Environment Canada Environnement Canada

National Interlaboratory Quality Control Study No. 29

Sodium, Potassium, Magnesium, Calcium and Hardness in Natural and Spiked Water Samples

V. Cheam and A.S.Y. Chau

REPORT SERIES NO. 74

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Abstract

This report describes an interlaboratory comparison of the analysis of Na, K, Mg, Ca and hardness of water. Some fifty Canadian laboratories participated in the analysis of six unpreserved water samples. The analyte concentrations were designed to be approximately at the middle of the wide concentration range encountered in environmental studies. Analytical data were assessed by several statistical treatments to identify outlying results and laboratory performance. Some laboratories performed extremely well, whereas the performance of others indicated a need to reevaluate seriously their internal quality control practices. It is the application of an analytical method, not the method itself, that usually determines how a laboratory performs.

Résumé

Ce rapport décrit une étude interlaboratoires de contrôle de la qualité des déterminations de la teneur en Na, en K, en Mg et en Ca ainsi que de la dureté de l'eau. Quelque 50 laboratoires canadiens y ont participé en analysant six échantillons d'eau non stabilisés. Les concentrations des constituants se trouvaient à peu près au centre de l'intervalle étendu des concentrations que l'on peut trouver dans l'environnement. Plusieurs traitements statistiques des données d'analyse ont été effectués afin de déterminer les résultats aberrants et la performance des laboratoires. Certains laboratoires se sont révélés extrêmement compétents. D'autres ont manifestement besoin de réévaluer leurs modes de contrôle interne de la qualité. C'est l'application d'une méthode d'analyse et non la méthode elle-même qui détermine ordinairement la compétence d'un laboratoire.

List of Symbols

n Number of results used in calculating the sample mean ($\bar{x}$)

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

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

S_j Standard deviation of sample j, j = 1 - 6

S_g Standard deviation using difference and average difference between m paired results,

$$S_g = 0.886 \sum_{j=1}^{m} \frac{|di - d|}{m}$$

where di is algebraic difference between results of sample j + 1 and sample j, and

$$d = \frac{\sum_{i}^{m} di}{m}$$

C.V. Coefficient of variation, C.V. = $(S/\bar{x})$ 100

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

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INTRODUCTION

This study forms part of the national interlaboratory quality control program of the Quality Assurance Program at the National Water Research Institute (NWRI). It supplements studies Nos. 1, 7 and 14 published in 1970, 1974 and 1978, respectively (1, 2, 3). Since the 1978 study, the number of new participants and new analytical methodologies has greatly increased. The present study offers a continuing intercomparison program to the national participants, and an opportunity to assess data comparability and data compatibility between conventional and new techniques. New approaches to assessing data are presented along with conventional ones.

STUDY DESIGN

Six test samples were used (Table 1). The samples were synthetic, natural or spiked. The concentration range was designed to be approximately at the middle of the wide concentration range encountered by the participants — low levels in very soft waters and high levels in sewage samples. The design also was such that a sample could be statistically evaluated on a single sample basis, or paired with another sample, or combined with the rest in a ranking process. The test samples are described in Table 1.

Table 1. Description of Samples

Test sample	Type
1	Synthetic
2	Synthetic
3	Synthetic
4	Lake Superior water
5	Spiked Lake Superior water
6	Spiked Lake Superior water

No preservative was used, but participants were requested to store samples at 4°C until analysis. Each laboratory selected its own analytical method.

EXPERIMENTAL

Chemicals

The chemicals used were purchased from the Fisher Scientific Co.: NaCl (S-271), $MgSO_4 \cdot 7H_2O$ (M-63), $CaCl_2 \cdot 2H_2O$ (C-79), KNO_3 (P-263 and KCl (P-217).

Sample Preparation

All containers, glassware and plasticware were chromerge cleaned, rinsed with hot tap water and deionized distilled water, and stored with deionized distilled water for several weeks before use (4).

Both synthetic and spiked bulk samples were prepared in large polyethylene containers. Appropriate stock solutions were added to each bulk water sample, the volume of which was estimated from its weight and density. Each solution was well homogenized by a closed circuit mixing before being subsampled into polyethylene test samples. Most test bottles were of 500-mL size, except a few larger ones, as requested by some participants.

Analysis

Each participant had a choice of analytical method(s) and was encouraged to use more than one technique. A brief outline of each method was requested from the participants.

For the analysis of sodium and potassium, flame photometry and atomic absorption spectrometry were used more than other methods, which include ion chromatography (IC), inductively coupled argon plasma (ICAP), flame emission, and instrumental neutron activation analysis (INAA).

Most laboratories used atomic absorption spectrometry for calcium and magnesium analysis. Other methodologies employed were atomic emission, EDTA titration, ion chromatography, neutron activation or calculation.

About 40% of participants determined hardness by EDTA titration, whereas the rest calculated from atomic absorption data.

DATA EVALUATION

All positive analytical data reported by the participants were statistically treated for determination of outliers. (The "less than" values are not included in the statistical analyses.) The data evaluation begins with single sample treatment (Greenberg [5, 6] or 2S and Grubbs procedures [7]), then considers the paired sample treatment (Greenberg [5]; Cheam and Aspila [8]), and finally assesses all samples simultaneously by a ranking procedure (9) to determine laboratories with pronounced systematic errors.

The Greenberg criterion of data unacceptability for single samples is used here to determine unacceptable results, i.e., those outside the range $\bar{x}_j \pm 2\,S_j$. The standard deviation, S_j, was calculated after discarding suspect results by twice applying the 2S procedure. This standard deviation was further used in paired sample treatment, where the sum of two standard deviations is taken as the radius of a circle.

RESULTS AND DISCUSSION

Sodium

Table 2 presents all sodium analytical results reported by the participating laboratories along with their analytical method, detection limit and the derived interlaboratory statistics. Tables 2 to 26 may be found on pages 25 to 44. The mean and standard deviation values were obtained after the raw data had been treated by the 2S procedure. The letter "R" beside an analytical result indicates that the result was determined to be an outlier according to the Grubbs test (7), whereas underlining indicates use of the 2S procedure.

The single sample treatment of data detected several suspect results, as summarized in Table 3. Each line in the table identifies a suspect analytical result (by 2S and/or Grubbs test) produced by a certain laboratory in a water sample.

The sodium analytical data were further treated by graphical presentation of paired results (10) from paired samples of similar composition. Figures 1, 2 and 3 each paired two synthetic samples, whereas Figure 4 paired two spiked samples. Each figure contains ample information about laboratory and method performance with respect to means and medians and their circles of acceptability limit.

There are two circles in each figure. The first circle has its centre at the intersection of the dashed lines whose coordinates are the mean value of each of the paired samples. Its radius is the sum of two standard deviations. To facilitate identification in the figures, this type of circle is tagged with "Σs" throughout. Take Figure 1 as a specific example. The centre of the Σs circle is the intersection of the mean in sample 1 and the mean in sample 2, whereas the radius is equal to $S_1 + S_2$, where S_1 is standard deviation for sample 1 and S_2 is that for sample 2.

The second circle, on the other hand, is centred by the intersection of the median values. Its radius is equal to 2 Sg, where Sg was calculated from the difference and average difference between the paired results (5).

In a study of arsenic and selenium in water, Cheam and Aspila (8) discussed in detail the use of the two types of circles to treat paired data. They concluded that the Σs circles adequately identified unacceptable paired results. Furthermore, with respect to data handling, it is much easier to handle the Σs than the Sg data treatment. Thus in this study, we solely used the Σs treatment for the evaluation summary of sodium results (Table 6) as well as those of other constituents to be discussed below. The circles with 2 Sg as radius were illustrated for direct visual comparison with Σs circles only.

In Figures 1 to 4, the paired results tend to cluster in quadrant I and quadrant III as if they could be best represented by 45° lines passing through either one of the circle centres. This behaviour, in general terms, indicates that the participants are able to produce precise, although not necessarily accurate, results (10). Some tend to produce precise but biased high results (for example Laboratory 52), whereas others produce precise but biased low results (for example Laboratory 80). The absolute accuracy could not be calculated here because the samples used were not certified materials. Nevertheless, since the means and medians are very close to each other and the recoveries are from 96% to 98%, indications are that the Σs circles envelop paired results that have acceptable precision and accuracy. The paired results outside the circles thus have questionable accuracy (Table 4).

The ion chromatography technique, represented by solid squares in the figures, is used by two laboratories for sodium analysis. Laboratory 4B managed fairly well, producing three pairs inside and one pair outside the Σs circles. Laboratory 60, however, produced all four pairs outside the circles and appeared to experience significant systematic errors (Figs. 3 and 4) as well as random ones (Figs. 1 and 2).

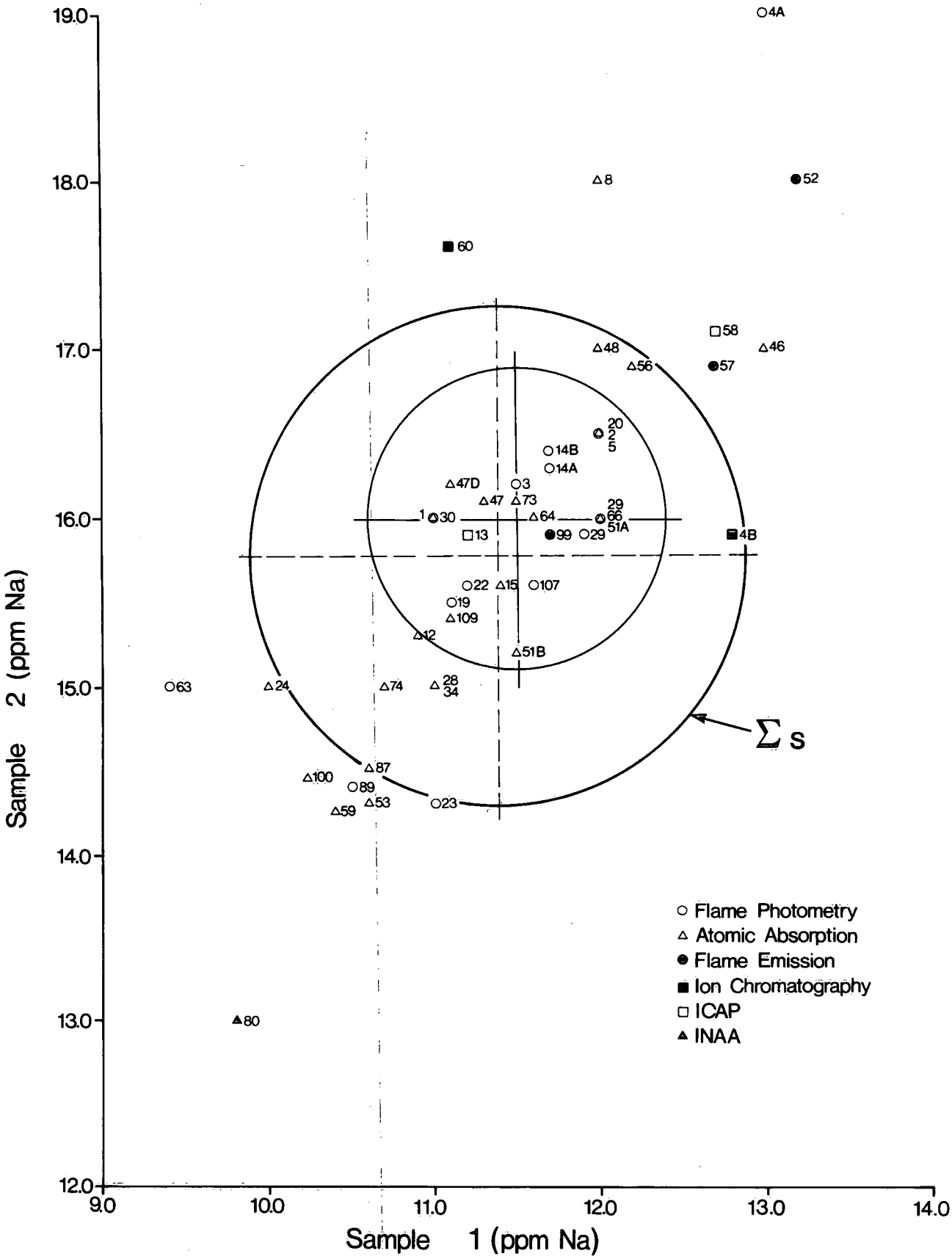

Figure 1. Sodium paired sample plot for samples 1 and 2.

In another incidence, however, Laboratory 4B generated a pair of results uncharacteristically located in quadrant II (Fig. 2), which might suggest that some element of random error is present. As a direct contrast, consider Laboratory 4A, which used flame photometry for sodium analysis. All four 4A locations are in quadrant I (Figs. 1 to 4) and outside the circles, which implies predominance of systematic errors. It thus seems that some random

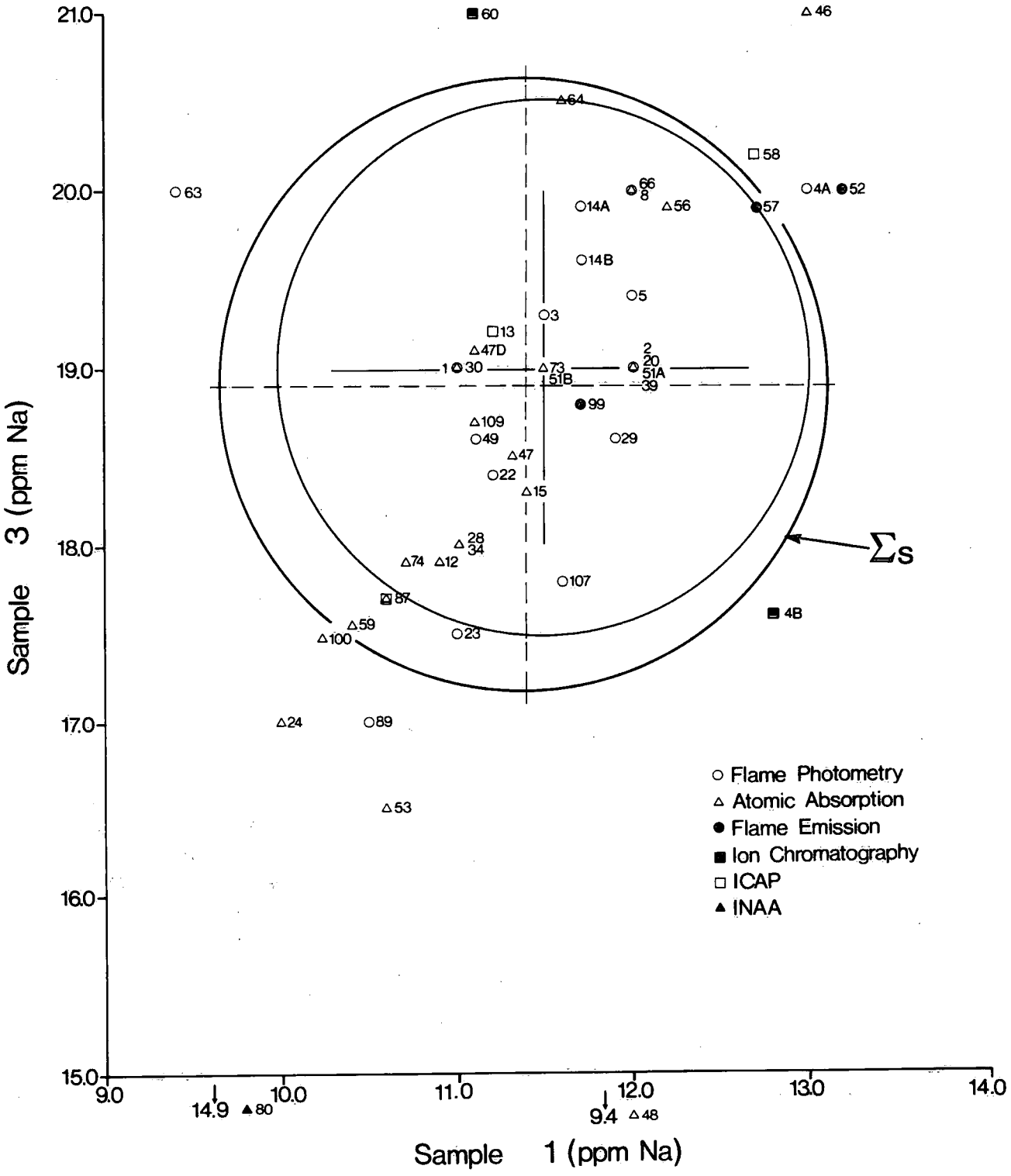

Figure 2. Sodium paired sample plot for samples 1 and 3.

errors exist in the IC system. Perhaps a more concrete conclusion could be made if more participants had used the ion chromatography technique.

