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NATIONAL INTERLABORATORY QUALITY CONTROL STUDY NO. 33 - SULFATE IN COLORED WATERS.

by
V. Cheam and A.S.Y. Chau

Analytical Methods Division
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada

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MANAGEMENT PERSPECTIVE

This national interlaboratory quality control study dealt with the analysis of SO_4 in coloured waters. Sulfate data are important in the study of acid rain. Some 70 Canadian laboratories participated in the study. The interferences from coloured matter in the waters caused some methodologies to produce results which were biased high, in particular the Methyl Thymol Blue colorimetry. Other methodologies were however less affected by these interferences, in particular the ion chromatography method. The study helped the participants to assess the performance of their laboratories and the methods they used in the analysis of sulfate.

PERSPECTIVE-GESTION

Cette étude nationale de contrôle interlaboratoire de la qualité traite de l'analyse du SO_4 dans les eaux colorées. Les données sur les sulfates sont très utiles pour analyser les pluies acides. Quelque soixante-dix laboratoires canadiens ont accepté de participer à cette étude. Les résultats obtenus grâce à certaines méthodes, dont la méthode d'analyse des sulfates par colorimétrie au bleu de thymol, indiquent un biais positif en raison des interférences causées par les colorants dans l'eau. D'autres techniques, en particulier la chromatographie par échange d'ions, ont été moins perturbées par ces interférences. Cette étude a aidé les participants à évaluer le rendement de leur laboratoire et à se prononcer sur la valeur des méthodes qu'ils emploient pour analyser les sulfates.

Titre : Étude nationale de contrôle interlaboratoire de la qualité n° 33 - Les sulfates dans les eaux colorées.

ABSTRACT

This report describes an interlaboratory comparison study for the analysis of SO_4 in organic contaminated coloured waters. Some 70 Canadian laboratories participated in the analysis of five unpreserved water samples. Because of the interference from coloured matter in the waters, some methodologies, in particular the Methyl Thymol Blue colorimetry, were identified as producing results which were biased high. Some other methodologies performed well, particularly ion chromatography.

RÉSUMÉ

Ce rapport décrit une étude sur la comparaison, entre divers laboratoires, des méthodes d'analyse du SO_4 dans des eaux colorées contaminées par des substances organiques. Quelque soixante-dix laboratoires canadiens ont participé à l'analyse de cinq échantillons d'eau non préservés. On a remarqué que les résultats obtenus grâce à certaines méthodes, dont la méthode d'analyse des sulfates par colorimétrie au bleu de thymol, indiquaient un biais positif en raison des interférences causées par les colorants dans l'eau. D'autres techniques ont donné de bons résultats, notamment la chromatographie par échange d'ions.

LIST OF SYMBOLS

n Number of results used

$\bar{x}$ Mean value, $\bar{x} = \sum x_i / n$

S Standard deviation, $S = \left\{ \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1} \right\}^{1/2}$

R Results with a flag R were statistically determined to be outliers.

VH Result with a flag VH was assessed to be very high.

VL Result with a flag VL was assessed to be very low.

INTRODUCTION

The analysis of SO_4 in coloured waters has recently created a great deal of discussion and concern (1-8). This is partly due to its importance in the study of acid rain, and partly because data generated by different analytical methods are not always compatible due to interference from coloured matter in the waters. This intercomparison study offered each participant an opportunity to analyse coloured waters and to assess their methods and data against those of other laboratories.

STUDY DESIGN

This study involved five test samples of natural and spiked natural waters (Table 1). The waters were filtered, unpreserved, and the participants were instructed to store the test samples at 4°C until analysis. Each laboratory chose its own analytical method but was encouraged to use more than one method.

EXPERIMENTAL

Chemicals

Reagent grade chemicals used were purchased from J.T. Baker Chemical Company: Na_2SO_4, Na_2CO_3 and $NaHCO_3$.

TABLE 1 Description of Samples

Test Samples	Type
1	Spiked natural sample
2	Mixture of natural waters sample
3	Natural sample (Sand Pond)
4	Spiked natural sample
5	Spiked natural sample

Sample Preparation

All containers, glassware and plasticware were cleaned, rinsed with hot tap water and deionized distilled water, and stored with deionized distilled water for several weeks before use (9).

The waters were collected from Ontario and Atlantic regions and filtered through 0.45 μm filter paper. Spiked waters and mixed waters were prepared from the individual regional waters in large polyethylene containers. Each water was homogenized and subsampled into 200 mL plastic test bottles. Five percent of test samples were randomly selected and analysed for confirmation of sample homogeneity and integrity.

Analyses

Several participants used more than one analytical method for sulfate analysis. Thirty-one laboratories used ion chromatography and 17 used MTB (methyl thymol blue) colorimetry. Other methods used were: calmagite colorimetry (1 laboratory); turbidimetry (10 laboratories); gravimetry (10 laboratories); Thorin titration (1 laboratory); colour-corrected MTB (1 laboratory); pretreatment of samples by UV/H_2O_2 oxidation followed by MTB analysis (1 laboratory); and inductively coupled Argon Plasma, ICAP (1 laboratory).

DATA EVALUATION

The median value for each sample was determined using all data (except the 'less than' values) reported by the participants. The mean and standard deviation were calculated after rejection of outliers (identified as R on Tables 3 - 7) using Grubbs procedure (10). The results of each sample from all the laboratories were ranked according to Youden (11). All the results were evaluated using the flagging technique (12) as applied in our other Quality Assurance (QA) programs for Long Range Transport of Atmospheric Pollutants (LRTAP) and International Joint Commission (IJC). By this technique, the results are classified into five categories; namely, unflagged, L(low), VL(very low), H(high), VH(very high) based on comparison with

the medians. Since medians are often good estimates of the true values in unknown samples, the flagging technique provides some evaluation of each result based on median values. Thus, the most accurate results are those which are not flagged whereas the VH or VL results are farther away from the medians and are interpreted as less accurate.

The ranking procedure (11, 12) also assesses simultaneously the results of all samples analysed by the same methodology to determine laboratories with pronounced systematic errors. The optimal values used in the ranking process were 2.00 for the Lower Limit for Use of Basic Acceptable Error (LLBAE), 0.76 for Basic Acceptable Error (BAE), and 0.20 for Concentration Error Increment (CEI).

Another data evaluation technique used in this study was based on Youden's pair sample technique (13) by assessing the paired analytical results and their medians against design values. The latter values were estimated from the many in-house analyses and investigations including multiple standard additions (8), colour and organic carbon removal.

RESULTS AND DISCUSSION

Combined Analytical Data

Table 2 presents the combined data reported by the participants and the corresponding sample statistics - mean, standard deviation and

median along with design value. As can be seen, standard deviation for each sample is large indicating data incompatibility.

The data incompatibility is clearly evident when the data are graphically presented as paired sample plots in Figures 1 - 3. The results are very scattered and have quite a large range. Thus the design values are used and are represented by two perpendicular segments in each figure. The segments represent ±10% range of the design values.

