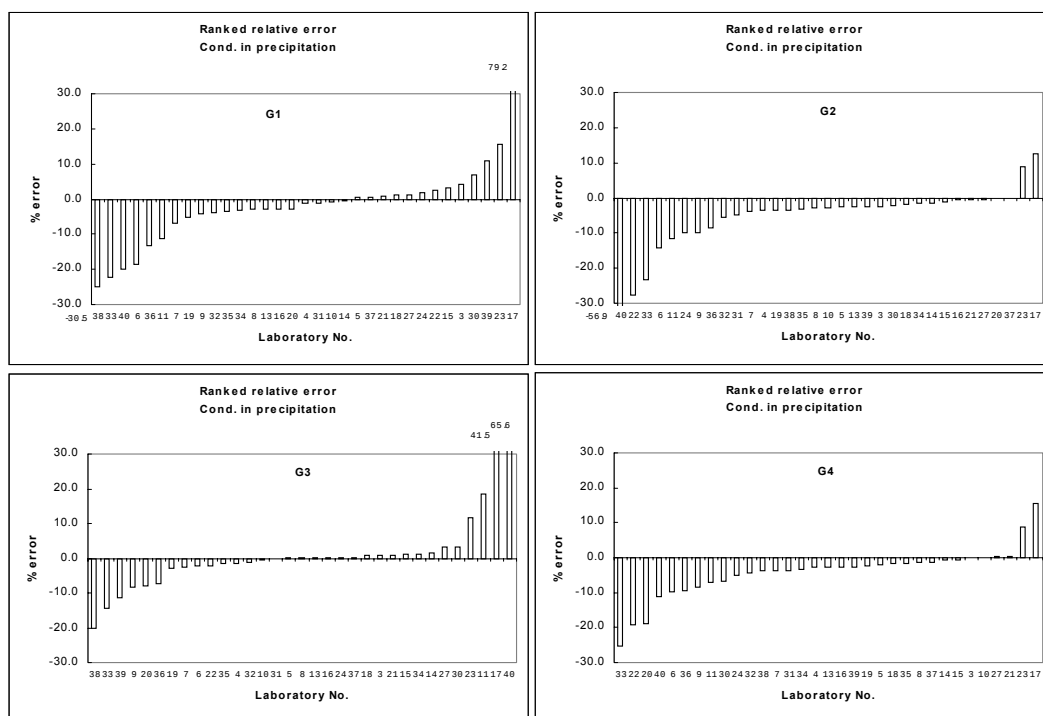


Figure 16.