Instrumental neutron activation analysis was used by one laboratory only, Laboratory 80. The paired results are all in quadrant III (Figs. 1 to 4) and show the existence of pronounced systematic errors.

Two participants used inductively coupled argon plasma. Laboratory 13 produced excellent results with all four pairs anchored right in the middle of circles. Laboratory 58, on the other hand, seemed to experience some systematic errors, as three out of four pairs are outside the Σs circles and in quadrant I.

The more conventional methods—flame photometry, atomic absorption and flame emission—were used by most participants, and mostly generated acceptable results. Nevertheless, a few laboratories did report significantly low or high results (Figs. 1 to 4). Table 4 summarizes all suspect sodium results as determined by paired sample treatment.

The sodium interlaboratory data have so far been treated first on a single, then a paired sample basis. Now we wish to treat the whole ensemble of data simultaneously,

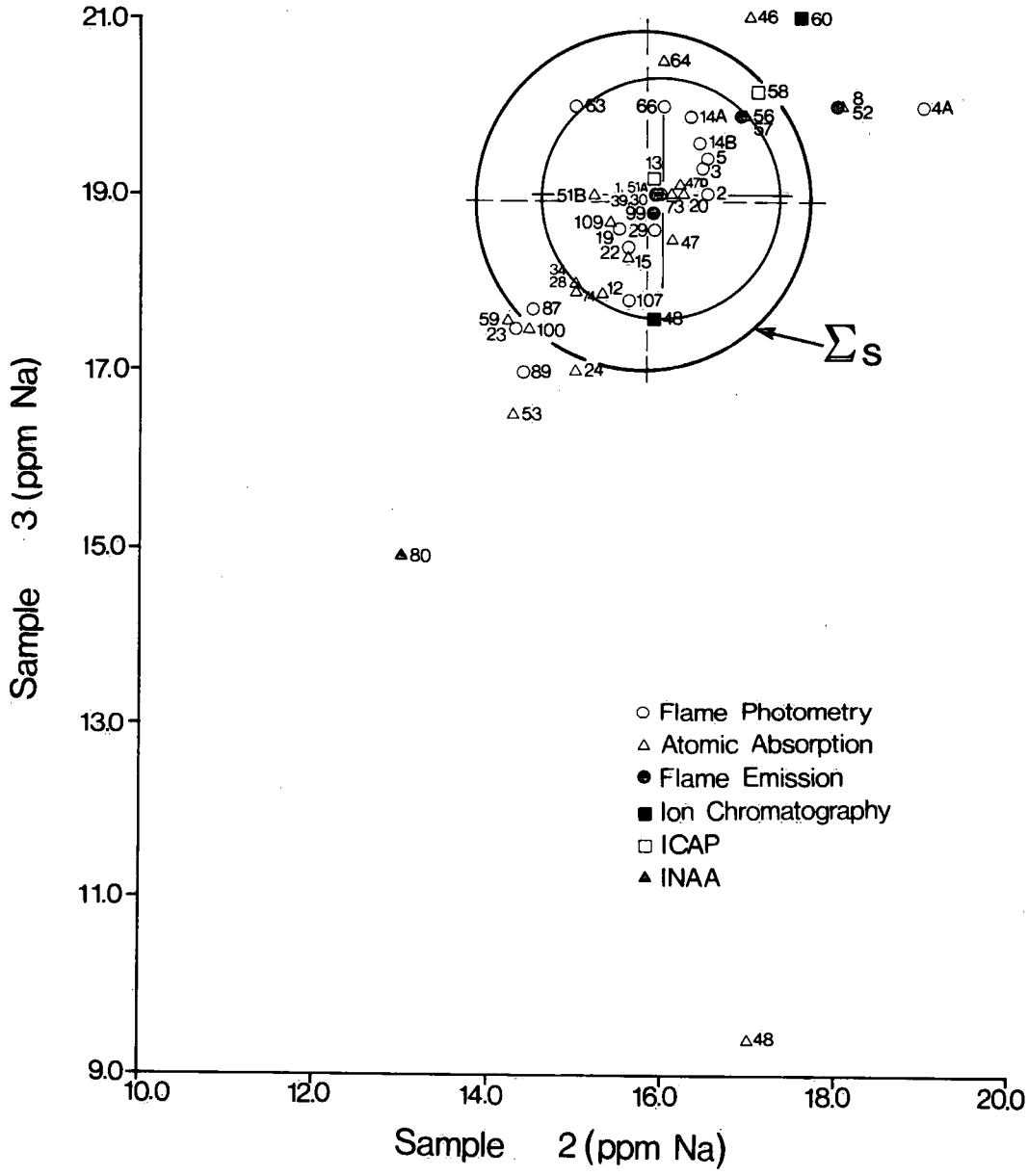

Figure 3. Sodium paired sample plot for samples 2 and 3.

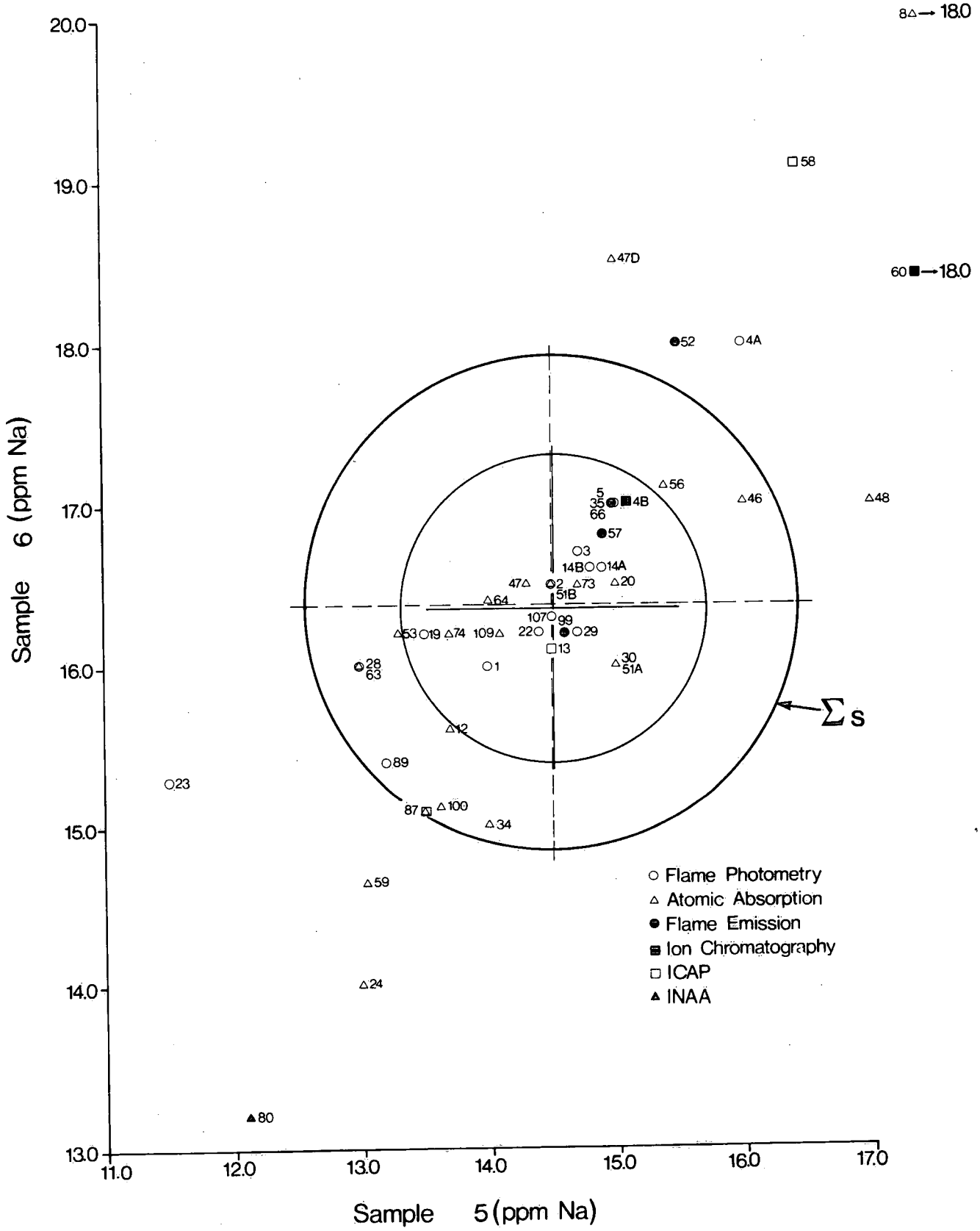

Figure 4. Sodium paired sample plot for samples 5 and 6.

using the basic ranking procedure originated by Youden (9). Table 5 shows the sodium ranking results with a summary of flagging and identification of laboratories with pronounced systematic errors. Laboratories with low average rank values of 4.6 to 6.0 were flagged several times with "VL" (very low) and were determined as having consistently biased low results (top of table). Laboratories with high average rank values of 43.7 to 38.4 were flagged several times with "VH" (very high) and were determined to be biased high (bottom of table). Those laboratories producing average values around 24 had none, or very few, of the six analytical results flagged; in fact, these laboratories must have produced paired results located well within the circles most of the time (Figs. 1 to 4).

Table 6 summarizes the evaluation results by the various statistical tests. The flagging frequency for each test is given for the laboratories listed in the upper part of the table. The unflagged laboratories, producing no suspect results, are listed at the bottom of the table.

Potassium

The analytical data reported by the participants are given in Table 7 along with the resulting statistics. The means and medians are essentially identical and the recoveries range from 98% to 106% for the six samples. Table 8 summarizes the single sample treatment results.

Figures 5 to 7 illustrate the graphical diagnosis of paired potassium results from samples 1, 2 and 3. The results from samples 4, 5 and 6 were not considered because the concentrations were very different from each other and for samples 1 to 3, so that the Youden plot could not be applied. As in the case of sodium, the circles tagged with "Σs" have the intersection of means as their centres and the sum of standard deviation as their radii. Similarly, the other circles are related to medians and Sg defined earlier.

The figures clearly bring out the presence of systematic errors in some laboratories. Laboratory 99 has all

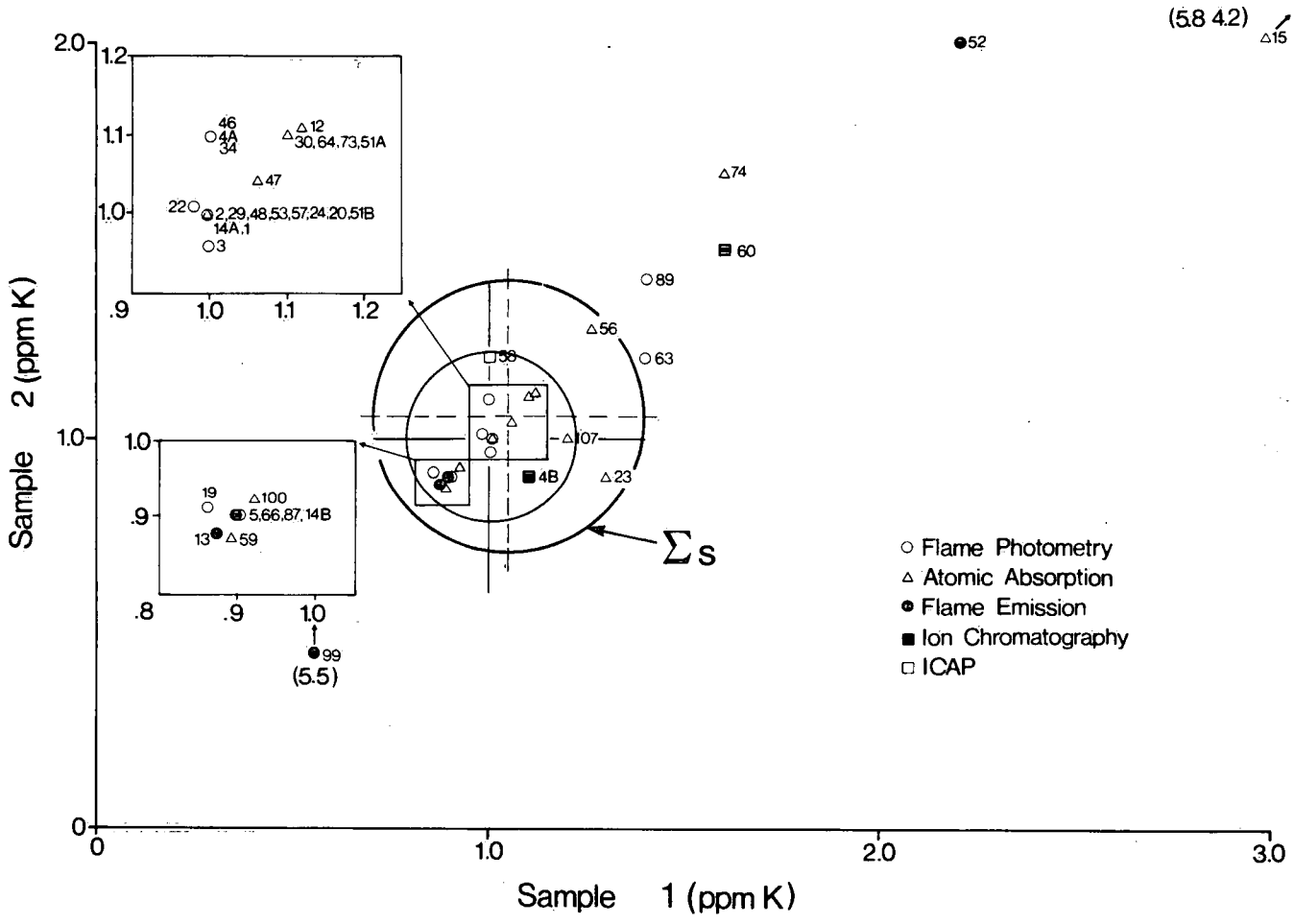

Figure 5. Potassium paired sample plot for samples 1 and 2.

three points in quadrant III and outside the circles, indicating negative systematic errors. Positive systematic errors are found in Laboratories 15, 52, 60, 74 and 89, which have coordinates in quadrant I and beyond the acceptability circles. Table 9 summarizes the paired sample treatment results.

Ion chromatography was utilized by Laboratories 4B and 60, yielding quite contrasting results. The system was successfully applied by Laboratory 4B, which has its Cartesian points well within the circles of Figures 5 to 7. In contrast, its application by participant 60 was not so successful, apparently being plagued with serious positive systematic errors.

The ICAP system applied by Laboratory 58 yielded acceptable paired results, as indicated by their points in the circles, but produced two suspect results in samples 4 and 5 (Table 7). This is further confirmed by the ranking test, which identifies the two results as very low (Table 10).