Each of Figures 1 - 3 shows that the combined data could be represented by a 45° line passing through the intersection of the two segments. This behaviour indicates that some methods and/or some laboratories have produced precise but biased results. The bias and the assessment of each methodology will be discussed below in more detail.

Methodology Comparison

The ion chromatography data are presented in Table 3 along with their statistics and the design values. The suspected results are flagged with R, VH, VL, H and L as explained in the Data Evaluation Section. For each sample, the mean and median agree well with the design value, indicating good performance by most laboratories and good accuracy by the IC methodology.

The colorimetric (MTB) results are likewise presented in Table 4. The means and medians clearly indicate that the MTB results

are biased high, which confirms the previous findings (3, 8). Table 5 gives the colorimetric (calmagite) results, which are close to, but consistently lower than, the design values. Only one laboratory used this method.

The turbidimetric results appear in Table 6 and indicate fairly good agreement with the design values, although the imprecision is generally quite high. The gravimetric data (Table 7) are very imprecise, and the means and medians indicate consistently high results. Table 8 presents the Thorin titration results, which are a lot closer to design values than MTB results. Table 9 combines the results by other methods, including MTB method with colour correction, MTB method with UV/H_2O_2 sample pretreatment, and ICAP (inductively coupled argon plasma) method. The results by these methods were slightly higher than the design values.

To clearly illustrate the methodology comparison, the design values and the median result of each methodology are plotted for samples 1 and 2 in Figure 4. Each design value is presented by a segmented line representing ±10% range. The intersection of the two segmented lines thus represents the design values and is taken as the centre of the oval shown on the Figure. If the oval defines the acceptability limit, it's clear that the IC and turbidimetry methodologies perform acceptably, with the calmagite method being just outside the limit.

As in Figure 4, two other paired sample plots were made (Figures 5 and 6). It is clear from the three figures that the IC and

turbidimetry methodologies perform well as they are consistently within the acceptability limits. It should be noted however that the turbidimetric results, although acceptable, are quite imprecise (Table 6) particularly compared with the IC results. Thus, from the standpoint of data reliability, which requires both good precision and accuracy, IC is superior to turbidimetry.

The calmagite method, used by laboratory 51, also performed well as two out of three points are within the acceptability limit (Figs. 5 and 6). The Thorin titration method and the MTB (UV/H_2O_2, colour corrected) methods also produced some promising results. It's interesting to note that the titration results were more random than the corrected MTB results, the latter being consistently at the upper right quadrant of the design values axes (Figs. 4-6).

The three figures clearly show the high bias characteristic of the unmodified MTB method as all the points are at the upper right hand corner far away from the ovals. The figures also indicate that the gravimetric method is biased high in particular at lower SO_4 levels (Figs. 4 and 5). At higher levels (Fig. 6), the gravimetric method has its points very close to the acceptability limit, and this seems to support the fact that the method is capable of producing accurate results at high concentrations (14). The ICAP method gives consistently high results, though not as high as MTB results.

Ranking and Systematic Errors

The results for each type of methodology are assessed by the ranking procedure (11, 12). Table 10 gives the ranking results of IC analytical data. Laboratory 18 was assessed to have positive systematic errors (high results) even though each of its sample results was not flagged at all (Table 3). This is because each result is slightly but consistently high. This phenomenon was also observed in other studies (15, 16). Likewise, Laboratories 64 and 72 were assessed as having negative systematic errors (low results), even though not a single one of their results was flagged (Table 3).

The ranking results of MTB data (Table 11) show Laboratory 8, flagged five times in Table 4, to have negative systematic errors. Laboratory 13 (flagged once) and laboratory 112 (flagged five times) were shown to have positive systematic errors. The ranking results of turbidimetric data (Table 12a) show that Laboratory 98, with four flags shown in Table 6 has positive systematic errors.

The ranking results of gravimetric data, although showing many flags, do not indicate that the laboratories have systematic errors (Table 12b). The data of other methods (Table 12c) have no flag or did not show systematic errors. The results by Calmagite and Thorin titration methods of course were not ranked because only single results were available.

CONCLUSION

This interlaboratory study helped the participants to assess their laboratories and methods in the analysis of SO_4 in coloured waters. The ion chromatography methodology as well as turbidimetry and calmagite colorimetry performed acceptably. The turbidimetric results were however imprecise. The colorimetric (Methyl Thymol Blue) results were biased high.

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TABLE 2 Combined sulfate results* (all methods), mg/L

Laboratory Number	Sample Results				
	1	2	3	4	5
02	4.45	2.8	2.3	5.85	9.2
02B	6.5	4.6	5.4	7.1	10.0
03	4.25	2.91	2.47	5.48	7.76
03B	6.8	5.6	7.1	8.2	11.8
04	4.36	3.19	2.45	6.07	8.97
04B	6.6	5.3	6.4	8.1	10.8
04C	4.8	3.5	3.6	6.1	8.7
05	4.55	2.85	2.44	6.19	9.04
05B	6.6	4.2	4.4	6.9	9.7
08	5.0	3.9	4.4	5.1	7.6
10	4.21	2.7	2.05	5.65	8.77
10B	6.15	5.19	6.40	8.10	10.3
12	4.48	2.92	2.42	6.38	9.25
12B	6.39	4.55	5.60	8.24	11.7
13	8.0	7.0	9.0	10.0	13.0
15	4.2	2.7	2.2	5.6	8.9
15B	7.0	4.0	5.0	9.0	13.0
18	4.81	3.29	3.05	6.44	9.71
19	7.4	5.6	7.4	8.5	11.5
19B	4.3	2.7	2.4	5.7	8.5
22	4.7	3.3	3.0	6.2	9.1
23	2.8	4.1	2.4	5.6	8.5
25	5.34	3.79	3.36	6.45	9.84
26	<5.0	<5.0	<5.0	<5.0	<5.0
29	81.9	2.1	1.6	3.3	7.4
30	5.0	4.0	5.0	6.0	8.0
34	4.27	2.89	2.48	5.79	8.78
41	3.5	2.5	2.0	4.9	8.6
43	4.5	3.4	2.8	5.9	9.0
47	4.2	2.9	3.3	5.9	9.0
47B	3.75	1.55	0.4	5.5	7.75
48	3.7	6.4	8.2	9.7	12.6
51	4.0	2.4	1.8	5.4	8.4
51B	4.3	3.1	2.5	6.1	8.7
52	6.6	5.6	7.1	8.5	9.9
53	3.0	1.2	0.9	5.6	7.9
53B	4.0	1.0	2.0	6.0	10.0
58	6.3	3.4	3.0	6.1	8.9
58B	6.1	3.8	2.2	6.1	9.1
58C	4.1	4.9	4.9	11.5	19.7
60	4.39	2.78	2.35	5.68	8.77
64	4.0	2.6	2.2	5.4	8.3
70	3.99	2.8	2.44	5.54	8.20
70B	7.5	6.5	8.0	9.5	12.0
72	4.0	2.65	2.25	5.45	8.0
72B	3.0	1.0	1.0	5.0	9.5