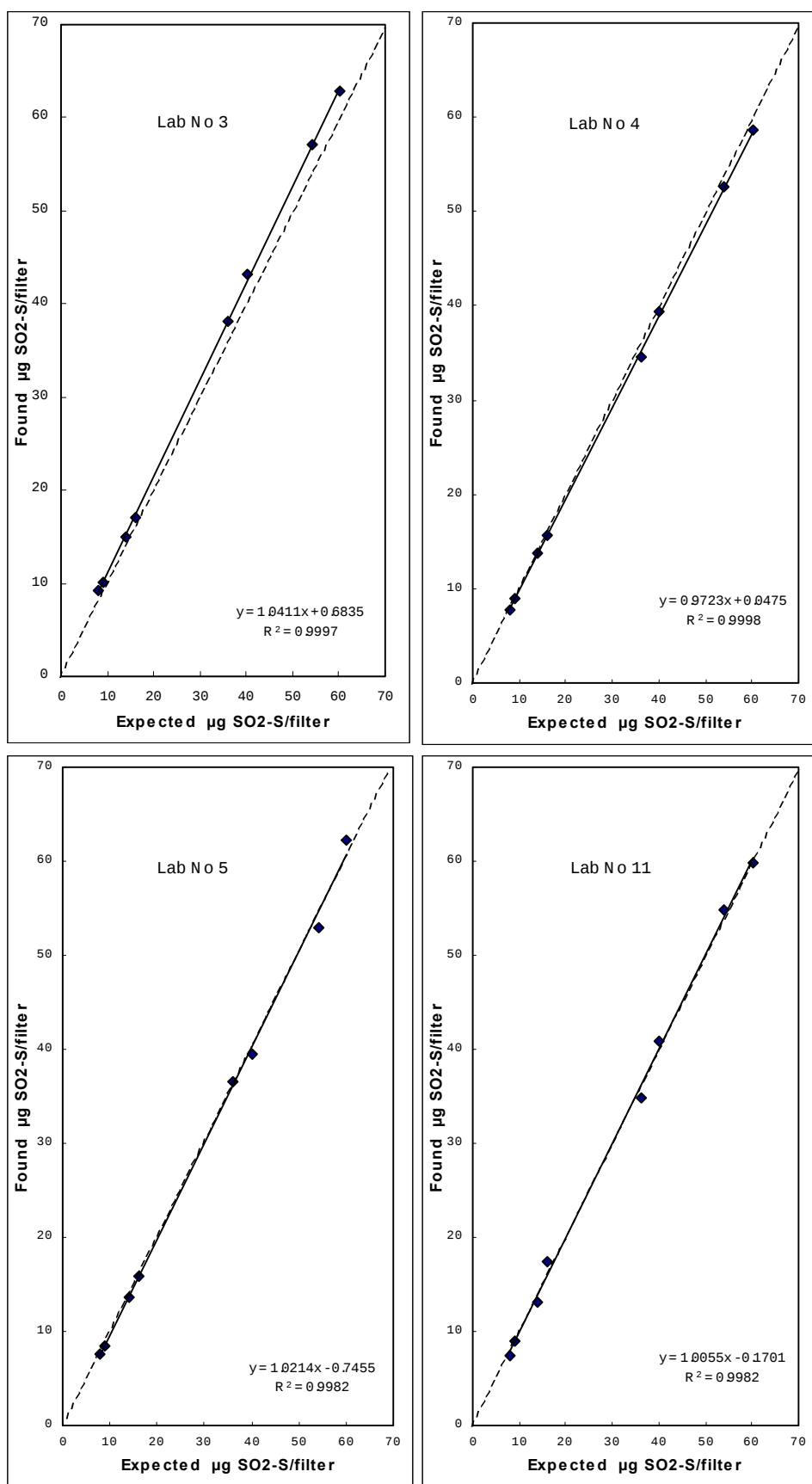


Figure 17.