The ranking process takes every sample into account, ranks each analytical result relative to others within a sample, and totals the ranks for each participant. The average ranks are then calculated and are arranged in ascending order so that the smallest (on top) and the largest (at bottom) may be easily identified as being biased low and biased high, respectively. Table 10 suggests that

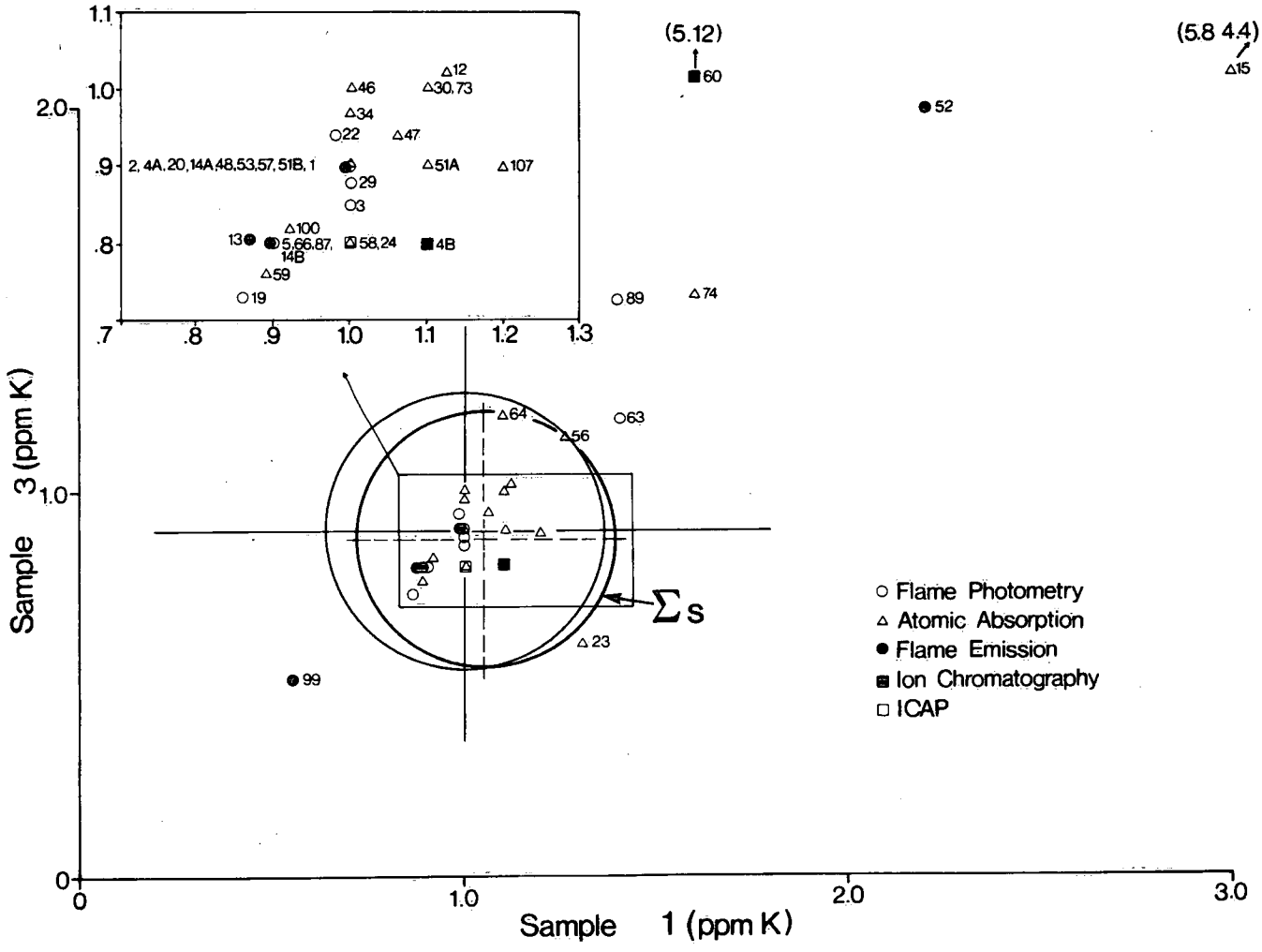

Figure 6. Potassium paired sample plot for samples 1 and 3.

eight of the participants (four on top, four at bottom) had serious systematic errors.

Laboratories 19, 59 and 13 were rarely flagged – in fact, only four times with "L" out of a total of 18 – and yet they were determined to be biased low (Table 10). A similar result appeared in an earlier study on arsenic (8) where a laboratory seemed to do well, as it had no outliers nor unacceptable individual results, yet a ranking process identified it to be biased low. Here, Laboratory 59 has not even a single flag "L", yet is tagged as biased low. A look at their raw data reveals that they are not excessively, but consistently low. This once again shows the usefulness of the ranking technique in identifying the presence of systematic errors. However, it is not suitable for identifying random errors, as will be seen later under discussions on calcium.

On the other hand, when a laboratory is not tagged with "biased low" or "biased high," it does not necessarily indicate that the laboratory altogether eliminates systematic elements in the methodology application. Table 10 illustrates this point for Laboratories 56 and 89, which were not tagged but were flagged with numerous "VH" (very high) results. A check with Table 7 will offer further confirmation.

Unflagged laboratories producing no suspect results in any of the data treatments are listed in Table 11, where the evaluation summary is given also.

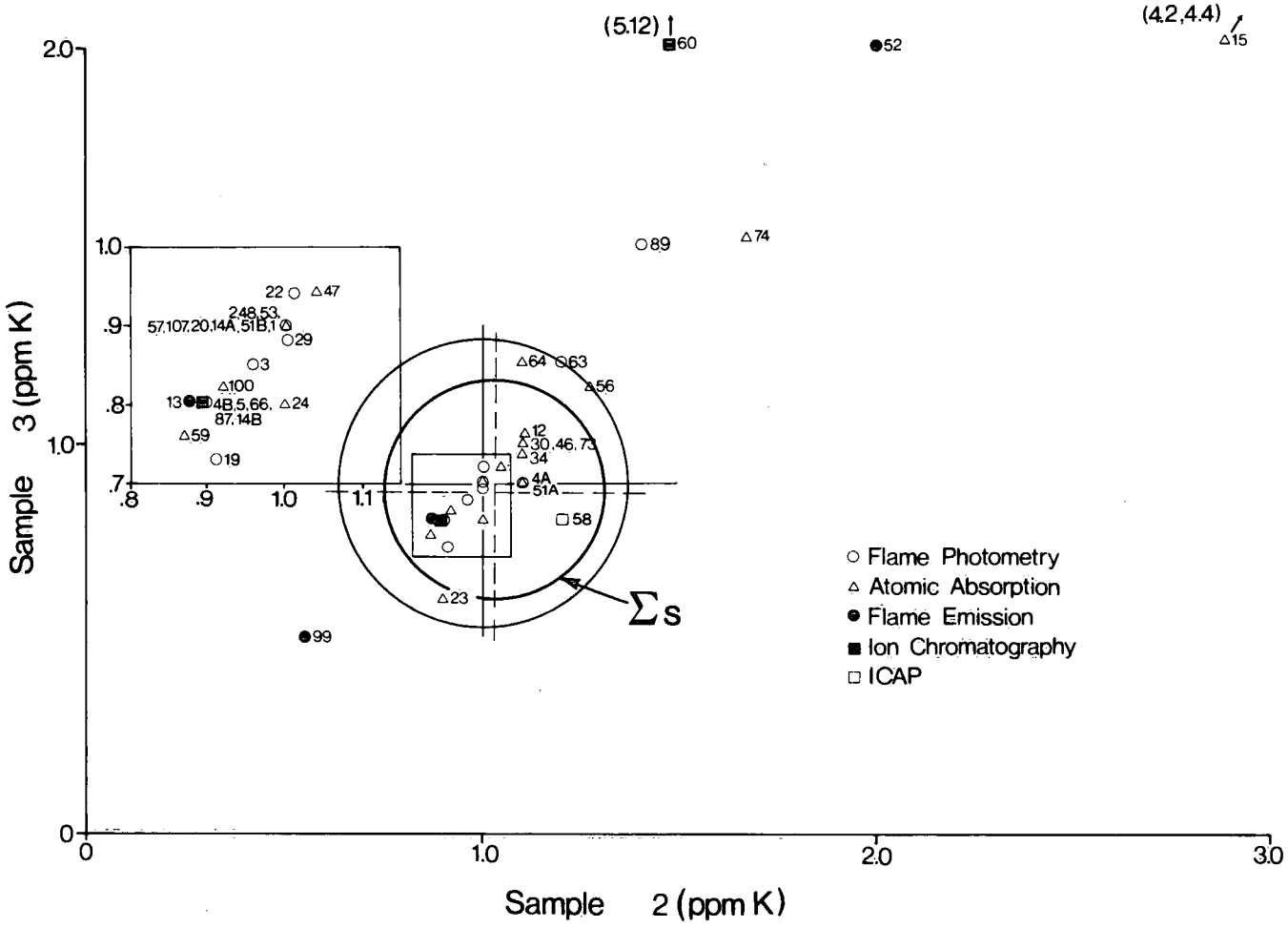

Figure 7. Potassium paired sample plot for samples 2 and 3.

Magnesium

Table 12 presents the raw interlaboratory data along with the median and mean values and other related statistics. It also indicates that suspect results by "R" and underlining, which are summarized in Table 13.

Figures 8 to 11 are paired sample plots for paired results of samples 1 and 2, 1 and 3, 2 and 3, and 5 and 6. As mentioned above, two circles were drawn about the intersection of means and medians. The points are again spread about the imaginary lines going through quadrants I and III in all four figures indicating the presence of systematic errors, in particular for those that are consistently outside the acceptability Σs circles. For example, all four points for Laboratory 66 are in quadrant III and those for Laboratory 58 are in I.

The ion chromatography system has been successfully applied by participant 19B, as all their four points lie well within the circles. Neutron activation results of Laboratory 80 are also assessed acceptable, since they are in the Σs circles.

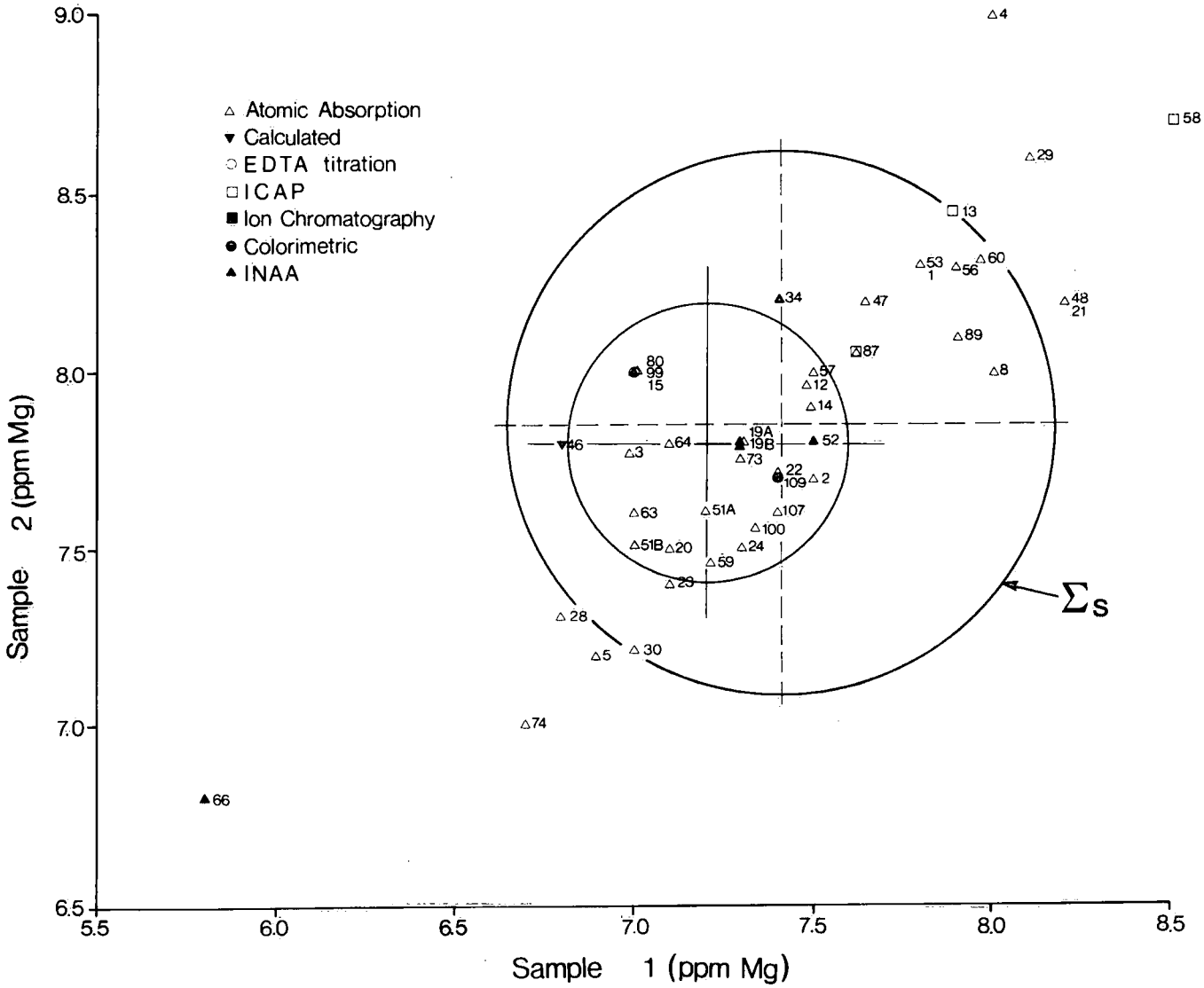

Figure 8. Magnesium paired sample plot for samples 1 and 2.

The plasma system (ICAP) was used by three laboratories, but their results were quite different. All four paired results of Laboratory 87 were acceptable (well inside Σs circle), whereas those of Laboratory 13 were borderline and those of Laboratory 58, clearly unacceptable.

Atomic absorption spectrophotometry was used by most participants with different degrees of performance. Colorimetry, on the other hand, was used by only one laboratory, Laboratory 22, and with excellent results.

The results of paired sample treatment are listed in Table 14. The ranking results are given in Table 15. Note that one laboratory was determined to be biased low even though it is flagged only once with "L". Table 16 summarizes all evaluation results.

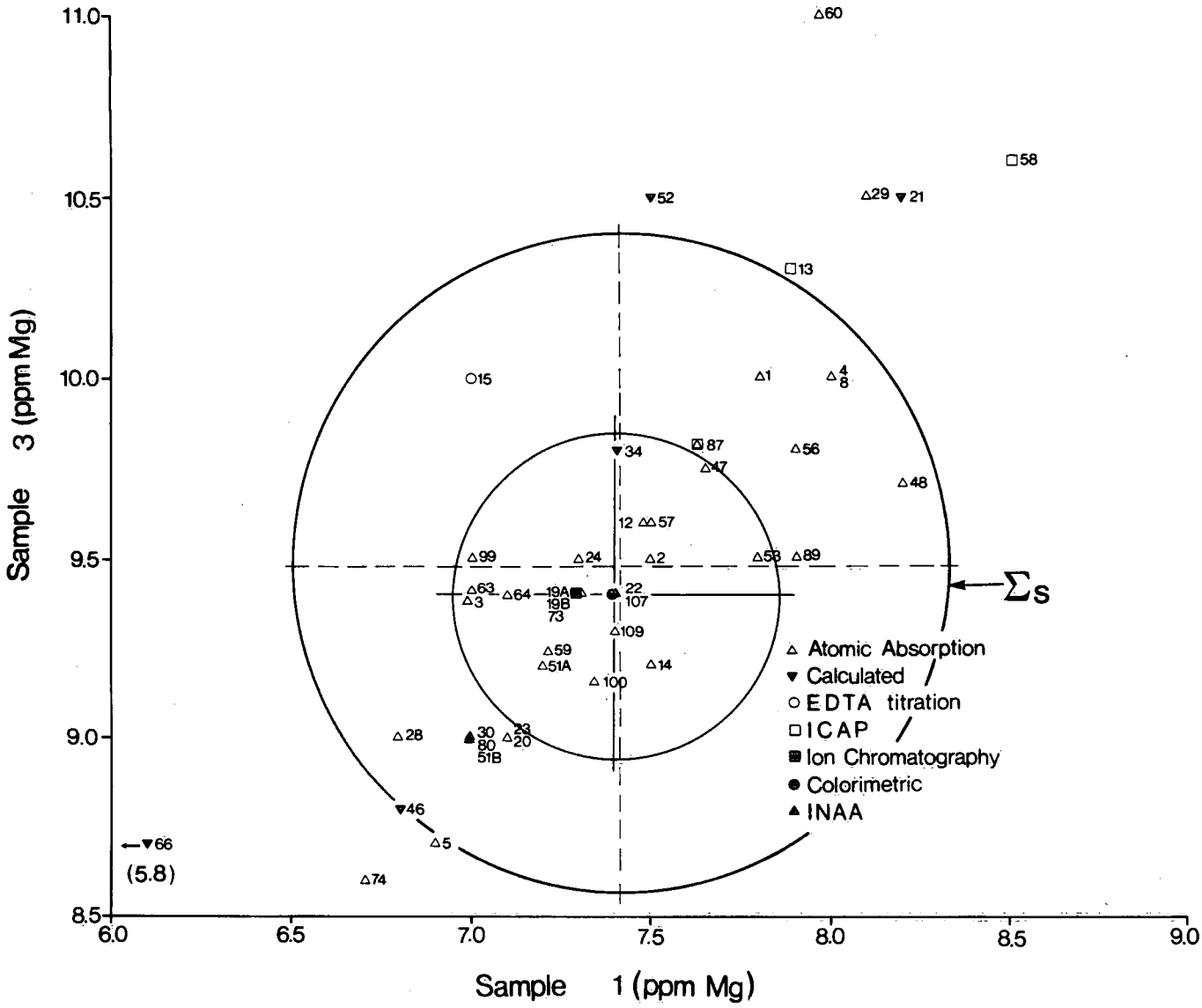

Figure 9. Magnesium paired sample plot for samples 1 and 3.