TABLE 2 Combined sulfate results* (all methods), mg/L
Continued

Lab	Sample Results 1	2	3	4	5
74	4.1	2.8	2.8	5.4	8.3
85	3.8	3.1	2.5	29.0	8.7
89	4.34	2.72	2.33	5.61	8.5
90	4.03	2.62	2.22	5.61	8.26
96	4.42	2.75	2.54	6.23	9.28
98	6.0	4.0	5.0	7.0	12.0
100	6.7	5.6	7.6	8.1	10.0
100B	8.6	3.7	2.5	6.5	8.9
102	5.4	5.6	3.0	6.3	9.4
106	5.14	2.66	2.24	5.74	8.52
106B	7.92	5.46	6.94	8.37	11.0
109	5.14	2.91	1.30	9.97	10.19
110	6.27	5.33	7.0	6.63	9.93
112	10.8	8.0	9.6	9.6	14.8
112B	12.0	8.0	10.0	10.0	15.0
119	8.4	5.1	<2.0	<2.0	7.2
120	7.6	6.2	7.8	8.7	11.4
124	5.53	4.08	3.0	6.84	8.7
125	4.34	2.83	2.41	5.81	8.8
128	4.27	2.79	2.33	5.87	8.97
130	4.44	2.94	2.53	5.87	9.76
131	4.2	2.7	2.1	5.6	8.7
132	4.55	2.95	2.5	6.95	9.15
135	2.0	1.0	4.0	5.0	6.0
Total Labs	70	70	70	70	70
Results Used, n	69	69	68	68	69
Mean, $\bar{x}$	6.37	3.71	3.79	7.01	9.65
Std Dev, s	9.39	1.55	2.31	3.13	2.07
Median	4.55	3.19	2.54	6.10	9.00
Design	4.23	2.73	2.4	5.72	8.69

*After the study had been closed and the data analysed and plotted, two other laboratories reported the following data, very good data, by IC methodology.