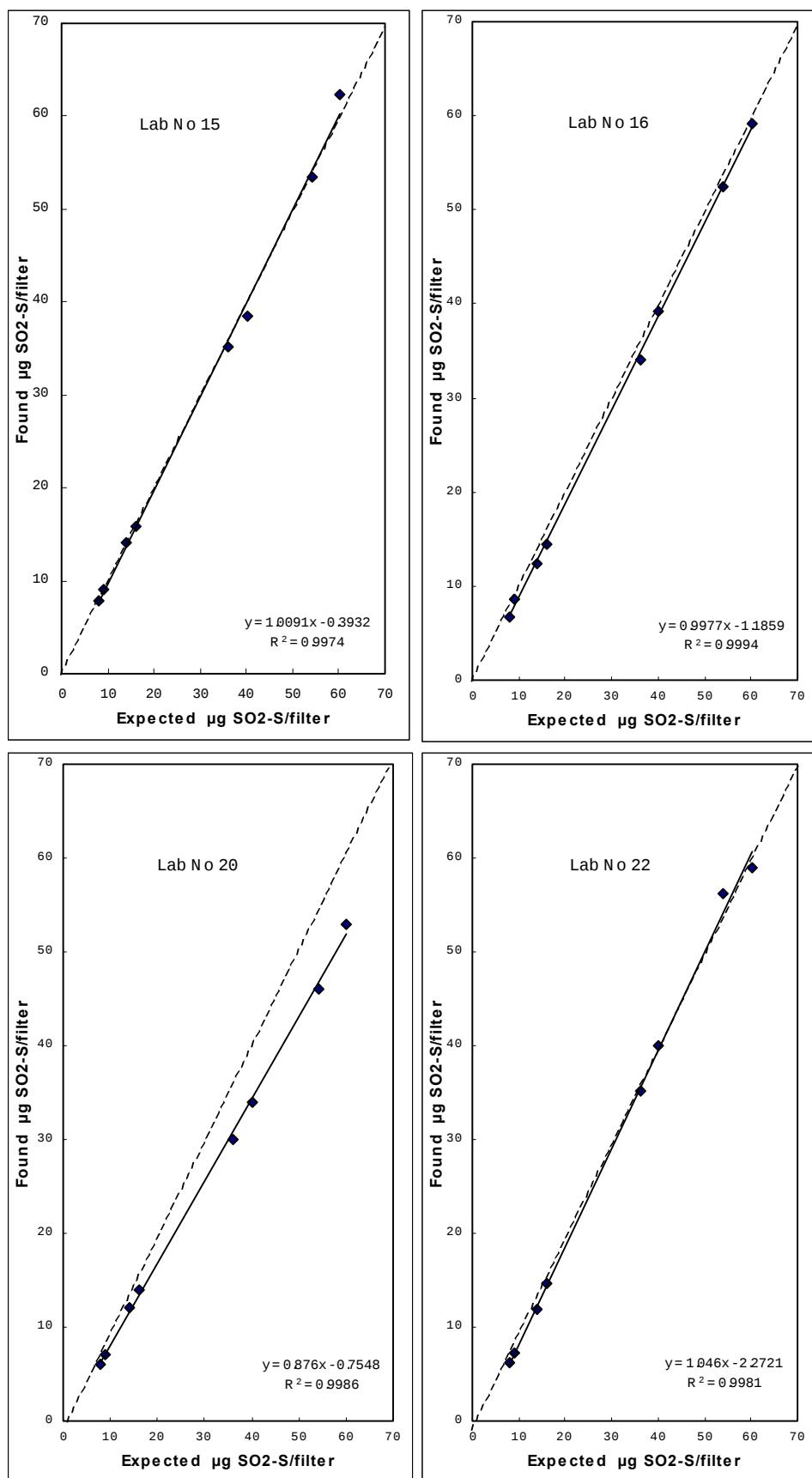


Figure 17, cont.

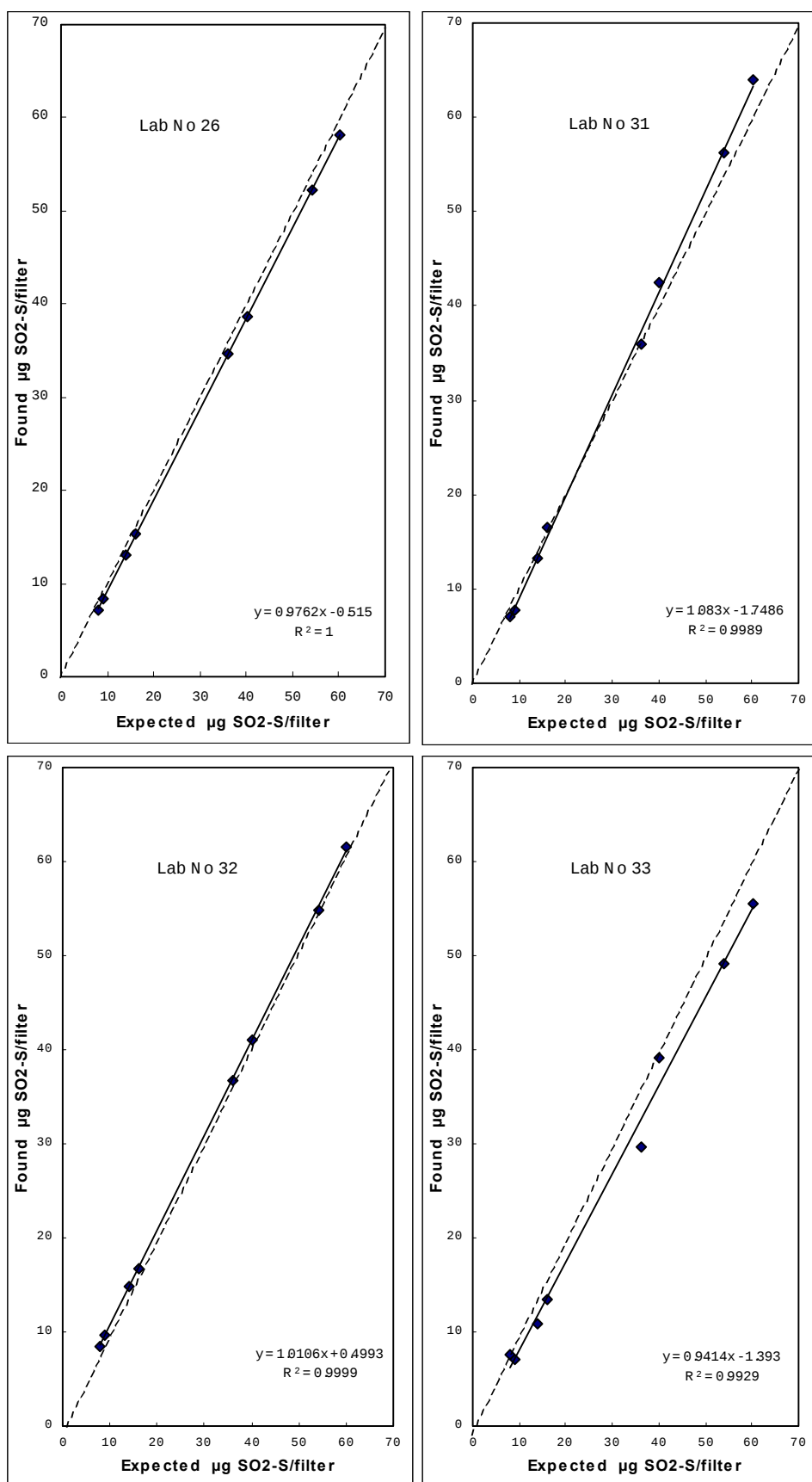


Figure 17, cont.