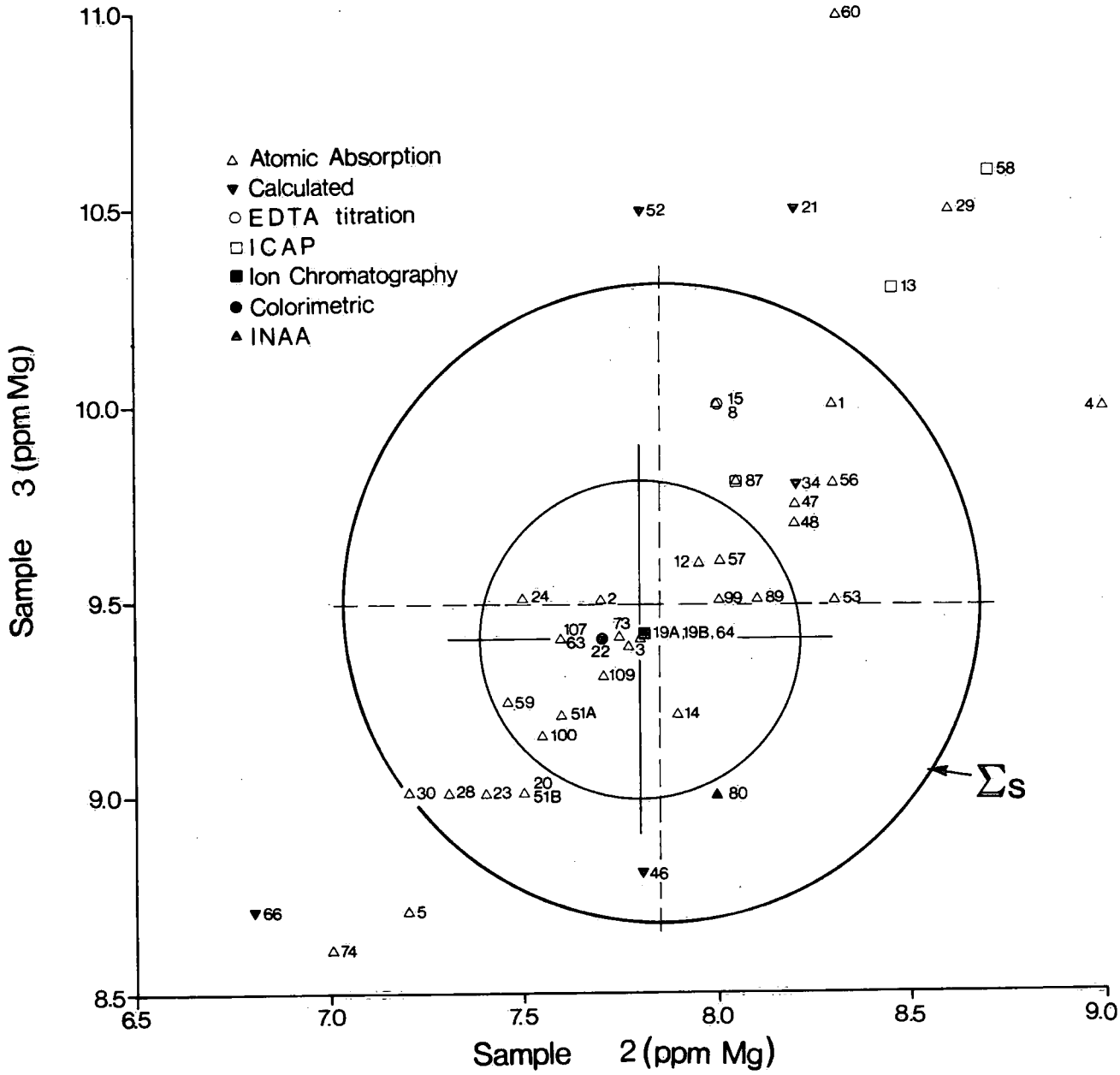

Figure 10. Magnesium paired sample plot for samples 2 and 3.

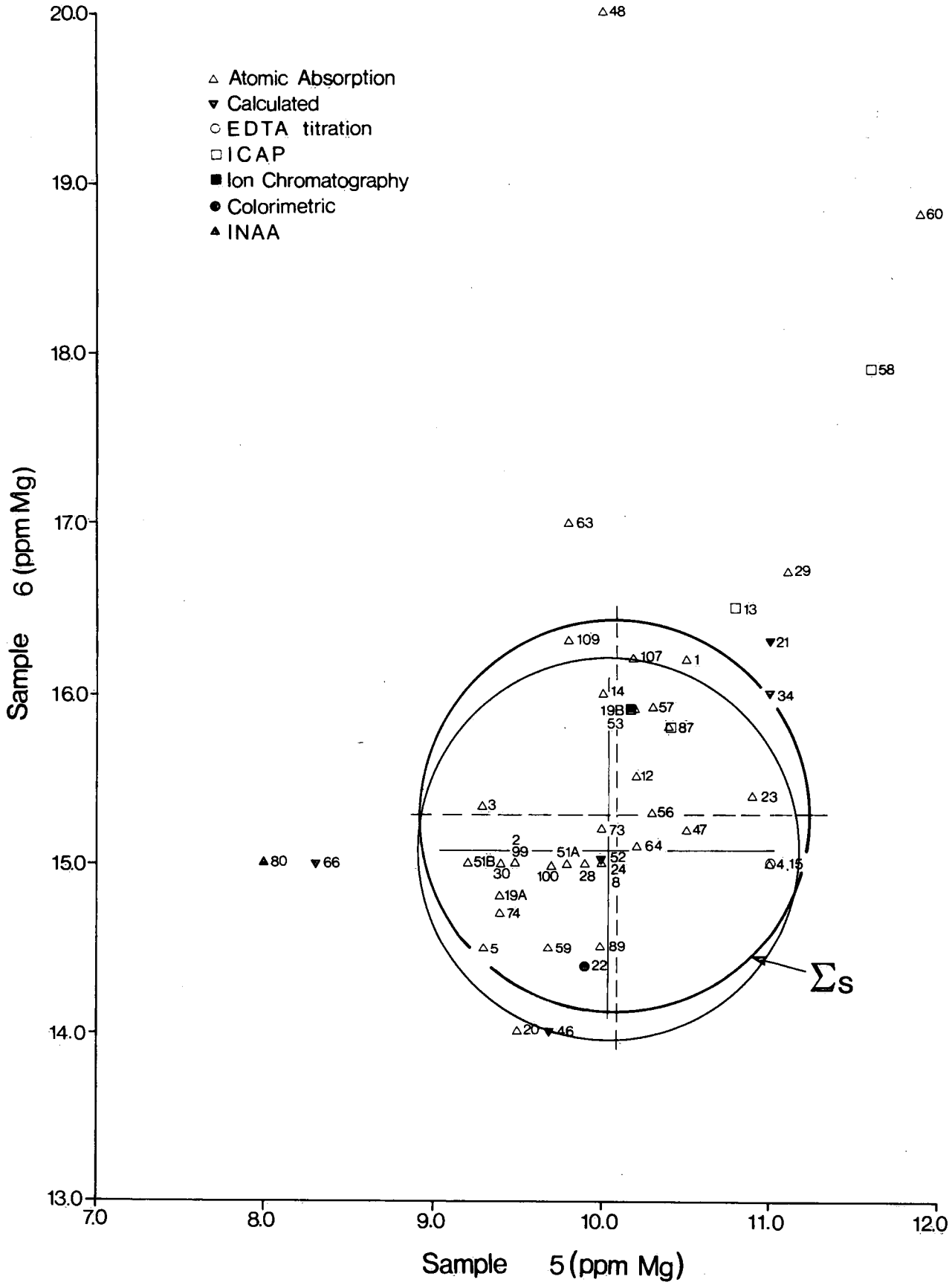

Figure 11. Magnesium paired sample plot for samples 5 and 6.

Calcium

The raw data are presented in Table 17, and the suspect results detected by the single sample treatment are given in Table 18.

Figures 12 to 14 represent paired sample plots for samples 1 vs. 2, 1 vs. 3, and 2 vs. 3, respectively. It can be seen from the figures that systematic elements exist in this ensemble for the interlaboratory data, as evidenced by the behaviour of points in quadrants I and III.

The intersection of means and that of medians in all three figures are close to each other, and they are respectively the centres of Σs and Sg circles. The results of Laboratories 58, 73 and 74 appear to be biased high, their points being in quadrant I and outside the circles. On the other hand, the results of Laboratories 60, 80 and 47D seem biased low, as they are in quadrant III and outside the circles. Laboratory 4 shows some pronounced random errors, as all three points are outside the circles, two being in quadrant II and one in quadrant III.

Ion chromatography is successfully applied by Laboratory 19B; all their results are very close to the means and medians of all samples (Fig. 12 to 14, Table 17).

The INAA produced comparable results, although a few tend to be low (Table 17, Figs. 12 to 14). The ICAP technique was used by Laboratories 13, 58 and 87; although Laboratory 87 results are within the Σs circles, the other results are mostly outside these circles, in particular Laboratory 58. Most laboratories used the atomic absorption technique with varying degrees of success.

Table 19 summarizes the results of paired sample treatment. The ranking results are given in Table 20, where the flagging results are summarized along with the identification of laboratories with pronounced bias results. Note that Laboratories 63 and 99 rank near the overall average, yet they are flagged many times randomly with "L" and "H" (Table 20). This again points out the specialty of the ranking technique in identifying systematic and not random errors. All evaluation results are summarized in Table 21.

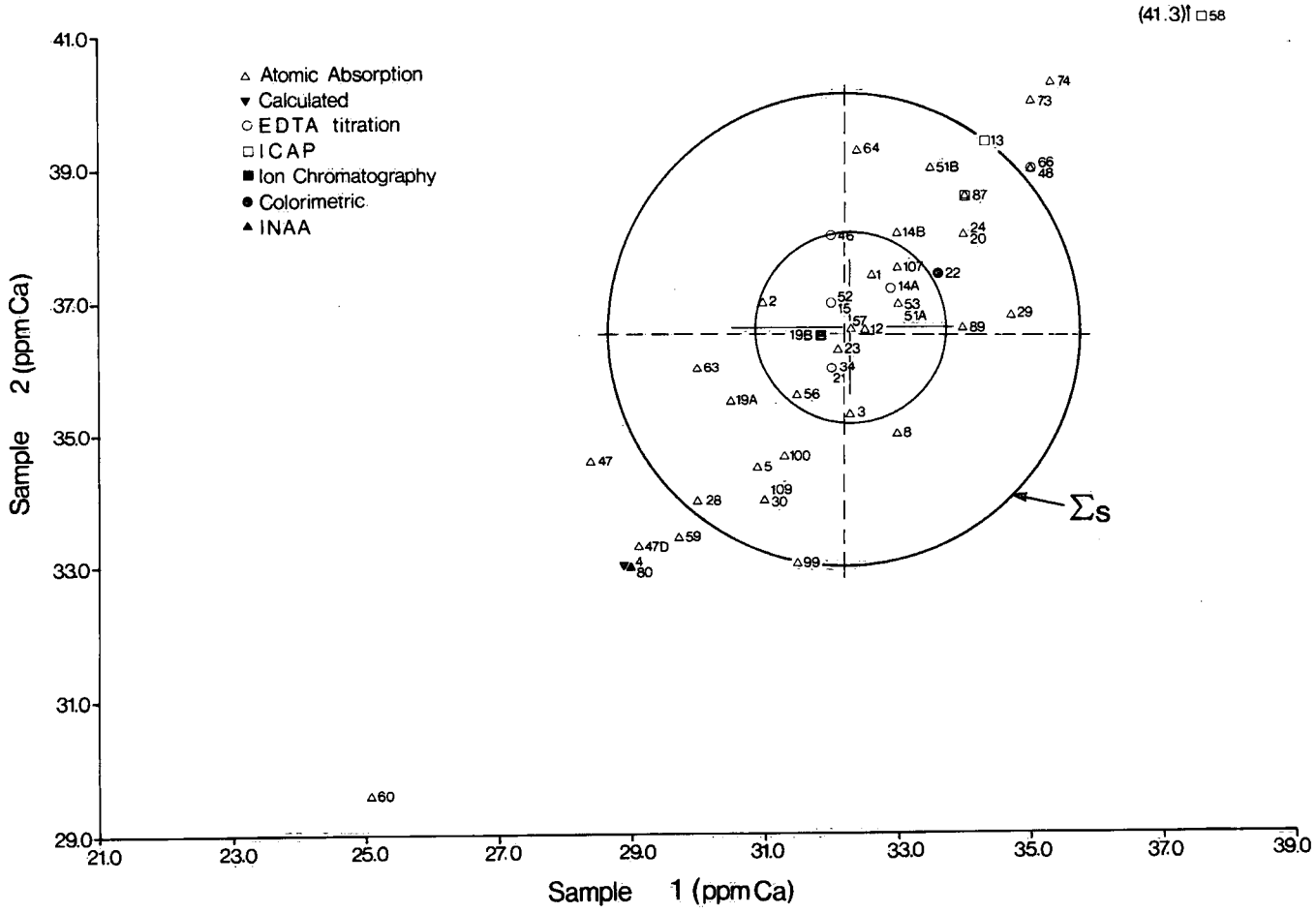

Figure 12. Calcium paired sample plot for samples 1 and 2.

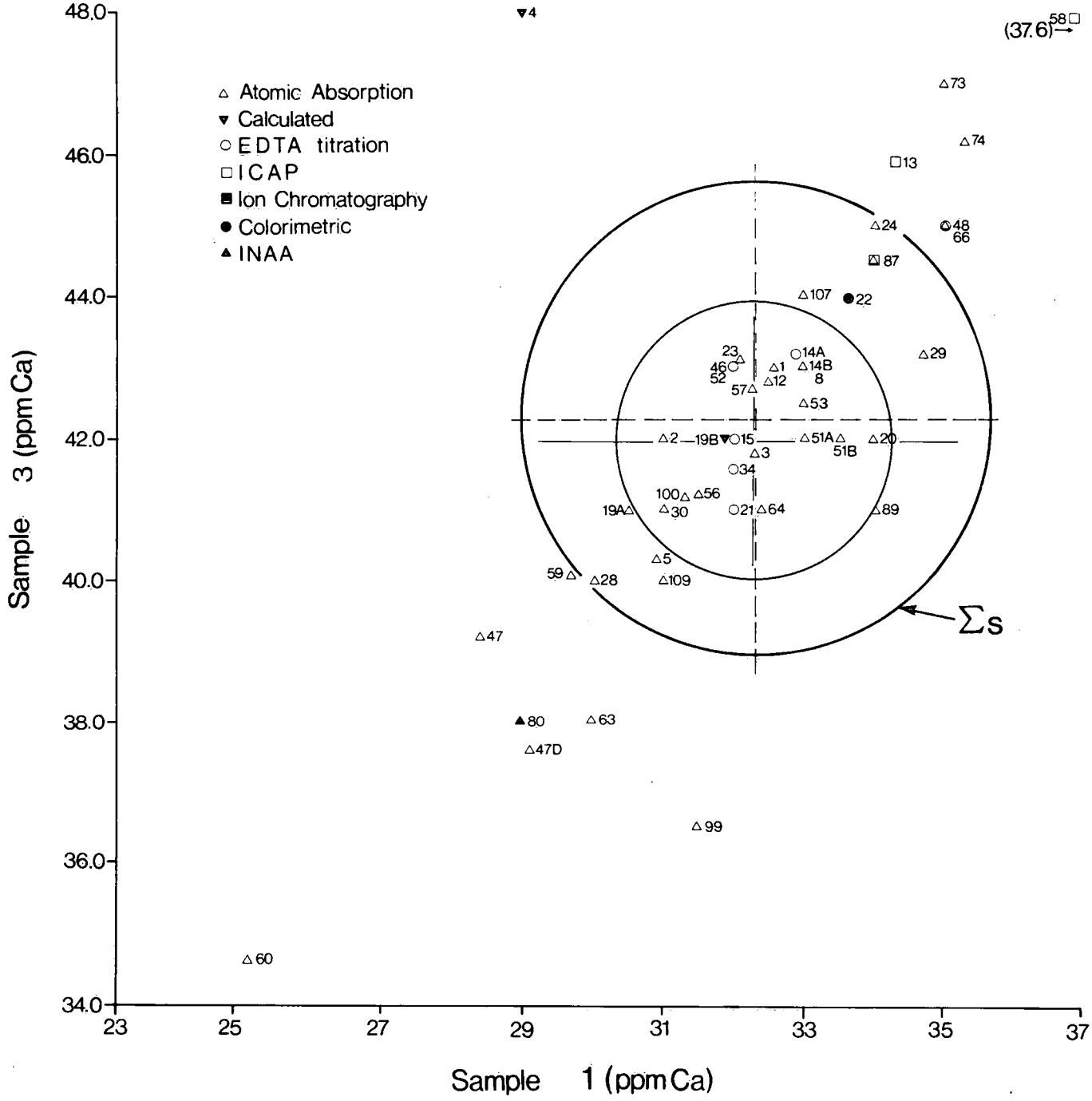

Figure 13. Calcium paired sample plot for samples 1 and 3.