Lab31	4.2	2.8	2.8	5.8	8.8
Lab111	4.3	2.8	2.4	5.9	8.8

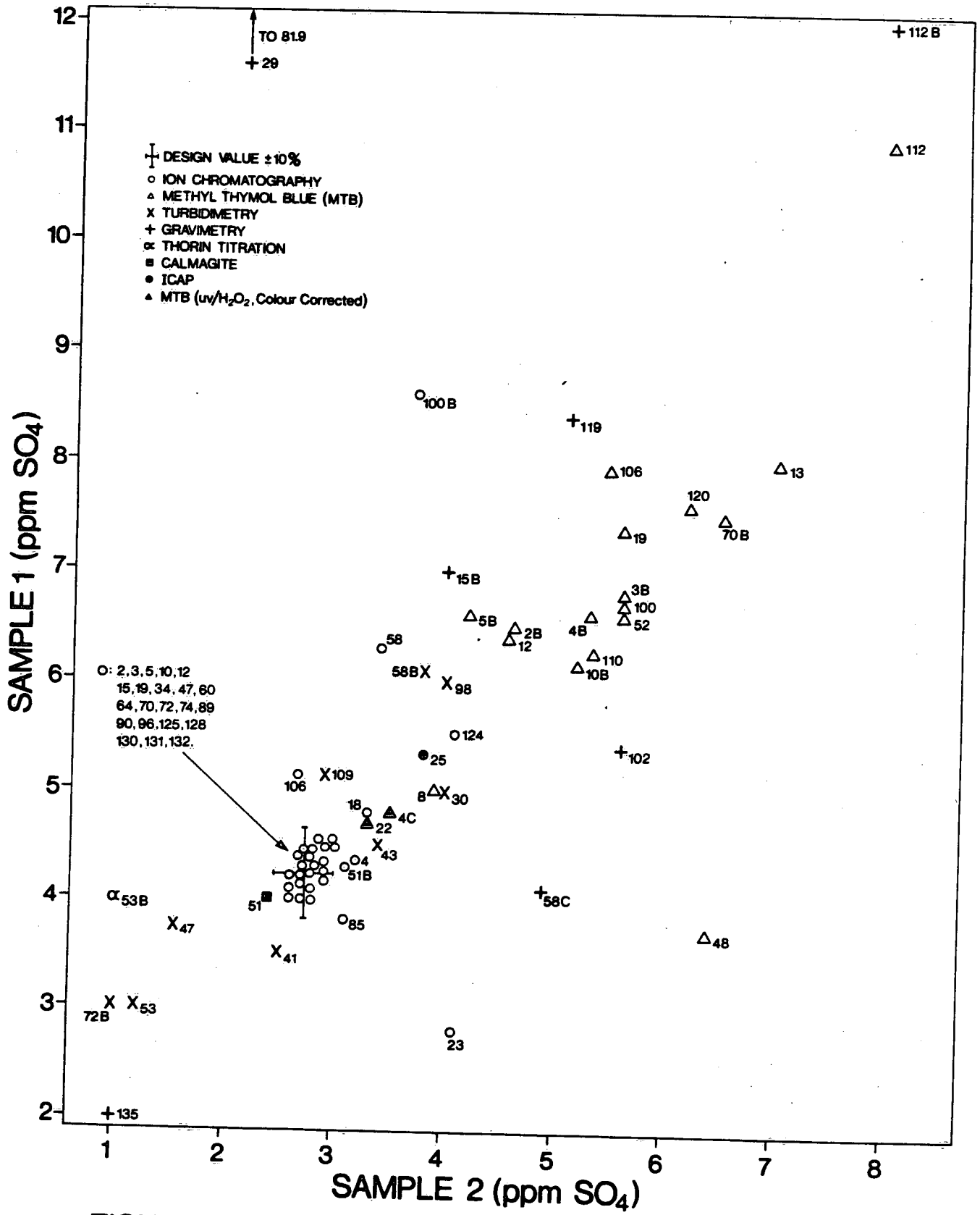

FIGURE 1. PAIRED SAMPLE PLOT FOR SAMPLES 2 AND 1

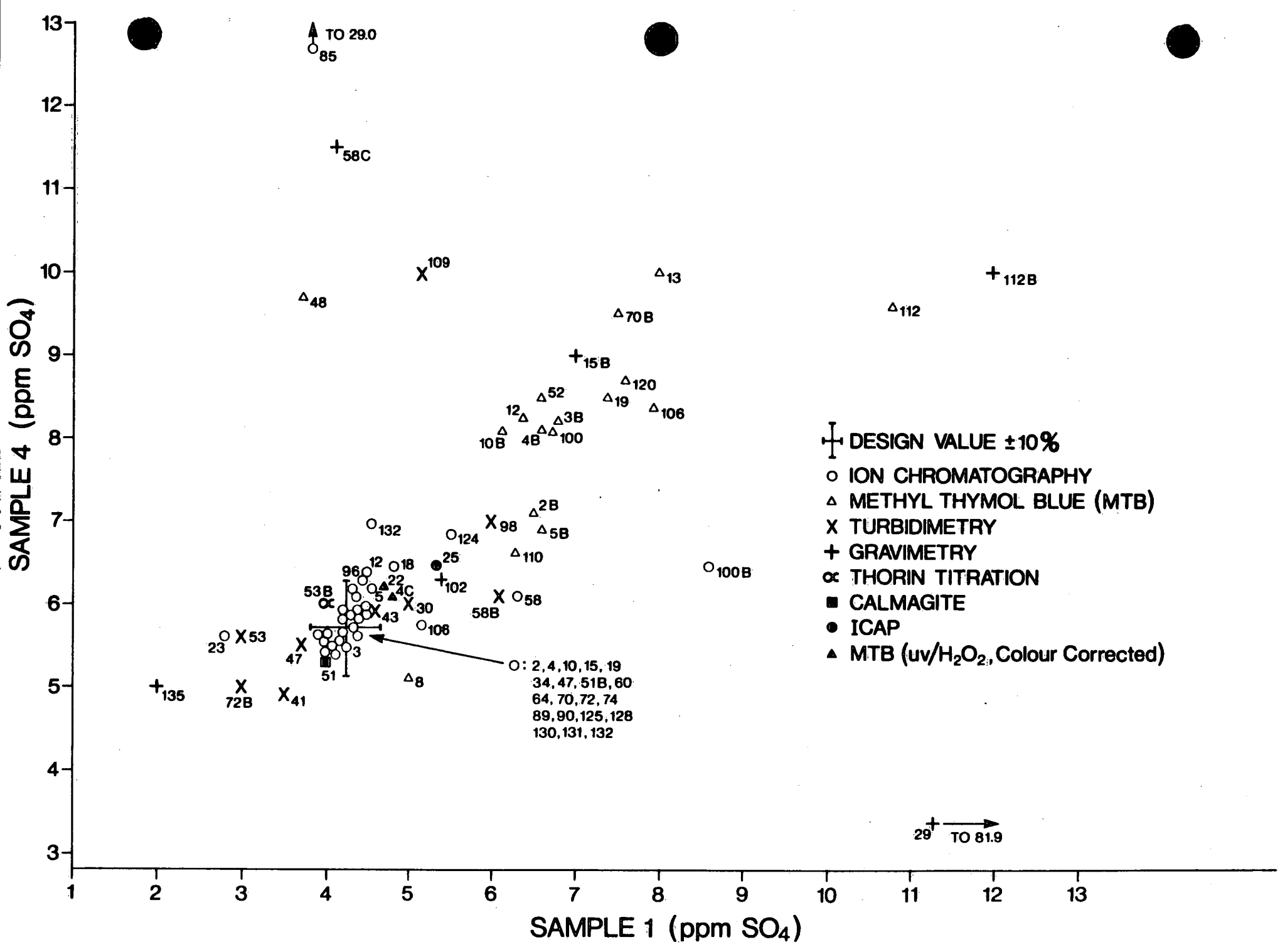

FIGURE 2. PAIRED SAMPLE PLOT FOR SAMPLES 1 AND 4