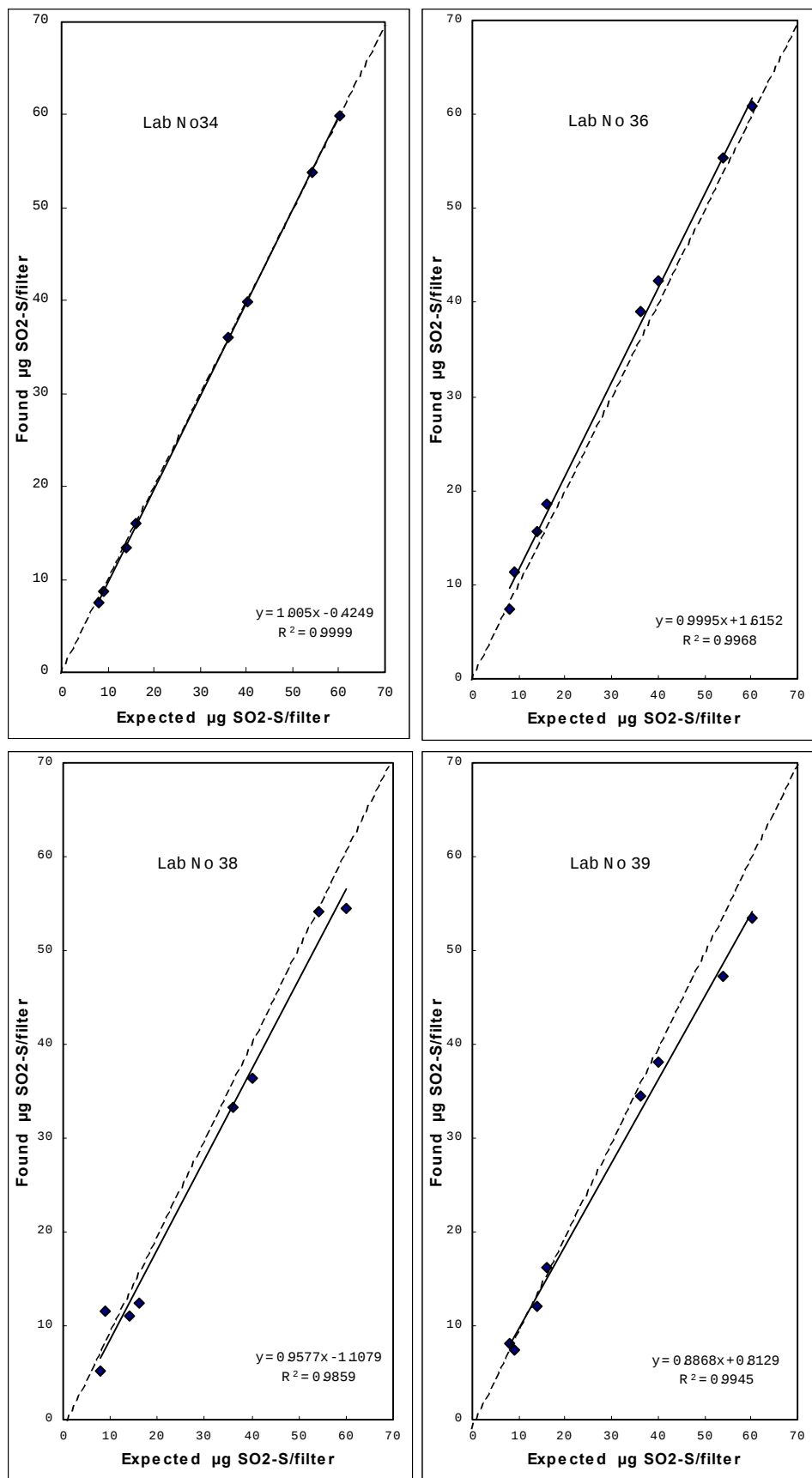


Figure 17, cont.