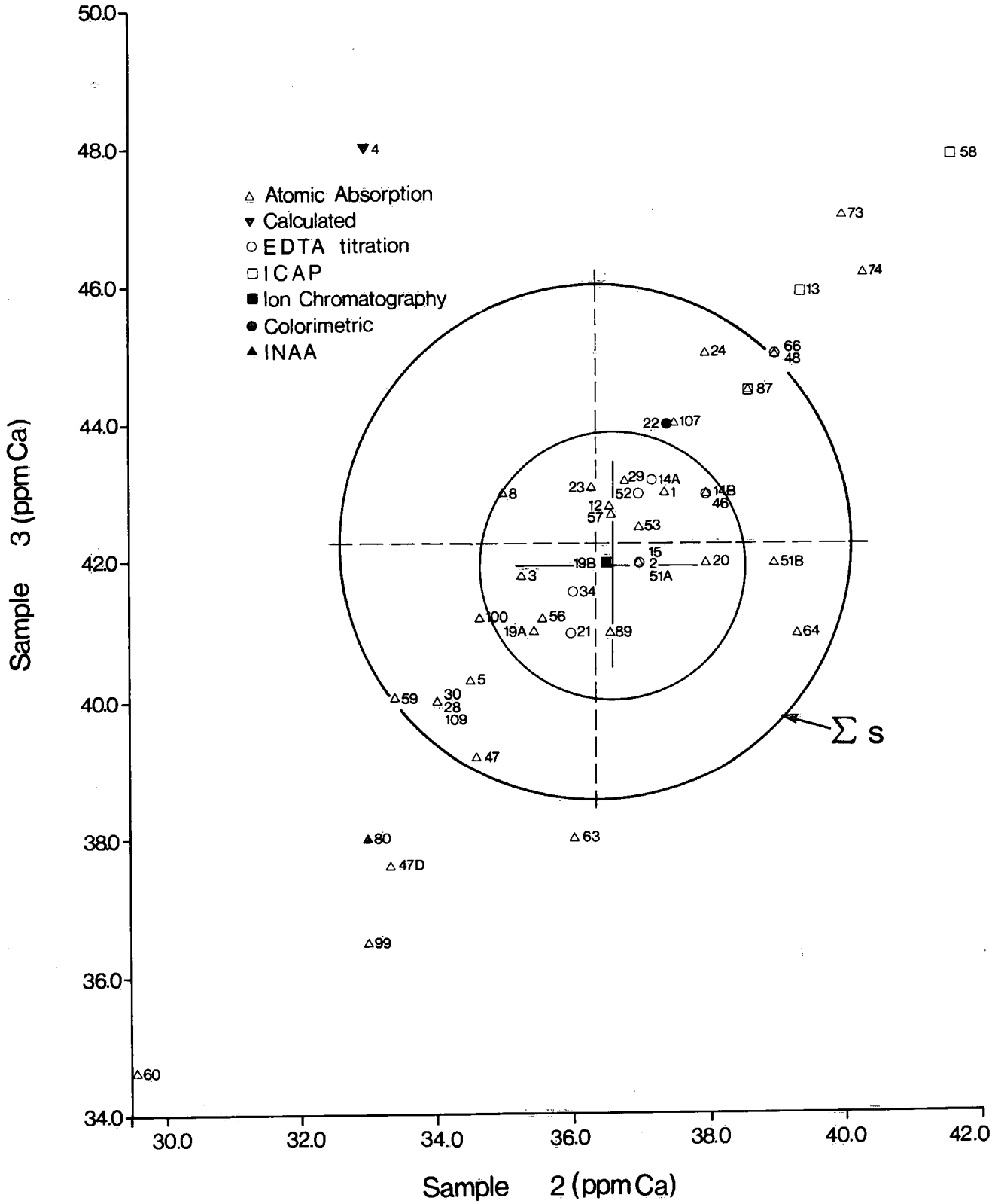

Figure 14. Calcium paired sample plot for samples 2 and 3.

Hardness

Table 22 presents all raw data along with the single sample suspect results (with "R" and/or underlining) and statistics (means, medians, S, percent C.V., mean errors and percent recoveries). The design values were calculated using the following formula: Total hardness ≡ 2.497 Ca (ppm) + 4.117 Mg (ppm). Table 23 summarizes the statistical results of individual samples.

The Youden paired sample treatment is illustrated in Figures 15 to 17 for samples 1, 2 and 3. The two types of circles defined earlier are shown in the figures. The general grouping of the points is seen here also straddling the imaginary 45° line, passing through quadrants I and III and practically by the intersection of means and medians, indicating the presence of systematic errors in the combined results plotted in each of the figures.

Laboratories 58, 13, 73 and 48 are in quadrant I outside the Σs circles, whereas Laboratories 59, 28, 80 and 47 are in quadrant III outside Σs circles. Except points 73 and 47, which represent EDTA titration, the rest of these points represent calculated values of total hardness.

Table 24 summarizes the results of the paired sample treatment, and Table 25, the ranking results. The evaluation summary is presented in Table 26.

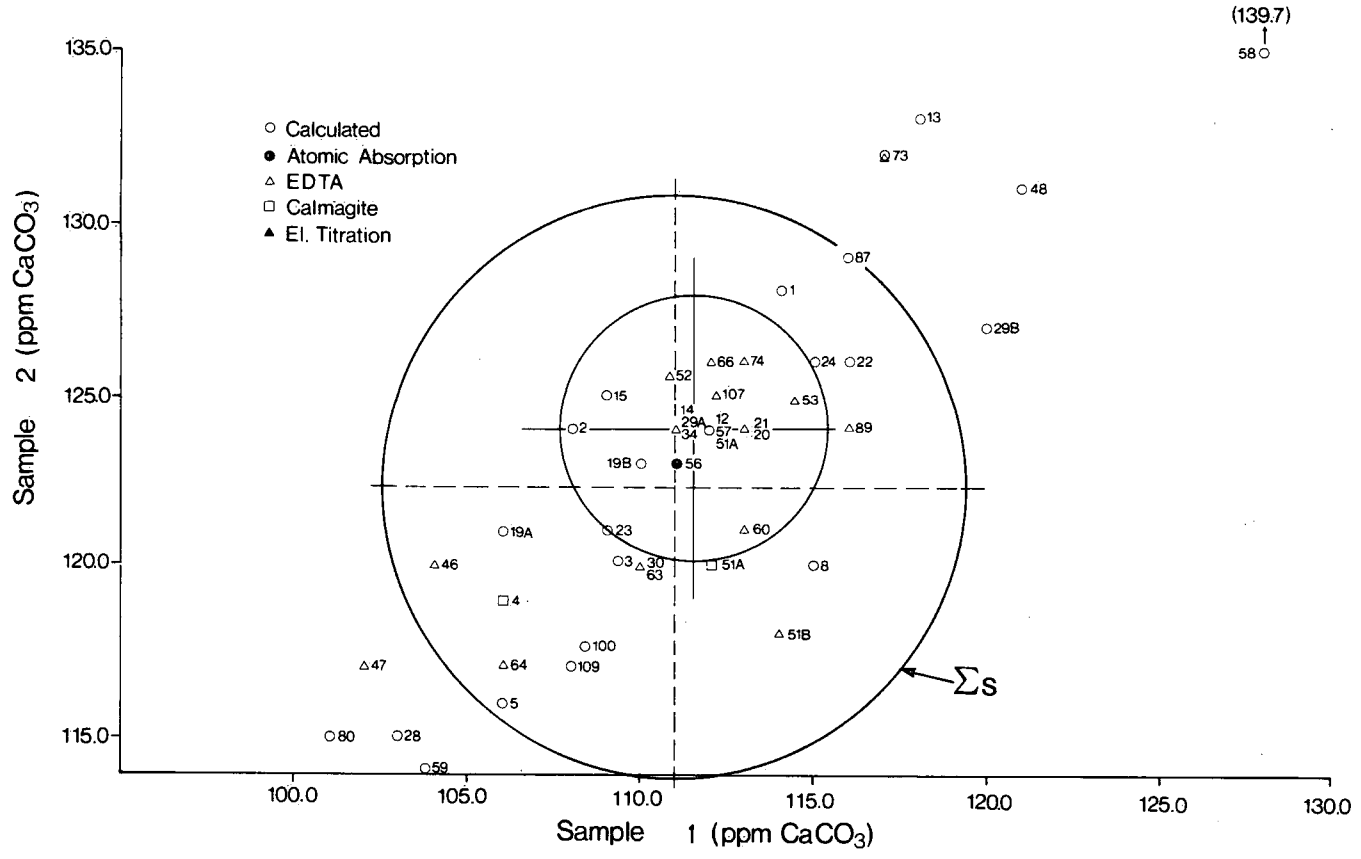

Figure 15. Total hardness paired sample plot for samples 1 and 2.

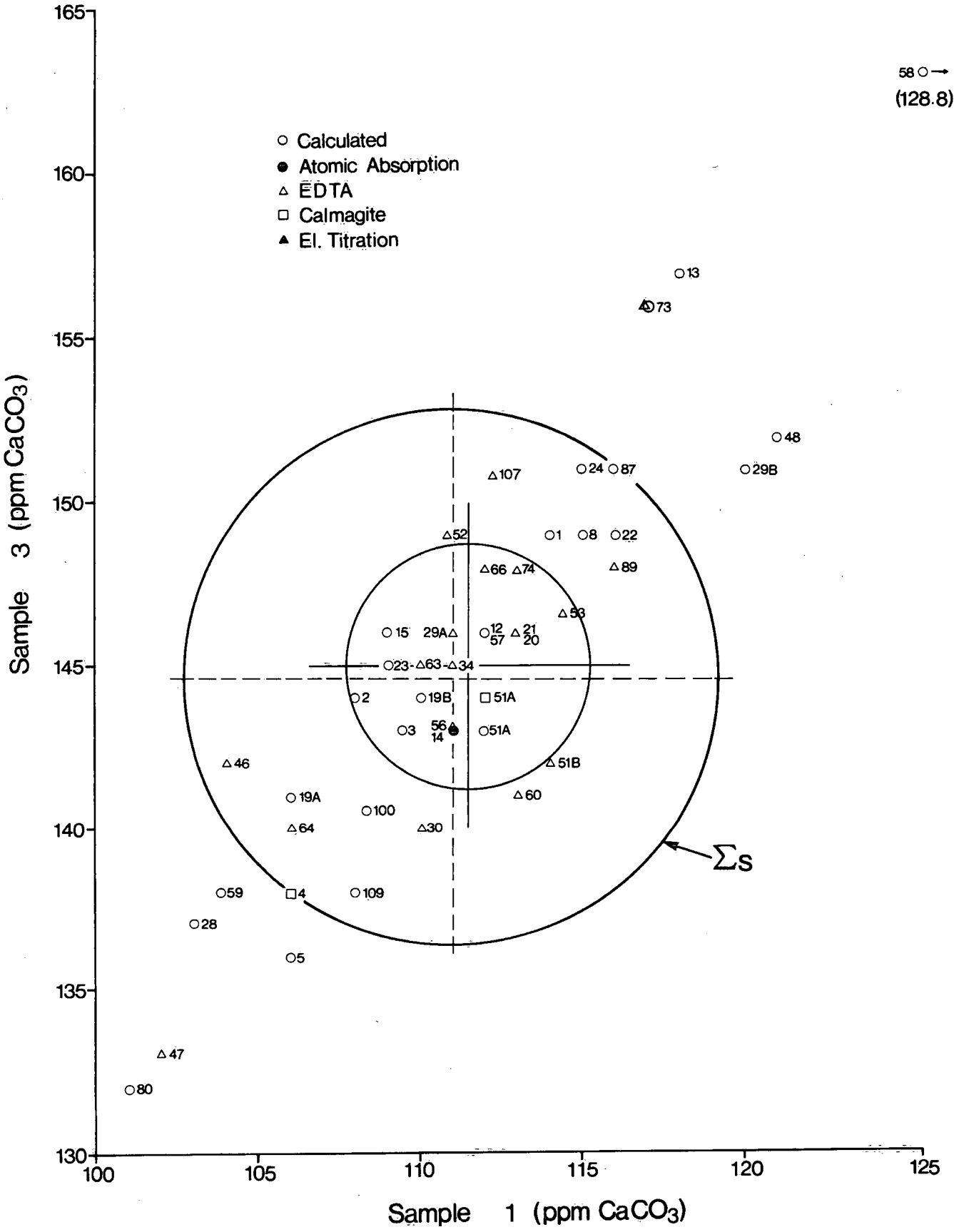

Figure 16. Total hardness paired sample plot for samples 1 and 3.

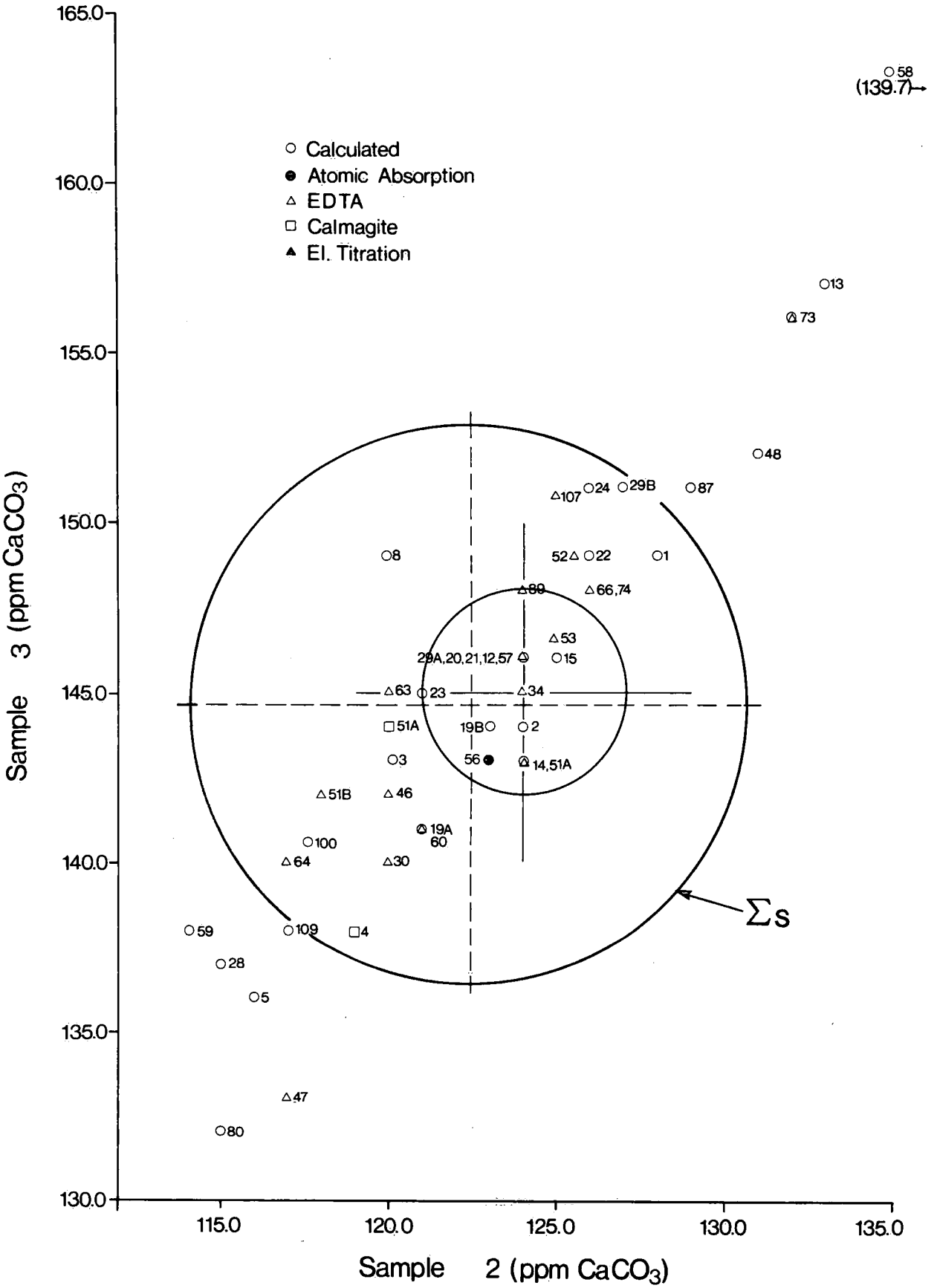

Figure 17. Total hardness paired sample plot for samples 2 and 3.