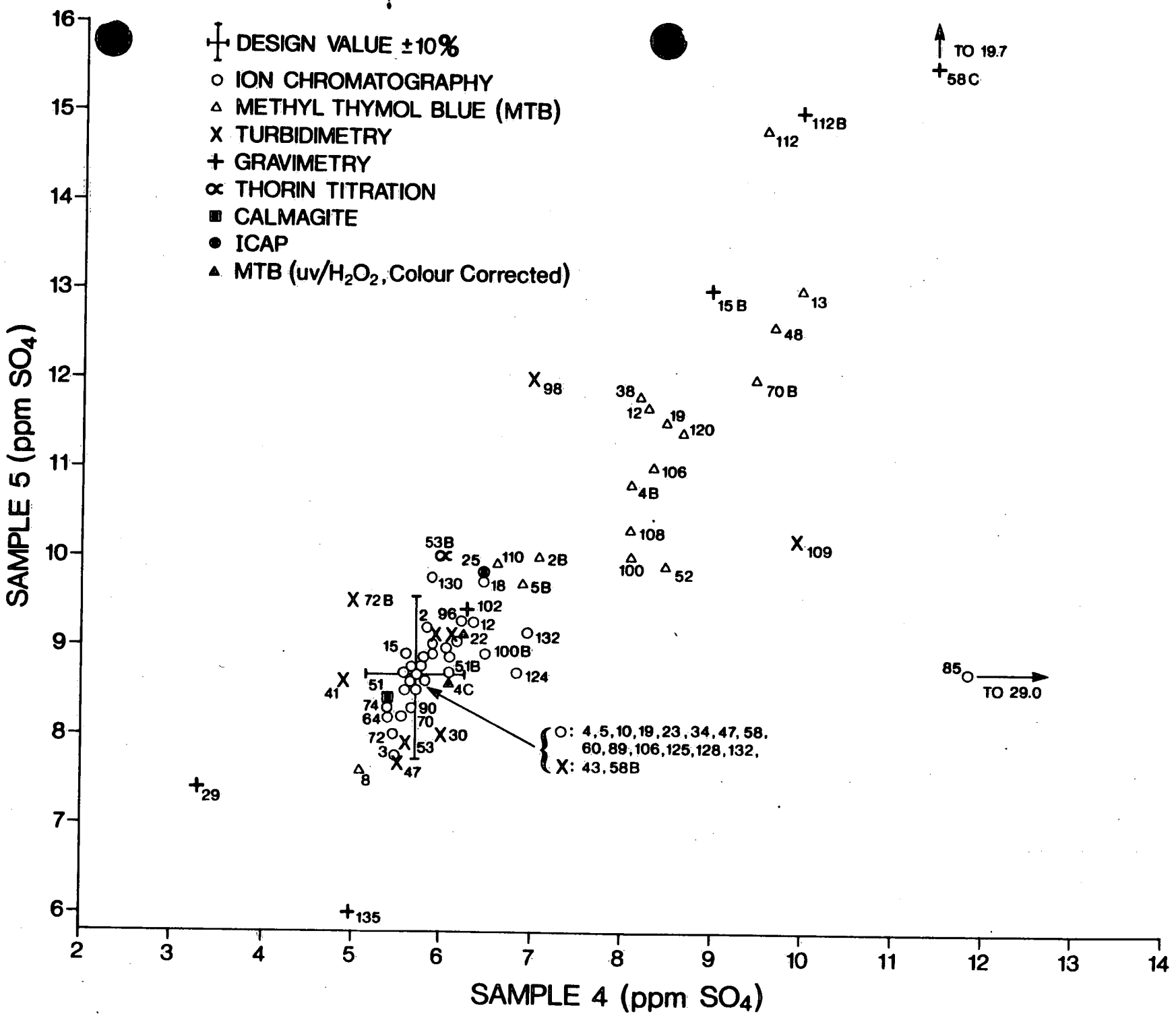

FIGURE 3. PAIRED SAMPLE PLOT FOR SAMPLES 4 AND 5

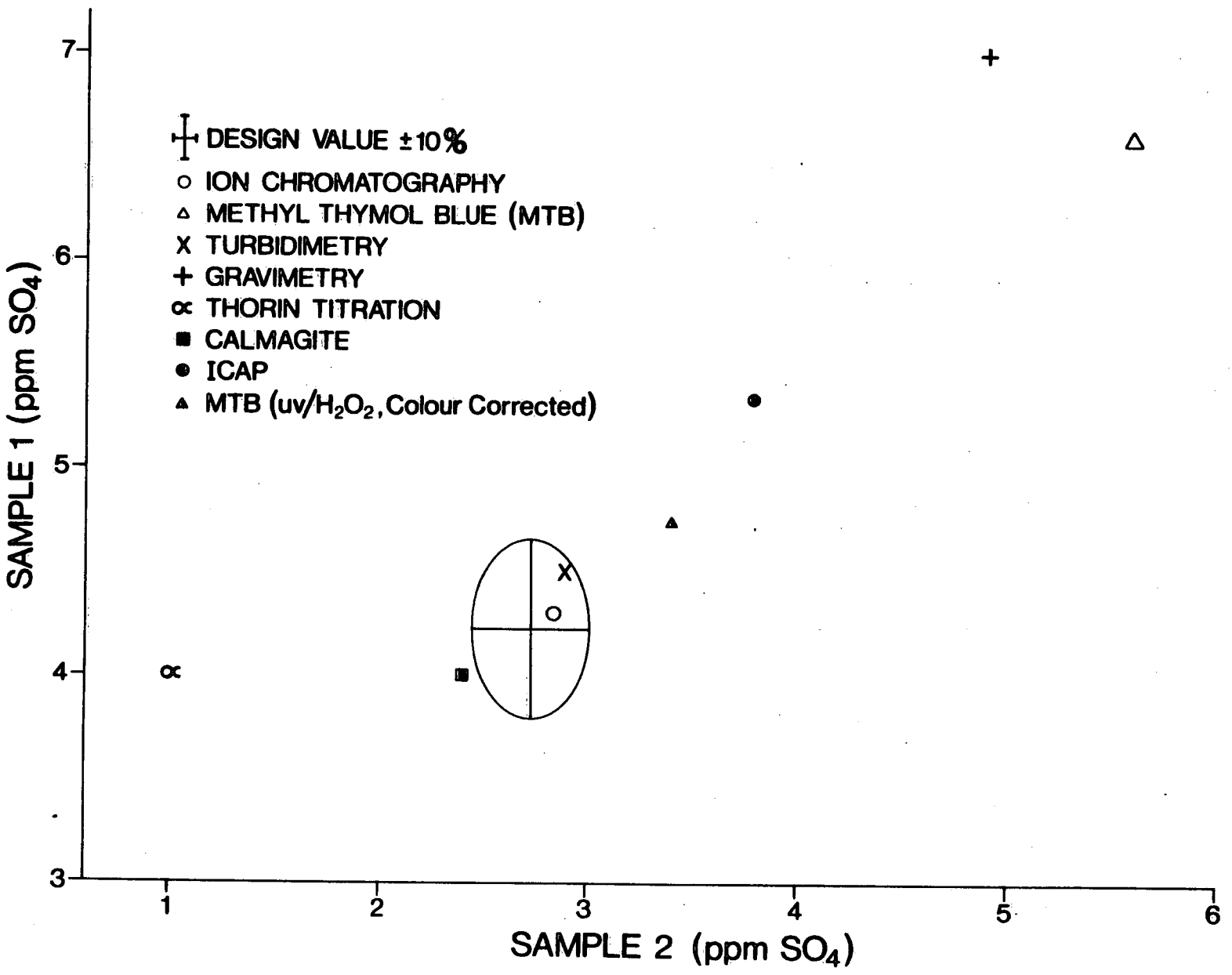

FIGURE 4. COMPARISON OF THE DESIGN VALUE WITH MEDIAN VALUES IN PAIRED SAMPLES 2 AND 1 DETERMINED BY VARIOUS METHODOLOGIES

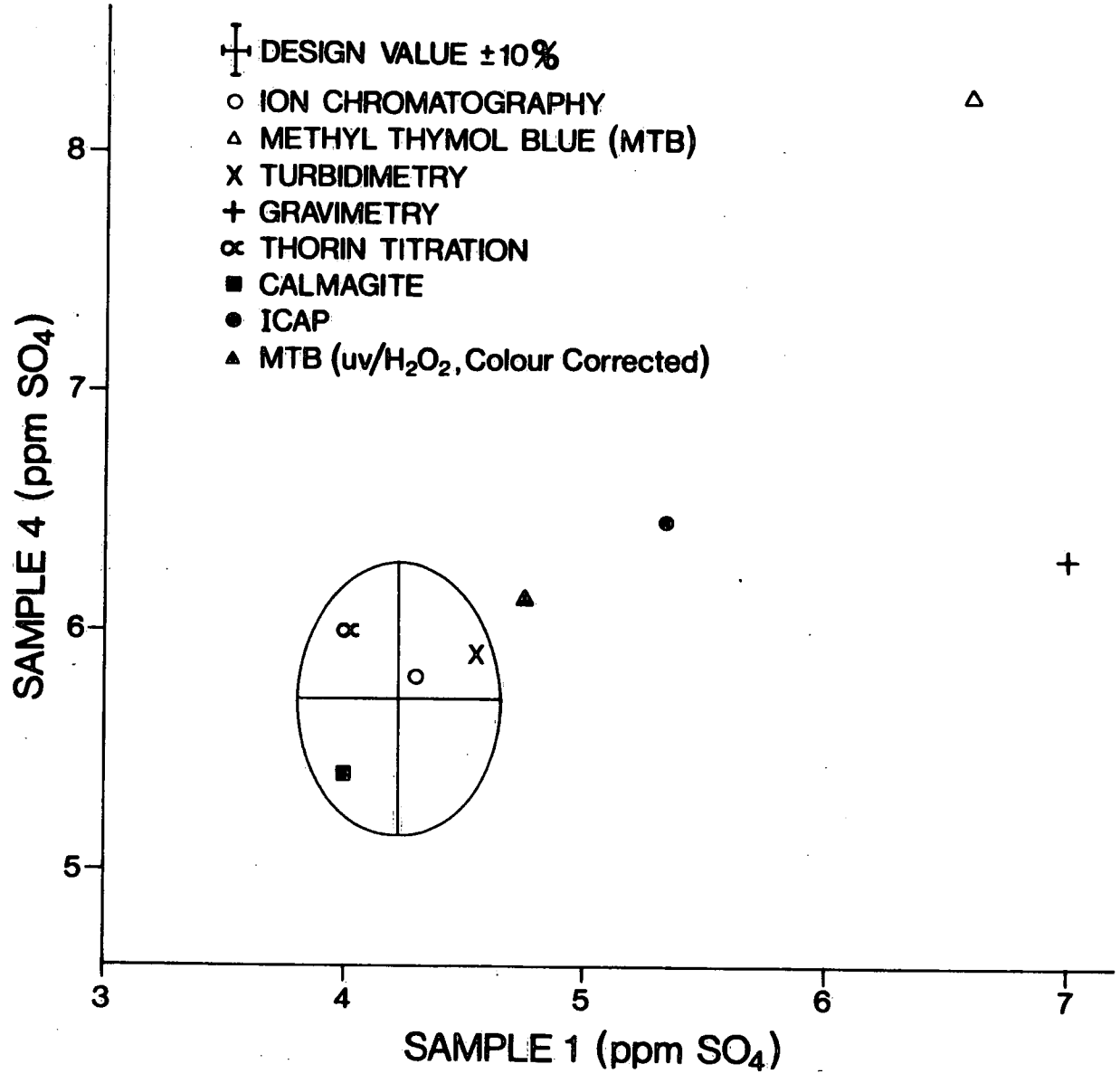

FIGURE 5. COMPARISON OF THE DESIGN VALUE WITH MEDIAN VALUES IN PAIRED SAMPLES 1 AND 4 DETERMINED BY VARIOUS METHODOLOGIES

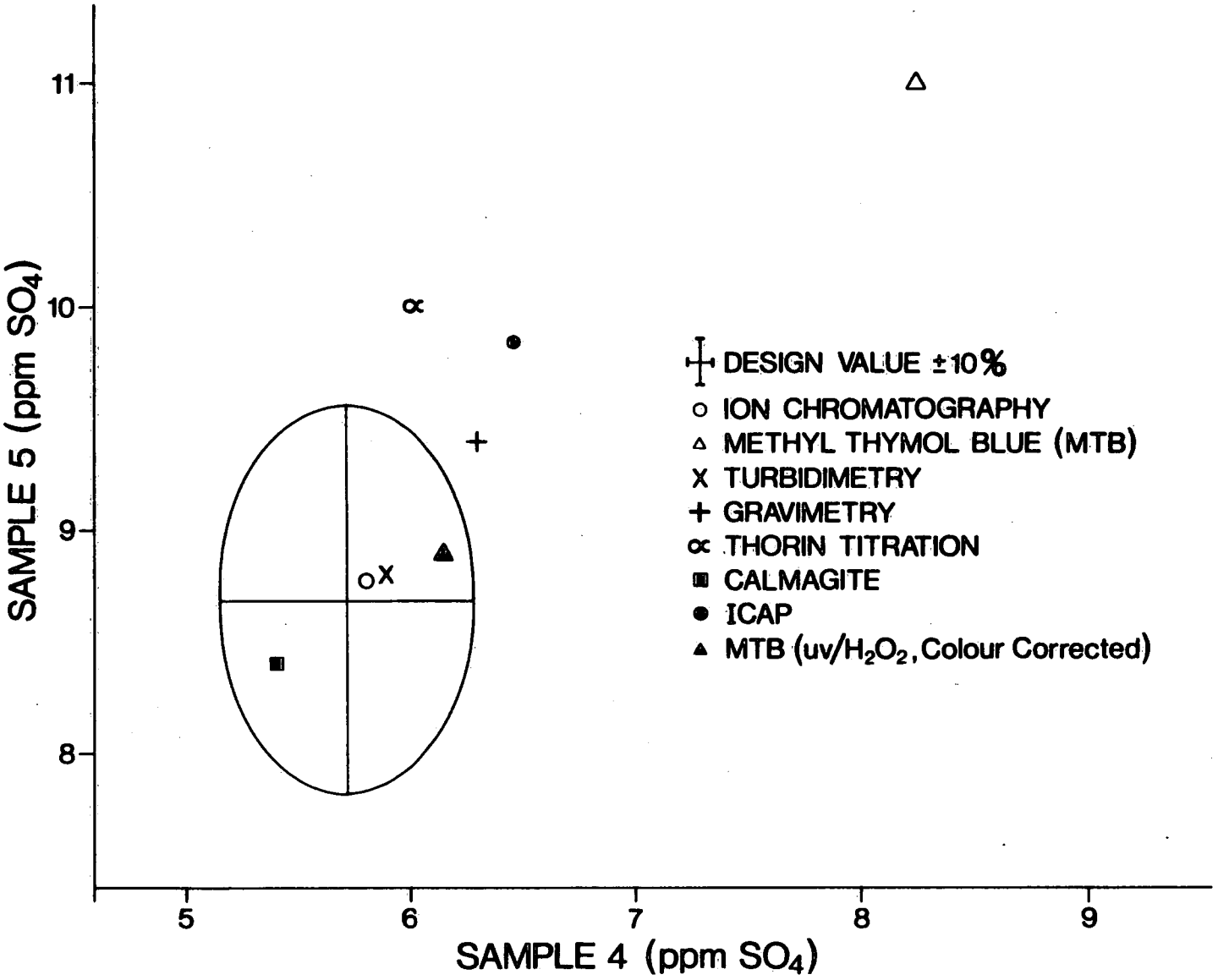

FIGURE 6 . COMPARISON OF THE DESIGN VALUE WITH MEDIAN VALUES IN PAIRED SAMPLES 4 AND 5 DETERMINED BY VARIOUS METHODOLOGIES

TABLE 3 Ion chromatographic results, mg/L

Laboratory Number	Sample Results 1	2	3	4	5
02	4.45	2.8	2.3	5.85	9.2
03	4.25	2.91	2.47	5.48	7.76
04	4.36	3.19	2.45	6.07	8.97
05	4.55	2.85	2.44	6.19	9.04
10	4.21	2.7	2.05	5.65	8.77
12	4.48	2.92	2.42	6.38	9.25
15	4.2	2.7	2.2	5.6	8.9
18	4.81	3.29	3.05	6.44	9.71
19	4.3	2.7	2.4	5.7	8.5
23	2.8 L	4.1 R,H	2.4	5.6	8.5
34	4.27	2.89	2.48	5.79	8.78
47	4.2	2.9	3.3 H	5.9	9.0
51B	4.3	3.1	2.5	6.1	8.7
58	6.3 R,VH	3.4	3.0	6.1	8.9
60	4.39	2.78	2.35	5.68	8.77
64	4.0	2.6	2.2	5.4	8.3
70	3.99	2.8	2.44	5.54	8.20
72	4.0	2.65	2.25	5.45	8.0
74	4.1	2.8	2.8	5.4	8.3
85	3.8	3.1	2.5	29.0 R,VH	8.7
89	4.34	2.72	2.33	5.61	8.5
90	4.03	2.62	2.22	5.61	8.26
96	4.42	2.75	2.54	6.23	9.28
100B	8.6 R,VH	3.7	2.5	6.5	8.9
106	5.14	2.66	2.24	5.74	8.52
124	5.53 H	4.08 R,H	3.0	6.84	8.7
125	4.34	2.83	2.41	5.81	8.8
128	4.27	2.79	2.33	5.87	8.97
130	4.44	2.94	2.53	5.87	9.76
131	4.2	2.7	2.1	5.6	8.7
132	4.55	2.95	2.5	6.95	9.15
Total Labs	31	31	31	31	31
Results Used, n	31	31	31	31	31
Mean, $\bar{x}$	4.30	2.89	2.47	5.90	8.77
Std Dev, s	0.45	0.25	0.28	0.41	0.44
Median	4.30	2.83	2.44	5.81	8.77
Design	4.23	2.73	2.4	5.72	8.69