Summary of Laboratory Performance

For each of five constituents studied here, there are laboratories that performed quite well, as their results were not flagged at all by the many statistical outlying tests. If a laboratory performs 82 tests unflagged (six samples, five parameters, four different tests), it deserves to be congratulated. There are three such laboratories, Nos. 12, 14 and 51A (Table 27), which scored the perfect score of 5 out of 5. Other participants that performed quite well were Laboratories 3, 8, 20, 34, 53, 56 and 57, having been flagged for one parameter out of five. Table 27 gives the rest of unflagged frequency.

Table 27. Summary of Unflagged (U) Frequency

Laboratory No.	Na	K	Mg	Ca	Hardness	Σu
1	U	U				2
2			U	U		2
3	U		U	U	U	4
4		U				1
5	U	U				2
8		U	U	U	U	4
12	U	U	U	U	U	5
13	U					1
14	U	U	U	U	U	5
15						0
19			U	U	U	3
20	U	U		U	U	4
21				U	U	2
22	U	U		U	U	4
23				U	U	2
24		U	U		U	3
28						0
29A	U	U			U	3
29B	U	U				2
30		U	U		U	3
34		U		U	U	3
39	U					1
46		U				1
47	U	U	U			3
48						0
51A	U	U	U	U	U	5
51B		U	U			2
52				U	U	2
53		U	U	U	U	4
56	U		U	U	U	4
57		U	U	U	U	4
58						0
59			U			1
60					U	1
63						0
64			U			1
66	U				U	2
73	U		U			2
74	U					1
80						0
87		U	U			2
89			U	U		2
99	U					1
100		U	U			2
107	U		U		U	3
109	U		U			2

In this study, we have again observed the effectiveness of the Youden ranking technique (9). This technique is very useful in identifying the existence of systematic errors, but not so for random errors. On the other hand, the technique of flagging suspected high or low results is useful in identifying random errors. Thus these two techniques complement each other. If only one technique is used in data evaluation, misleading laboratory assessment and interpretation of data quality will likely occur. Our experience in this study provides yet another example of the correct choice of techniques for data evaluation to avoid misleading assessment on data quality and laboratory performance.

CONCLUSIONS

Some novel analytical methods were used by the participating laboratories in addition to conventional ones. The detailed data treatment seems to indicate that most methods are capable of giving precise and accurate results, but the determining factor is their application by individual participants.

Many participants performed very well. In particular, three laboratories, namely, Laboratories 12, 14 and 51A, were not flagged once by the various statistical tests. Laboratories 12 and 51A used atomic absorption spectrometry, whereas Laboratory 14 used flame photometry, atomic absorption and EDTA titration methods.

Ion chromatography was successfully used by Laboratory 19 for Mg and Ca analysis. It was the only laboratory that used IC for divalent cations. Laboratory 4 also successfully applied the IC system for monovalent cations.

The interlaboratory study was extremely beneficial because it demonstrated the following:

(a) Some laboratories need to reevaluate seriously their internal quality control practices (Table 27)
(b) The application of an analytical method, not the method itself, usually determines laboratory performance.

ACKNOWLEDGMENTS

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Tables 2 to 26

Table 2. Sodium Analytical Results*

Laboratory No.	Method	Detection limit	Sample results (mg/L) 1	2	3	4	5	6
1	Flame photometry	0.1	11.0	16.0	19.0	1.30	14.0	16.0
2	Flame photometry	0.1	12.0	16.5	19.0	1.90	14.50	16.50
3	Flame photometry		11.5	16.2	19.3	1.40	14.70	16.70
4A	Flame photometry	<1.0	13.0 R	19.0 R	20.0	2.00	16.00	18.00
4B	IC		12.8	15.9	17.6	1.40	15.10	17.00
5	Flame photometry	0.1	12.0	16.5	19.4	1.30	15.00	17.00
8	Atomic absorption	10.0	12.0	18.0 R	20.0	<10.00	18.00	20.00 R
12	Atomic absorption	0.1	10.9	15.3	17.9	1.25	13.70	15.60
13	ICAP	0.030	11.2	15.9	19.2	1.22	14.50	16.10
14A	Flame photometry	0.2	11.7	16.3	19.9	1.30	14.90	16.60
14B	Flame photometry	0.2	11.7	16.4	19.6	1.30	14.80	16.60
15	Atomic absorption	0.1	11.4	15.6	18.3	1.00 R	13.50	
19	Flame photometry	0.1	11.1	15.5	18.6	1.20	13.50	16.20
20	Atomic absorption	0.1	12.0	16.5	19.0	1.20	15.0	16.50
22	Flame photometry	<0.5	11.2	15.6	18.4	1.10	14.40	16.20
23	Flame photometry	0.1	11.0	14.3	17.5	1.30	11.50 R	15.30
24	Atomic absorption	1.0	10.0	15.0	17.0	1.00 R	13.0	14.0 R
28	Atomic absorption	0.5	11.0	15.0	18.0	1.00 R	13.0	16.0
29	Flame photometry		11.9	15.9	18.6	1.20	14.70	16.20
30	Atomic absorption	0.05	11.0	16.0	19.0	1.60	15.0	16.0
34	Atomic absorption	0.5	11.0	15.0	18.0	1.30	14.0	15.0
39	Flame emission		12.0	16.0	19.0	1.20	15.0	17.0
46	Atomic absorption	1.0	13.0 R	17.0	21.0 R	2.0	16.0	17.0
47	Atomic absorption	0.002	11.3	16.1	18.5	1.20	14.30	16.50
47D	Atomic absorption	0.002	11.1	16.2	19.1	1.18	15.00	18.50
48	Atomic absorption	<0.1	12.0	17.0	9.4 R	1.40	17.0	17.0
51A	Atomic absorption	0.1	12.0	16.0	19.0	1.20	15.0	16.0
51B	Atomic absorption	0.1	11.5	15.2	19.0	0.90 R	14.50	16.50
52	Flame emission	0.005	13.2 R	18.0 R	20.0	2.10 R	15.50	18.0
53	Atomic absorption	0.1	10.6	14.3	16.5	1.30	13.30	16.20
56	Atomic absorption	1.0	12.2	16.9	19.9	1.30	15.40	17.10
57	Flame emission	0.2	12.7	16.9	19.9	1.40	14.90	16.80
58	ICAP	0.1	12.7	17.1	20.2	1.40	16.40	19.10
59	Atomic absorption	0.05	10.4	14.25 R	17.55	1.11	13.05	14.65
60	IC	0.05	11.1	17.6	21.0 R	1.34	18.00	18.40
63	Flame photometry	0.05	9.4 R	15.0	20.0	1.00 R	13.0	16.0
64	Atomic absorption	<0.01	11.6	16.0	20.5 R	1.70	14.00	16.40
66	Flame photometry	0.1	12.0	16.0	20.0	1.50	15.0	17.0
73	Atomic absorption	0.1	11.5	16.1	19.0	1.22	14.70	16.50
74	Atomic absorption	0.02	10.7	15.0	17.9	1.20	13.70	16.20
80	INAA	0.5	9.8 R	13.0 R	14.9	1.30	12.10 R	13.20 R
87	ICAP/atomic absorption	0.1	10.6	14.5	17.7	1.10	13.50	15.10
89	Flame photometry	0.1	10.5	14.4	17.0	1.00 R	13.20	15.40
99	Flame emission	0.01	11.7	15.9	18.8	1.50	14.60	16.20
100	Atomic absorption		10.23	14.46	17.48	1.19	13.63	15.11
107	Flame photometry	0.01	11.6	15.6	17.8	1.20	14.50	16.30
109	Atomic absorption	0.1	11.1	15.4	18.7	1.10	14.10	16.20
Design values (mg/L)†			11.9	16.4	19.3	1.27	15.03	16.9
Median values (mg/L)			11.5	16.0	19.0	1.275	14.5	16.35
$\bar{x}$, Mean values (mg/L)			11.42	15.77	18.92	1.23	14.42	16.36
S.D., Standard deviation (mg/L)			0.66	0.84	1.02	0.13	0.86	0.68
C.V., Coefficient of variation (%)			5.78	5.33	5.40	10.57	5.96	4.16
Mean error (mg/L)			0.48	0.63	0.38	0.04	0.61	0.54
Relative mean error (%)			4.0	3.8	2.0	3.1	4.0	3.2
Recovery (%)			96	96	98	97	96	97

*Results with a flag R and underlined were determined to be suspect by Grubbs and 2S procedures, respectively.
†Values for samples 1, 2, 3, 5 and 6 were calculated from estimated volume and amounts of chemicals added. The value for sample 4 is an average value of several in-house analyses.

IC – Ion chromatography.
ICAP – Inductively coupled argon plasma.
INAA – Instrumental neutron activation analysis.

Table 3. Summary of Suspect Sodium Results by Single Sample Treatment

Laboratory No.	Sample	Value	Rejection
2	4	1.9	2S, –
4A	1	13.0	2S, Grubbs
4A	2	19.0	2S, Grubbs
4A	4	2.0	2S, –
8	2	18.0	2S, Grubbs
8	5	18.0	2S, –
8	6	20.0	2S, Grubbs
15	4	1.0	–, Grubbs
23	5	11.5	2S, Grubbs
24	4	1.0	–, Grubbs
24	6	14.0	2S, Grubbs
28	4	1.0	–, Grubbs
30	4	1.6	2S, –
46	1	13.0	2S, Grubbs
46	3	21.0	–, Grubbs
46	4	2.0	2S, –
47D	6	18.5	2S, –
48	3	9.4	2S, Grubbs
48	5	17.0	2S, –
51B	4	0.9	2S, Grubbs
52	1	13.2	2S, Grubbs
52	2	18.0	2S, Grubbs
52	4	2.1	2S, Grubbs
53	3	16.5	2S, –
58	6	19.1	2S, –
59	2	14.25	–, Grubbs
59	6	14.65	2S, –
60	3	21.0	–, Grubbs
60	5	18.0	2S, –
60	6	18.4	2S, –
63	1	9.4	2S, Grubbs
63	4	1.0	–, Grubbs
64	3	20.5	–, Grubbs
64	4	1.7	2S, –
80	1	9.8	2S, Grubbs
80	2	13.0	2S, Grubbs
80	3	14.9	2S, –
80	5	12.1	2S, Grubbs
80	6	13.2	2S, Grubbs
89	4	1.0	–, Grubbs

Table 4. Summary of Suspect Sodium Results by Paired Sample Treatment

Laboratory No.	Number of paired results outside the circles	
	Greenberg *et al.* (5)*	S.D. sum (8)
4A	4 out of 4	4 out of 4
4B	2	1
8	3	3
12	1	0
23	3	1
24	4	4
28	2	0
34	2	0
46	4	3
47D	1	1
48	4	3
52	4	4
53	3	3
56	2	0
57	1	1
58	4	3
59	4	2
60	4	4
63	3	2
64	1	0
74	1	0
80	4	4
87	4	0
89	4	3
100	4	2

*Throughout the study, circles of radius are considered 2 Sg rather than 2.448 Sg.

Table 5. Sodium Ranking Results

Laboratory No.	Total rank	Average rank	No. of samples ranked	Summary of flagging*	Bias	Method
24	27.50	4.583	6	VLVLVLVL	Low	Atomic absorption
59	34.00	5.667	6	LVLLLVL	Low	Atomic absorption
89	34.50	5.750	6	LVLVLL	Low	Flame photometry
80	36.00	6.000	6	VLVLVLVLVL	Low	INAA
100	46.00	7.667	6	VLLLL		Atomic absorption
87	47.50	7.917	6	LLLLL		ICAP/atomic absorption
28	57.50	9.583	6	VL		Atomic absorption
23	59.50	9.917	6	VLLVL		Flame photometry
53	69.00	11.500	6	LVLVLL		Atomic absorption
63	72.00	12.000	6	VLVL		Flame photometry
74	80.50	13.417	6			Atomic absorption
12	82.00	13.667	6			Atomic absorption
15	71.00	14.200	5	L		Atomic absorption
34	85.50	14.250	6	L		Atomic absorption
19	98.50	16.417	6	L		Flame photometry
109	98.50	16.417	6			Atomic absorption
22	102.50	17.083	6			Flame photometry
51B	115.00	19.167	6			Atomic absorption
107	118.50	19.750	6			Flame photometry
1	122.00	20.333	6			Cadmium red
47	133.00	22.167	6			Atomic absorption
13	133.00	22.167	6			ICAP
29	135.50	22.583	6			Flame photometry
51A	153.00	25.500	6			Atomic absorption
30	154.00	25.667	6			Atomic absorption
99	157.00	26.167	6			Flame emission
73	157.50	26.250	6			Atomic absorption
47D	171.00	28.500	6	VH		Atomic absorption
39	177.50	29.583	6			Flame emission
20	178.50	29.750	6			Atomic absorption
64	181.00	30.167	6	H		Atomic absorption
3	185.50	30.917	6			Flame photometry
4B	186.00	31.000	6	VHL		IC
14B	187.50	31.250	6			Flame photometry
14A	190.00	31.667	6			Flame photometry
2	192.50	32.083	6	H		Flame photometry
48	196.50	32.750	6	VLVH		Atomic absorption
5	207.00	34.500	6			Flame photometry
66	215.00	35.833	6			Flame photometry
57	218.50	36.417	6	H		Flame emission
56	225.50	37.583	6			Atomic absorption
60	230.50	38.417	6	VHVHVHVH		IC
58	254.50	42.417	6	HHVHVH	High	ICAP
46	257.00	42.833	6	VHVHHVH	High	Atomic absorption
8	215.50	43.100	5	VHVHVH	High	Atomic absorption
4A	262.00	43.667	6	VHVHHVHVH	High	Flame photometry
52	262.00	43.667	6	VHVHVHHVH	High	Flame emission

*L – One low result; VL – One very low result; H – One high result; VH – One very high result.

INAA – Instrumental neutron activation analysis.
ICAP – Inductively coupled argon plasma.
IC – Ion chromatography.

Note: Overall average rank is 23.836.

Table 6. Evaluation Summary of Sodium Results*

Laboratory No.	2S	Grubbs	Paired results S.D. sum	Rank L/H	Rank VL/VH
2	1			1	
4A	3	2	4	1	4
4B			1	1	1
8	3	2	3		3
15		1		1	
19				1	
23	1	1	1	1	2
24	1	2	4		4
28		1			1
30	1				
34				1	
46	2	2	3	1	3
47D	1		1		1
48	2	1	3		2
51B	1	1			
52	3	3	4	1	4
53	1		3	2	2
57			1	1	
58	1		3	2	2
59	1	1	2	3	2
60	2	1	4		4
63	1	2	2		2
64	1	1		1	
80	5	4	4		5
87				5	
89		1	3	2	2
100			2	3	1

*Laboratories Nos. 1, 3, 5, 12, 13, 14A, 14B, 20, 22, 29, 39, 47, 51A, 56, 66, 73, 74, 99, 107 and 109 are unflagged, having produced no suspect results by procedures of 2S, Grubbs, standard deviation sum or ranking.

Table 7. Potassium Analytical Results*

Laboratory No.	Method	Detection limit	Sample results (mg/L) 1	2	3	4	5	6
1	Flame photometry	0.1	1.0	1.0	0.90	0.50	1.50	6.90
2	Flame photometry	0.1	1.00	1.00	0.90	0.30 R	1.20	7.00
3	Flame photometry		1.00	0.96	0.85	0.49	1.40	2.60 R
4A	Flame photometry	0.2	1.00	1.10	0.90	0.50	1.40	6.80
4B	IC		1.10	0.90	0.80	0.50	1.50	6.90
5	Flame photometry	0.1	0.90	0.90	0.80	0.50	1.40	7.00
8	Atomic absorption	2.0	<2.00	<2.00	<2.00	<2.00	<2.00	7.30
12	Atomic absorption	0.01	1.12	1.11	1.02	0.62	1.53	7.37
13	Flame emission	0.010	0.872	0.879	0.802	0.436	1.26	6.02
14A	Flame photometry	0.2	1.00	1.00	0.90	0.60	1.40	7.00
14B	Flame photometry	0.2	0.90	0.90	0.80	0.50	1.30	6.90
15	Atomic absorption	0.1	5.80 R	4.20 R	4.40	2.00 R	5.80 R	
19	Flame photometry	0.01	0.86 R	0.91	0.73	0.30 R	1.30	6.30
20	Atomic absorption	0.1	1.00	1.00	0.90	0.50	1.50	7.0
22	Flame photometry	<0.05	0.98	1.01	0.94	0.47	1.52	6.35
23	Atomic absorption	0.1	1.30	0.90	0.60 R	0.40	1.50	7.10
24	Atomic absorption	1.0	1.00	1.00	0.80	0.60	1.50	7.20
29	Flame photometry		1.00	1.00	0.88	0.58	1.50	7.60
30	Atomic absorption	0.5	1.10	1.10	1.00	0.60	1.50	7.40
34	Atomic absorption	0.3	1.00	1.10	0.97	0.51	1.60	7.30
46	Atomic absorption	1.0	1.00	1.10	1.00	0.50	1.50	7.40
47	Atomic absorption	0.002	1.06	1.04	0.94	0.39	1.57	6.95
48	Atomic absorption	0.1	1.00	1.00	0.90	0.60	1.50	5.00
51A	Atomic absorption	0.1	1.10	1.10	0.90	0.60	1.50	7.10
51B	Atomic absorption	0.1	1.00	1.00	0.90	0.50	1.50	6.40
52	Flame emission	0.03	2.20	2.00	2.00	0.88	2.70	10.00 R
53	Atomic absorption	0.1	1.00	1.00	0.90	0.40	1.60	6.90
56	Atomic absorption	0.1	1.26	1.27	1.14	0.63	1.91	8.20
57	Flame emission	0.2	1.00	1.00	0.90	0.50	1.50	7.00
58	ICAP	0.1	1.00	1.20	0.80	0.10 R	1.10 R	7.30
59	Atomic absorption	0.05	0.89	0.87 R	0.76	0.41	1.33	6.46
60	IC	0.1	1.60	1.48	5.12 R	0.83	2.03	8.25
63	Flame photometry	0.1	1.40	1.20	1.20	0.60	1.40	6.00
64	Atomic absorption	<0.01	1.10	1.10	1.20	0.60	1.30	7.80
66	Flame photometry	0.1	0.90	0.90	0.80	0.90	1.30	6.60
73	Atomic absorption	0.5	1.10	1.10	1.00	0.80	1.60	7.70
74	Atomic absorption	0.10	1.60	1.67	1.52	0.62	2.35	9.80 R
87	Flame emission	0.01	0.90	0.90	0.80	0.44	1.36	6.55
89	Flame photometry	0.1	1.40	1.40	1.50	0.70	2.00	7.50
99	Flame emission	0.01	0.55 R	0.55 R	0.50 R	0.30 R	0.80 R	3.65
100	Atomic absorption	0.01	0.92	0.92	0.82	0.42	1.42	6.40
107	Atomic absorption	0.05	1.20	1.00	0.90	0.60	1.50	7.20
Design values (mg/L)†			0.99	0.99	0.874	0.52	1.508	7.11
Median values (mg/L)			1.0	1.0	0.90	0.50	1.5	7.0
$\bar{x}$, Mean values (mg/L)			1.05	1.04	0.88	0.52	1.48	7.00
S.D., Standard deviation (mg/L)			0.20	0.14	0.14	0.12	0.19	0.50
C.V., Coefficient of variation (%)			19.05	13.46	15.91	23.08	12.84	7.14
Mean error (mg/L)			0.06	0.05	0.006	0	0.028	0.11
Relative mean error (%)			6.1	5.1	0.6	0	1.8	1.5
Recovery (%)			106	105	100	100	98	98

*Results with a flag R and underlined were determined to be suspect by Grubbs and 2S procedures, respectively.
†Values for samples 1, 2, 3, 5 and 6 were calculated from estimated volume and amounts of chemicals added. The value for sample 4 is an average value of several in-house analyses.

IC – Ion chromatography.
ICAP – Inductively coupled argon plasma.

Table 8. Summary of Suspect Potassium Results by Single Sample Treatment

Laboratory No.	Sample	Value	Rejection
2	4	0.3	−, Grubbs
3	6	2.6	2S, Grubbs
15	1	5.8	2S, Grubbs
15	2	4.2	2S, Grubbs
15	3	4.4	2S, −
15	4	2.0	2S, Grubbs
15	5	5.8	2S, Grubbs
19	1	0.86	−, Grubbs
19	4	0.3	−, Grubbs
23	3	0.6	−, Grubbs
48	6	5.0	2S, −
52	1	2.2	2S, −
52	2	2.0	2S, −
52	3	2.0	2S, −
52	4	0.88	2S, −
52	5	2.7	2S, −
52	6	10.0	2S, Grubbs
58	4	0.1	2S, Grubbs
58	5	1.1	−, Grubbs
59	2	0.87	−, Grubbs
60	3	5.12	2S, Grubbs
60	6	8.25	2S, −
66	4	0.9	2S, −
74	2	1.67	2S, −
74	3	1.52	2S, −
74	5	2.35	2S, −
74	6	9.8	2S, Grubbs
89	3	1.5	2S, −
99	1	0.55	−, Grubbs
99	2	0.55	2S, Grubbs
99	3	0.50	−, Grubbs
99	4	0.30	−, Grubbs
99	5	0.8	2S, Grubbs
99	6	3.65	2S, −

Table 9. Summary of Suspect Potassium Results by Paired Sample Treatment

	Number of paired results outside the circles	
Laboratory No.	Greenberg *et al.* (5)*	S.D. sum (8)
15	3 out of 3	3 out of 3
23	2	1
52	3	3
56	2	0
60	3	3
63	3	2
64	1	0
74	3	3
89	3	3
99	3	3

*Throughout the study, circles of radius are considered 2 Sg rather than 2.448 Sg.

Table 10. Potassium Ranking Results

Laboratory No.	Total rank	Average rank	No. of samples ranked	Summary of flagging*	Bias	Method
99	9.00	1.500	6	VLVLVLLVLVL	Low	Flame emission
19	30.50	5.083	6	LL	Low	Flame photometry
59	37.00	6.167	6		Low	Atomic absorption
13	37.00	6.167	6	LL	Low	Flame emission
87	53.00	8.833	6			Flame emission
14B	61.00	10.167	6			Flame photometry
100	66.50	11.083	6			Atomic absorption
3	71.00	11.833	6	VL		Flame photometry
5	73.00	12.167	6			Flame photometry
66	79.50	13.250	6	VH		Flame photometry
2	84.00	14.000	6	LL		Flame photometry
58	92.50	15.417	6	HVLVL		ICAP
23	97.50	16.250	6	VHVL		Atomic absorption
4B	100.00	16.667	6			IC
51B	106.50	17.750	6			Atomic absorption
22	110.50	18.417	6			Flame photometry
48	111.50	18.583	6	VL		Atomic absorption
4A	112.00	18.667	6			Flame photometry
53	113.00	18.833	6			Atomic absorption
1	113.50	18.917	6			Cadmium red
20	119.00	19.833	6			Atomic absorption
57	119.00	19.833	6			Flame emission
14A	119.50	19.917	6			Flame photometry
24	122.00	20.333	6			Atomic absorption
29	133.00	22.167	6			Flame photometry
47	133.50	22.250	6			Atomic absorption
107	150.00	25.000	6	H		Atomic absorption
46	151.50	25.250	6			Atomic absorption
63	152.00	25.333	6			Flame photometry
51A	155.00	25.833	6	VHHVHL		Atomic absorption
34	162.00	27.000	6			Atomic absorption
64	165.50	27.583	6	VHH		Atomic absorption
30	173.00	28.833	6			Atomic absorption
8	29.00	29.000	1			Atomic absorption
12	193.50	32.250	6			Atomic absorption
73	196.00	32.667	6	VH		Atomic absorption
56	213.00	35.500	6	VHVHVHVHVH		Atomic absorption
89	217.50	36.250	6	VHVHVHHVH		Flame photometry
74	228.00	38.000	6	VHVHVHVHVH	High	Atomic absorption
60	232.50	38.750	6	VHVHVHVHVHVH	High	IC
52	239.00	39.833	6	VHVHVHVHVHVH	High	Flame emission
15	204.00	40.800	5	VHVHVHVHVH	High	Atomic absorption

*L – One low result; VL – One very low result; H – One high result; VH – One very high result.

ICAP – Inductively coupled argon plasma.
IC – Ion chromatography.

Note: Overall average rank is 21.000.

Table 11. Evaluation Summary of Potassium Results*

Laboratory No.	2S	Grubbs	Paired results S.D. sum	Rank L/H	Rank VL/VH
2		1		2	
3	1	1			1
13				2	
15	5	4	3		5
19		2		2	
23		1	2		2
48	1				1
52	6	1	3		6
56			1		5
58	1	2		1	2
59		1			
60	2	1	3		6
63			3	2	2
64			1	1	1
66	1				1
73					1
74	4	1	3		5
89	1		3	1	4
99	3	5	3	1	5
107				1	

*Laboratories Nos. 1, 4A, 4B, 5, 8, 12, 14A, 14B, 20, 22, 24, 29, 30, 34, 46, 47, 51A, 51B, 53, 57, 87 and 100 are unflagged, having produced no suspect results by procedures of 2S, Grubbs, standard deviation sum or ranking.

Table 12. Magnesium Analytical Results*

Laboratory No.	Method	Detection limit	Sample results (mg/L) 1	2	3	4	5	6
1	Atomic absorption	0.1	7.80	8.30	10.0	3.30	10.50	16.20
2	Atomic absorption	0.1	7.50	7.70	9.50	2.60	9.50	15.0
3	Atomic absorption		6.99	7.77	9.38	2.61	9.30	15.33
4	Atomic absorption	1.0	8.00	9.00 R	10.00	3.00	11.00	15.00
5	Atomic absorption	<0.02	6.90	7.20	8.70 R	2.50 R	9.30	14.50
8	Atomic absorption	5.0	8.0	8.0	10.0	2.80	10.0	15.0
12	Atomic absorption	0.01	7.48	7.96	9.60	2.74	10.20	15.50
13	ICAP	0.025	7.89	8.45	10.30	3.00	10.80	16.50
14	Atomic absorption	0.001	7.50	7.90	9.20	2.60	10.0	16.0
15	EDTA titration	1.0	7.0	8.0	10.0	3.0	11.0	15.0
19A	Atomic absorption	0.01	7.30	7.80	9.40	2.70	9.40	14.80
19B	IC		7.30	7.80	9.40	2.70	10.20	15.90
20	Atomic absorption	0.1	7.10	7.50	9.00	2.60	9.50	14.0 R
21	Calculated		8.20 R	8.20	10.50	3.10	11.0	16.30
22	Colorimetric	<0.1	7.40	7.70	9.40	2.90	9.90	14.40 R
23	Atomic absorption	0.1	7.10	7.40	9.00	2.60	10.90	15.40
24	Atomic absorption	0.2	7.30	7.50	9.50	2.80	10.0	15.0
28	Atomic absorption	0.5	6.80	7.30	9.00	2.80	9.90	15.0
29	Atomic absorption		8.10	8.60	10.50	3.00	11.10	16.70
30	Atomic absorption	0.1	7.00	7.20	9.00	2.80	9.40	15.0
34	Calculated	1.0	7.40	8.20	9.80	2.50 R	11.0	16.0
46	Calculated	2.0	6.80	7.80	8.80	3.90 R	9.70	14.0 R
47	Atomic absorption	0.001	7.65	8.20	9.75	2.84	10.50	15.20
48	Atomic absorption	0.1	8.20 R	8.20	9.70	3.00	10.0	20.0 R
51A	Atomic absorption	0.1	7.20	7.60	9.20	2.70	9.80	15.0
51B	Atomic absorption	0.2	7.00	7.50	9.00	2.80	9.20	15.00
52	Calculated	5.0	7.50	7.80	10.50	2.20R	10.00	15.00
53	Atomic absorption	0.1	7.80	8.30	9.50	3.00	10.20	15.90
56	Atomic absorption	1.0	7.90	8.30	9.80	2.90	10.30	15.30
57	Atomic absorption	0.2	7.50	8.00	9.60	2.80	10.30	15.90
58	ICAP	0.1	8.50 R	8.70 R	10.60 R	3.10	11.60 R	17.90
59	Atomic absorption	0.02	7.21	7.46	9.24	2.62	9.68	14.50
60	Atomic absorption	0.01	7.97	8.31	11.00 R	3.14	11.90 R	18.80
63	Atomic absorption	0.02	7.00	7.60	9.40	2.80	9.80	17.0
64	Atomic absorption	0.01	7.10	7.80	9.40	2.60	10.20	15.10
66	Calculated	0.1	5.80 R	6.80 R	8.70 R	1.00 W	8.30	15.0
73	Atomic absorption	0.1	7.30	7.75	9.40	2.80	10.00	15.20
74	Atomic absorption	0.005	6.70 R	7.00 R	8.60 R	2.50 R	9.40	14.70
80	INAA	1.0	7.0	8.0	9.0	3.0	8.0	15.0
87	ICAP/atomic absorption	0.001	7.62	8.05	9.81	2.84	10.40	15.80
89	Atomic absorption	0.1	7.90	8.10	9.50	2.70	10.00	14.50
99	Atomic absorption	0.02	7.00	8.00	9.50	3.80	9.50	15.00
100	Atomic absorption	0.01	7.34	7.55	9.15	2.62	9.71	14.98
107	Atomic absorption	0.01	7.40	7.60	9.40	2.80	10.20	16.20
109	Atomic absorption	0.1	7.40	7.70	9.30	2.60	9.80	15.20
Design values (mg/L)†			7.5	7.9	9.5	2.63	10.09	15.5
Median values (mg/L)			7.4	7.8	9.4	2.8	10.0	15.1
$\bar{x}$, Mean values (mg/L)			7.41	7.86	9.48	2.79	10.06	15.21
S.D., Standard deviation (mg/L)			0.41	0.34	0.48	0.18	0.53	0.60
C.V., Coefficient of variation (%)			5.53	4.32	5.06	6.45	5.27	3.94
Mean error (mg/L)			0.09	0.04	0.02	0.16	0.03	0.29
Relative mean error (%)			1.2	0.5	0.2	6.1	3.0	1.9
Recovery (%)			99	99	100	106	100	98

*Results with a flag R and underlined were determined to be suspect by Grubbs and 2S procedures, respectively. A W code is used with a reported result to indicate no possible measurement owing to the lack of response of the instrument to the sample.

†Values for samples 1, 2, 3, 5 and 6 were calculated from estimated volume and amounts of chemicals added. The value for sample 4 is an average value of several in-house analyses.

ICAP – Inductively coupled argon plasma.
IC – Ion chromatography.
INAA – Instrumental neutron activation analysis.