TABLE 4 MTB colorimetric results, mg/L

Laboratory Number	Sample Results 1	2	3	4	5
02B	6.5	4.6	5.4	7.1	10.0
03B	6.8	5.6	7.1	8.2	11.8
04B	6.6	5.3	6.4	8.1	10.8
05B	6.6	4.2	4.4 VL	6.9	9.7
08	5.0	3.9 L	4.4 VL	5.1 R,VL	7.6 L
10B	6.15	5.19	6.40	8.10	10.3
12	6.39	4.55	5.60	8.24	11.7
13	8.0	7.0	9.0 H	10.0	13.0
19	7.4	5.6	7.4	8.5	11.5
48	3.7 R,VL	6.4	8.2	9.7	12.6
52	6.6	5.6	7.1	8.5	9.9
70B	7.5	6.5	8.0	9.5	12.0
100	6.7	5.6	7.6	8.1	10.0
106	7.92	5.46	6.94	8.37	11.0
110	6.27	5.33	7.0	6.63	9.93
112	10.8 R,VH	8.0 VH	9.6 H	9.6	14.8 H
120	7.6	6.2	7.8	8.7	11.4
Total Labs	17	17	17	17	17
Results Used, n	17	17	17	17	17
Mean, $\bar{x}$	6.80	5.59	6.96	8.39	11.06
Std Dev, s	0.78	1.03	1.44	0.98	1.61
Median	6.60	5.60	7.10	8.24	11.00
Design	4.23	2.73	2.4	5.72	8.69

TABLE 5 Calmagite colorimeric results, mg/L

Laboratory Number	Sample Results				
	1	2	3	4	5
51	4.0	2.4	1.8	5.4	8.4
Total Lab	1	1	1	1	1
Results Used, n	1	1	1	1	1
Mean, $\bar{x}$	4.0	2.4	1.8	5.4	8.4
Std Dev, s	0.0	0.0	0.0	0.0	0.0
Median	4.0	2.4	1.8	5.4	8.4
Design	4.23	2.73	2.4	5.72	8.69

TABLE 6 Turbidimetric results, mg/L

Laboratory Number	Sample Results 1	2	3	4	5
26	< 5.0	<5.0	<5.0	<5.0	<5.0 VL
30	5.0	4.0 H	5.0 VH	6.0	8.0
41	3.5	2.5	2.0	4.9	8.6
43	4.5	3.4	2.8 H	5.9	9.0
47B	3.75	1.55 L	0.4 VL	5.5	7.75
53	3.0	1.2 VL	0.9	5.6	7.9
58B	6.1	3.8	2.2	6.1	9.1
72B	3.0 L	1.0 VL	1.0 L	5.0	9.5
98	6.0 H	4.0 H	5.0 VH	7.0	12.0 R,VH
109	5.14	2.91	1.30	9.97 R,VH	10.19
Labs Reporting	10	10	10	10	10
Results Used, n	9	9	9	9	9
Mean, $\bar{x}$	4.44	2.71	2.29	5.75	8.75
Std Dev, s	1.20	1.21	1.70	0.67	0.86
Median	4.50	2.91	2.00	5.90	9.00
Design	4.23	2.73	2.4	5.72	8.69

TABLE 7 Gravimetric results, mg/L

Laboratory Number	Sample Results 1	2	3	4	5
15B	7.0	4.0	5.0	9.0 VH	13.0 VH
29	81.9 R,VH	2.1 VL	1.6 VL	3.3 VL	7.4
58C	4.1 VL	4.9	4.9	11.5 VH	19.7 VH
102	5.4	5.6	3.0 L	6.3	9.4
112B	12.0 VH	8.0 VH	10.0 VH	10.0 VH	15.0 VH
119	8.4	5.1	<2.0	<2.0 VL	7.2
135	2.0 VL	1.0 VL	4.0	5.0	6.0 VL
Total Labs	7	7	7	7	7
Results Used, n	7	7	7	7	7
Mean, $\bar{x}$	6.48	4.39	4.75	7.52	11.10
Std Dev, s	3.50	2.31	2.87	3.16	5.01
Median	7.00	4.90	4.45	7.65	9.40
Design	4.23	2.73	2.4	5.72	8.69

TABLE 8 Thorin titration results, mg/L

Laboratory Number	Sample Results				
	1	2	3	4	5
53B	4.0	1.0	2.0	6.0	10.0
Total Labs	1	1	1	1	1
Results Used, n	1	1	1	1	1
Mean, $\bar{x}$	4.0	1.0	2.0	6.0	10.0
Std Dev, s	0.0	0.0	0.0	0.0	0.0
Median	4.0	1.0	2.0	6.0	10.0
Design	4.23	2.73	2.4	5.72	8.69

TABLE 10 IC ranking results

Laboratory Number	Total Rank	Average Rank	No. of Samples Ranked	Bias
2	89.0	17.80	5	
3	56.0	11.2	5	
4	106.5	21.3	5	
5	108.0	21.6	5	
10	45.0	9.0	5	
12	114.0	22.8	5	
15	46.0	9.2	5	
18	141.0	28.2	5	High
19	55.5	11.1	5	
23	59.5	11.9	5	
34	83.5	16.7	5	
47	103.0	20.6	5	
51B	97.5	19.5	5	
58	129.0	25.8	5	
60	69.5	13.9	5	
64	16.0	3.2	5	Low
70	41.5	8.3	5	
72	19.5	3.9	5	Low
74	55.0	11.0	5	
85	92.5	18.5	5	
89	53.5	10.7	5	
90	26.5	5.3	5	
96	111.0	22.2	5	
100B	130.5	26.1	5	
106	62.0	12.4	5	
124	129.0	25.8	5	
125	81.5	16.3	5	
128	76.0	15.2	5	
130	118.5	23.7	5	
131	37.0	7.4	5	
132	127.0	25.4	5	

TABLE 9 Results by other methods*, mg/L

Laboratory Number	Sample Results				
	1	2	3	4	5
4C	4.8	3.5	3.6	6.1	8.7
22	4.7	3.3	3.0	6.2	9.1
25	5.34	3.79	3.36	6.45	9.84
Total Labs	3	3	3	3	3
Results Used, n	3	3	3	3	3
Mean, $\bar{x}$	4.95	3.53	3.32	6.25	9.21
Std Dev, s	0.34	0.25	0.30	0.18	0.58
Median	4.80	3.50	3.36	6.20	9.10
Design	4.23	2.73	2.4	5.72	8.69

*Lab 4C = colour corrected results by MTB
Lab 22 = results on samples pretreated by UV/H_2O_2 followed by MTB analysis
Lab 25 = results by ICAP (Inductively coupled Argon plasma)

TABLE 11 MTB ranking results

Laboratory Number	Total Rank	Average Rank	No. of Samples Ranked	Bias
2B	22.5	4.5	5	
3B	52.0	10.4	5	
4B	33.5	6.7	5	
5B	16.5	3.3	5	
8	6.5	1.3	5	Low
10B	26.5	5.3	5	
12	33.0	6.6	5	
13	81.0	16.2	5	High
19	56.0	11.2	5	
48	61.0	12.2	5	
52	42.5	8.5	5	
70B	70.0	14.0	5	
100	44.0	8.8	5	
106	49.0	9.8	5	
110	25.0	5.0	5	
112	83.0	16.6	5	High
120	63.0	12.6	5	

TABLE 12a Turbidity ranking results

Laboratory Number	Total Rank	Average Rank	No. of Samples Ranked	Bias
26	1.0	1.0	1	Insufficient data
30	33.0	6.6	5	
41	18.0	3.6	5	
43	29.0	5.8	5	
47	13.0	2.6	5	
53	12.5	2.5	5	
58B	36.0	7.2	5	
72B	15.5	3.1	5	
98	43.0	8.6	5	High
109	34.0	6.8	5	

TABLE 12b Gravimetry ranking results

Laboratory Number	Total Rank	Average Rank	No. of Samples Ranked	Bias
15B	22.0	4.4	5	
29	15.0	3.0	5	
58C	24.0	4.8	5	
102	19.0	3.8	5	
112B	31.0	6.2	5	
119	13.0	3.25	5	
135	9.0	1.8	5	

TABLE 12c Ranking results for other methods*

Laboratory Number	Total Rank	Average Rank	No. of Samples Ranked	Bias
4C	9.0	1.8	5	
22	7.0	1.4	5	
25	14.0	2.8	5	

*Lab 4 = colour corrected results by MTB
Lab 22 = results on samples pretreated by UV/H_2O_2 followed by MTB analysis
Lab 25 = results by ICAP

APPENDIX

LIST OF PARTICIPANTS

Agriculture Canada

Newfoundland Forest Research Centre (St. John's, Nfld.)

Environment Canada

Environmental Conservation Service
- Atlantic Region, Water Quality Branch Laboratory (Moncton, N.B.)
- National Hydrology Research Institute, River Road Laboratory (Ottawa, Ontario)
- Quebec Region, Water Quality Branch Laboratory (Longueuil, Quebec)
- Water Quality National Laboratory, Water Quality Branch (Burlington, Ontario)

Environmental Protection Service
- Atlantic Region, Chemistry Laboratory (Dartmouth, Nova Scotia)
- Pacific Region, Laboratory Services (West Vancouver, B.C.)
- Northern Forest Research Centre (Edmonton, Alberta)
- Technical Service Branch (Ottawa, Ontario)

Canadian Forestry Service
- Great Lakes Forest Research Centre (Sault Ste. Marie, Ontario)
- Laurentian Forest Research Centre (Ste-Foy, Quebec)

Department of Fisheries and Oceans

Direction de la recherche (Québec, Québec)
Freshwater Institute (Winnipeg, Manitoba)

Indian and Northern Affairs Canada

Water Laboratory, Northern Affairs Program (Yellowknife, N.W. Territories)

Provincial Government Laboratories

Alberta Environment Centre, Water Analysis and Research Group (Vegreville, Alberta)
B.C. Ministry of the Environment, Environmental Laboratory (Vancouver, B.C.)*
Manitoba Department of Environment, Technical Services Laboratory (Winnipeg, Manitoba)
New Brunswick Department of Environment, Environmental Laboratory (Fredericton, N.B.)
Nova Scotia Department of Agriculture and Marketing, Soils and Crops Branch (Truro, N.S.)

Ontario Ministry of Environment, Anion Unit (Rexdale, Ontario)
Ontario Ministry of Environment, Rivers and Lakes Unit (Rexdale, Ontario)
Ontario Ministry of Environment (Thunder Bay, Ontario)
Québec Ministère de l'environnement, Section assurance de la qualité (Ste-Foy, Québec).
Victoria General Hospital, Environmental Chemistry Laboratory (Halifax, N.S.)

Municipal Laboratories

Communauté urbaine de Montréal, Montréal, Québec
Laboratorie C.J. des Baillets (Ville la Salle, Québec)

Industrial and Consulting Laboratories

Acres International Ltd. (Niagara Falls, Ontario)
Association Industrielle Lavale (Pointe-aux-Trembles, Québec)
Atlantic Analytical Services Ltd. (St. John, N.B.)
Barringer Magenta Ltd. (Rexdale, Ontario)
B.C. Research, Chemical Technology Division (Vancouver, B.C.)
Beak Consultants Ltd. (Mississauga, Ontario)
Bondar Clegg & Co. Ltd. (Ottawa, Ontario)
Brenda Mines Ltd. (Peachland, B.C.)
Chemex Labs (Alberta) Ltd. (Calgary, Alberta)
Chemex Labs Ltd. (North Vancouver, B.C.)
Chemical and Geological Labs Ltd. (Edmonton, Alberta)
Cominco Ltd., Exploration Research Laboratories (Vancouver, B.C.)
Concord Scientific Corporation (Downsview, Ontario)
Dearborn Chemical Co. Ltd. (Mississauga, Ontario)
Eco-recherches (Canada) Inc., (Pointe-claire, Québec)
Enviroclean Ltd., (London, Ontario)
Enviro-Test Labs (Edmonton, Alberta)
Monenco Analytical Laboratories (Calgary, Alberta)
Noranda Mines Ltd. (Noranda, Quebec)
Ontario Hydro (Etobicoke, Ontario)
Ontario Research Foundation (Mississauga, Ontario)
Shell Canada Ltd., Calgary Research Centre (Calgary, Alberta)
Stelco Inc. (Hamilton, Ontario)

University Laboratories

Dalhousie University, Biology Department (Halifax, N.S.)
École Polytechnique de Montréal, Labo du genie de l'environnement (Montréal, Québec)
Memorial University of Newfoundland, Chemistry Department (St. John's, Newfoundland)
Waterloo University, Department of Earth Science (Waterloo, Ontario)

* Participated in Study No. 29 also.