Table 13. Summary of Suspect Magnesium Results by Single Sample Treatment

Laboratory No.	Sample	Value	Rejection
1	4	3.3	2S, –
4	2	9.0	2S, Grubbs
5	3	8.7	–, Grubbs
5	4	2.5	–, Grubbs
20	6	14.0	–, Grubbs
21	1	8.2	–, Grubbs
22	6	14.4	–, Grubbs
29	6	16.7	2S, –
34	4	2.5	–, Grubbs
46	4	3.9	2S, Grubbs
46	6	14.0	–, Grubbs
48	1	8.2	–, Grubbs
48	6	20.0	2S, Grubbs
52	4	2.2	2S, Grubbs
58	1	8.5	2S, Grubbs
58	2	8.7	2S, Grubbs
58	3	10.6	2S, Grubbs
58	5	11.6	2S, Grubbs
58	6	17.9	2S, –
60	3	11.0	2S, Grubbs
60	5	11.9	2S, Grubbs
60	6	18.8	2S, –
63	6	17.0	2S, –
66	1	5.8	2S, Grubbs
66	2	6.8	2S, Grubbs
66	3	8.7	–, Grubbs
66	5	8.3	2S, –
74	1	6.7	–, Grubbs
74	2	7.0	2S, Grubbs
74	3	8.6	–, Grubbs
74	4	2.5	–, Grubbs
80	5	8.0	2S, –
99	4	3.8	2S, –

Table 14. Summary of Suspect Magnesium Results by Paired Sample Treatment

	Number of paired results outside the circles	
Laboratory No.	Greenberg *et al.* (5)*	S.D. sum (8)
1	4 out of 4	0 out of 4
4	3	2
5	3	3
8	3	0
13	4	3
15	2	0
20	3	1
21	4	4
23	3	0
28	3	1
29	4	4
30	3	0
34	3	0
46	2	1
47	2	0
48	4	2
51B	2	0
52	2	2
53	2	0
56	3	0
58	4	4
60	4	3
63	1	1
66	4	4
74	3	3
87	3	0
89	2	0
109	1	0

*Throughout the study, circles of radius are considered 2 Sg rather than 2.448 Sg.

Table 15. Magnesium Ranking Results

Laboratory No.	Total rank	Average rank	No. of samples ranked	Summary of flagging*	Bias	Method
74	23.00	3.833	6	L	Low	Atomic absorption
66	23.50	3.917	6	VLLVLVL	Low	Calculated
5	24.50	4.083	6		Low	Atomic absorption
20	50.50	8.417	6			Atomic absorption
30	67.50	11.250	6			Atomic absorption
59	68.50	11.417	6			Atomic absorption
51B	69.00	11.500	6			Atomic absorption
28	74.50	12.417	6			Atomic absorption
100	80.50	13.417	6			Atomic absorption
3	85.50	14.250	6			Atomic absorption
46	89.00	14.833	6	VH		Calculated
51A	90.00	15.000	6			Atomic absorption
19A	93.00	15.500	6			Atomic absorption
80	99.00	16.500	6	VL		INAA
23	103.00	17.167	6	H		Atomic absorption
109	105.00	17.500	6			Atomic absorption
2	106.00	17.667	6			Atomic absorption
22	113.50	18.917	6			Colorimetric
64	116.50	19.417	6			Atomic absorption
24	117.50	19.583	6			Atomic absorption
63	124.50	20.750	6	VH		Atomic absorption
73	129.50	21.583	6			Atomic absorption
14	134.00	22.333	6			Atomic absorption
52	134.50	22.417	6	HL		Calculated
99	134.50	22.417	6	VH		Atomic absorption
19B	140.00	23.333	6			IC
89	141.00	23.500	6			Atomic absorption
107	148.00	24.667	6			Atomic absorption
12	160.50	26.750	6			Atomic absorption
15	168.50	28.083	6	H		EDTA titration
8	170.00	28.333	6			Atomic absorption
34	173.50	28.917	6	H		Calculated
57	177.50	29.583	6			Atomic absorption
47	190.50	31.750	6			Atomic absorption
87	193.50	32.250	6			ICAP/atomic absorption
53	197.50	32.917	6			Atomic absorption
56	201.00	33.500	6			Atomic absorption
48	214.00	35.667	6	HVH		Atomic absorption
4	215.50	35.917	6	VHH		Atomic absorption
1	227.00	37.833	6			Cadmium red
13	231.00	38.500	6	HH		ICAP
21	241.00	40.167	6	HHHH	High	Calculated
29	247.00	41.167	6	HHHH	High	Atomic absorption
60	256.00	42.667	6	VHVHVH	High	Atomic absorption
58	260.50	43.417	6	VHHHVHVH	High	ICAP

*L – One low result; VL – One very low result; H – One high result; VH – One very high result.

INAA – Instrumental neutron activation analysis.
IC – Ion chromatography.
ICAP – Inductively coupled argon plasma.

Note: Overall average rank is 23.000.

Table 16. Evaluation Summary of Magnesium Results*

Laboratory No.	2S	Grubbs	Paired results S.D. sum	Rank L/H	Rank VL/VH
1	1				
4	1	1	2	1	1
5		2	3		
13			3	2	
15				1	
20		1	1		
21		1	4	4	
22		1			
23				1	
28			1		
29	1		4	4	
34		1		1	
46	1	2	1		1
48	1	2	2	1	1
52	1	1	2	2	
58	5	4	4	2	3
60	3	2	3		3
63	1		1		1
66	3	3	4	1	3
74	1	4	3	1	
80	1				1
99	1				1

*Laboratories Nos. 2, 3, 8, 12, 14, 19A, 19B, 24, 30, 47, 51A, 51B, 53, 56, 57, 59, 64, 73, 87, 89, 100, 107 and 109 are unflagged, having produced no suspect results by procedures of 2S, Grubbs, standard deviation sum or ranking.

Table 17. Calcium Analytical Results*

Laboratory No.	Method	Detection limit	Sample results (mg/L) 1	2	3	4	5	6
1	Atomic absorption	0.1	32.6	37.4	43.0	14.2	46.0	14.8
2	Atomic absorption	0.1	31.0	37.0	42.0	13.0	43.0	14.0
3	Atomic absorption		32.3	35.3	41.8	13.1	44.4	13.2
4	Calculated	1.0	29.0	33.0	48.0 R	8.0 R	40.0 R	10.0
5	Atomic absorption	<0.01	30.9	34.5	40.3	12.5	42.7	12.5
8	Atomic absorption	5.0	33.0	35.0	43.0	13.0	45.0	13.0
12	Atomic absorption	0.1	32.5	36.6	42.8	13.7	45.3	13.0
13	ICAP	0.025	34.3	39.4	45.9	14.5	48.6	14.5
14A	EDTA titration	1.0	32.9	37.2	43.2	13.5	46.8	13.5
14B	Atomic absorption		33.0	38.0	43.0	15.0	46.0	15.0 R
15	EDTA titration	1.0	32.0	37.0	42.0	14.0	45.0	15.0 R
19A	Atomic absorption	0.01	30.5	35.5	41.0	13.0	44.5	12.4
19B	IC	0.01	31.9	36.5	42.0	13.3	45.3	13.3
20	Atomic absorption	0.1	34.0	38.0	42.0	13.5	43.0	13.0
21	EDTA titration		32.0	36.0	41.0	13.0	45.0	13.0
22	Colorimetric	<0.4	33.6	37.4	44.0	13.6	46.0	13.8
23	Atomic absorption	0.1	32.1	36.3	43.1	12.5	43.4	13.0
24	Atomic absorption	1.0	34.0	38.0	45.0	14.0	47.0	14.0
28	Atomic absorption	0.5	30.0	34.0	40.0	13.0	45.0	12.0
29	Atomic absorption		34.7	36.8	43.2	13.3	44.9	13.0
30	Atomic absorption	0.1	31.0	34.0	40.0	12.0	44.0	12.0
34	EDTA titration	10.0	32.0	36.0	41.6	12.8	44.0	12.8
46	EDTA titration	2.0	32.0	38.0	43.0	11.0	44.0	13.0
47	Atomic absorption	0.002	28.4	34.6	39.2	10.3	41.8	12.6
47D	Atomic absorption	0.002	29.1	33.3	37.6	11.4	41.8	12.6
48	Atomic absorption	0.5	35.0	39.0	45.0	14.0	49.0	14.0
51A	Atomic absorption	0.1	33.0	37.0	42.0	13.0	45.0	14.0
51B	Atomic absorption	0.2	33.5	39.0	42.0	13.8	44.0	13.5
52	EDTA titration	5.0	32.0	37.0	43.0	13.2	46.0	13.0
53	Atomic absorption	0.5	33.0	37.0	42.5	13.5	45.5	12.5
56	Atomic absorption	1.0	31.5	35.6	41.2	12.8	43.8	12.8
57	Atomic absorption	0.2	32.3	36.6	42.7	13.0	45.0	12.9
58	ICAP	0.1	37.6 R	41.6 R	47.9 R	15.1	52.0 R	14.9
59	Atomic absorption	0.05	29.7	33.4	40.05	12.22	42.45	12.05
60	Atomic absorption	0.01	25.1 R	29.6 R	34.6 R	11.1	36.8 R	10.6
63	Atomic absorption	0.5	30.0	36.0	38.0	16.0	42.0	16.0 R
64	Atomic absorption	<0.01	32.4	39.3	41.0	12.6	44.4	13.2
66	EDTA titration	1.0	35.0	39.0	45.0	16.0	50.0 R	15.0 R
73	Atomic absorption	0.1	35.0	40.0	47.0	14.5	50.0 R	14.5
74	Atomic absorption	0.1	35.3 R	40.3 R	46.2	14.4	49.3	14.4
80	INAA	0.1	29.0	33.0	38.0	13.0	43.0	13.0
87	ICAP/atomic absorption	0.01	34.0	38.6	44.5	13.6	47.3	13.5
89	Atomic absorption	0.1	34.0	36.6	41.0	13.4	44.3	13.2
99	Atomic absorption	0.05	31.5	33.0	36.5 R	19.0 R	44.0	14.5
100	Atomic absorption	0.04	31.3	34.66	41.21	12.29	42.21	12.7
107	Atomic absorption	0.02	33.0	37.5	44.0	13.8	47.8	13.7
109	Atomic absorption	0.1	31.0	34.0	40.0	12.0	42.0	12.0
Design values (mg/L)†			32.2	36.3	42.6	13.4	46.7	13.39
Median values (mg/L)			32.3	36.6	42.0	13.2	44.9	13.0
$\bar{x}$, Mean values (mg/L)			32.32	36.47	42.18	13.19	44.75	13.37
S.D., Standard deviation (mg/L)			1.68	1.98	1.92	0.93	1.91	0.87
C.V., Coefficient of variation (%)			5.20	5.43	4.55	7.05	4.27	6.51
Mean error (mg/L)			0.12	0.17	0.42	0.21	1.95	0.02
Relative mean error (%)			0.4	0.5	1.0	1.6	4.2	0.1
Recovery (%)			100	100	99	98	96	100

*Results with a flag R and underlined were determined to be suspect by Grubbs and 2S procedures, respectively.
†Values for samples 1, 2, 3, 5 and 6 were calculated from estimated volume and amounts of chemicals added. The value for sample 4 is an average value of several in-house analyses.

ICAP – Inductively coupled argon plasma.
IC – Ion chromatography.
INAA – Instrumental neutron activation analysis.

Table 18. Summary of Suspect Calcium Results by Single Sample Treatment

Laboratory No.	Sample	Value	Rejection
4	3	48.0	2S, Grubbs
4	4	8.0	2S, Grubbs
4	5	40.0	2S, Grubbs
4	6	10.0	2S, –
14B	6	15.0	–, Grubbs
15	6	15.0	–, Grubbs
47	1	28.4	2S, –
47	4	10.3	2S, –
47D	3	37.6	2S, –
58	1	37.6	2S, Grubbs
58	2	41.6	2S, Grubbs
58	3	47.9	2S, Grubbs
58	5	52.0	2S, Grubbs
60	1	25.1	2S, Grubbs
60	2	29.6	2S, Grubbs
60	3	34.6	2S, Grubbs
60	5	36.8	2S, Grubbs
60	6	10.6	2S, –
63	4	16.0	2S, –
63	6	16.0	2S, Grubbs
66	4	16.0	2S, –
66	5	50.0	2S, Grubbs
66	6	15.0	–, Grubbs
73	3	47.0	2S, –
73	5	50.0	2S, Grubbs
74	1	35.3	–, Grubbs
74	2	40.3	–, Grubbs
99	3	36.5	2S, Grubbs
99	4	19.0	2S, Grubbs

Table 19. Summary of Suspect Calcium Results by Paired Sample Treatment

Laboratory No.	Number of paired results outside the circles	
	Greenberg *et al.* (5)*	S.D. sum (8)
4	3 out of 3	3 out of 3
5	3	0
8	1	0
13	3	2
14B	1	0
19A	2	0
20	1	0
22	3	0
24	3	0
28	3	0
29	2	0
30	2	0
47	3	2
47D	3	3
48	3	2
51B	2	0
58	3	3
59	3	2
60	3	3
63	3	2
64	2	0
66	3	2
73	3	3
74	3	3
80	3	3
87	3	0
89	1	0
99	3	2
100	2	0
107	2	0
109	3	0

*Throughout the study, circles of radius are considered 2 Sg rather than 2.448 Sg.

Table 20. Calcium Ranking Results

Laboratory No.	Total rank	Average rank	No. of samples ranked	Summary of flagging*	Bias	Method
60	10.00	1.667	6	VLVLVLVLVLVL	Low	Atomic absorption
47D	32.00	5.333	6	VLVLVLVLL	Low	Atomic absorption
47	35.00	5.833	6	VLLVLL	Low	Atomic absorption
59	44.00	7.333	6	LVL		Atomic absorption
109	44.00	7.333	6	LLL		Atomic absorption
30	55.50	9.250	6	LL		Atomic absorption
4	57.50	9.583	6	VLVLVHVLVLVL		Calculated
5	59.00	9.833	6	L		Atomic absorption
80	60.50	10.083	6	VLVLVL		INAA
100	71.00	11.833	6	L		Atomic absorption
28	73.50	12.250	6	LL		Atomic absorption
19A	86.00	14.333	6			Atomic absorption
56	88.50	14.750	6			Atomic absorption
34	100.00	16.667	6			EDTA titration
21	117.50	19.583	6			EDTA titration
23	120.50	20.083	6			Atomic absorption
99	124.50	20.750	6	VLVLVHH		Atomic absorption
46	127.50	21.250	6	VL		EDTA titration
2	127.50	21.250	6			Atomic absorption
3	128.00	21.333	6			Atomic absorption
63	128.00	21.333	6	LVLVHLVH		Atomic absorption
57	135.50	22.583	6			Atomic absorption
8	142.00	23.667	6			Atomic absorption
64	142.00	23.667	6	H		Atomic absorption
19B	145.50	24.250	6			IC
89	148.00	24.667	6			Atomic absorption
53	156.50	26.083	6			Atomic absorption
20	157.50	26.250	6			Atomic absorption
52	158.50	26.417	6			EDTA titration
12	162.50	27.083	6			Atomic absorption
51A	164.00	27.333	6			Atomic absorption
29	172.00	28.667	6	H		Atomic absorption
51B	180.00	30.000	6	H		Atomic absorption
15	180.00	30.000	6	VH		EDTA titration
14A	192.50	32.083	6			EDTA titration
22	206.00	34.333	6			Colorimetric
1	208.00	34.667	6	VH		Cadmium red
107	211.00	35.167	6	H		Atomic absorption
87	218.00	36.333	6	H		ICAP/atomic absorption
14B	223.00	37.167	6	VHVH		Atomic absorption
24	227.50	37.917	6	H		Atomic absorption
48	241.50	40.250	6	HHHVH		Atomic absorption
13	251.50	41.917	6	HHVHHHH	High	ICAP
74	258.00	43.000	6	VHVHVHHVHH	High	Atomic absorption
73	261.00	43.500	6	HVHVHHVHH	High	Atomic absorption
66	262.00	43.667	6	HHHVHVHVH	High	EDTA titration
58	274.00	45.667	6	VHVHVHVHVHVH	High	ICAP

*L – One low result; VL – One very low result; H – One high result; VH – One very high result.

INAA – Instrumental neutron activation analysis.
IC – Ion chromatography.
ICAP – Inductively coupled argon plasma.

Note: Overall average rank is 24.000.

Table 21. Evaluation Summary of Calcium Results*

Laboratory No.	2S	Grubbs	Paired results S.D. sum	Rank L/H	Rank VL/VH
1					1
4	4	3	3		6
5				1	
13			2	5	1
14B		1			2
15		1			1
24				1	
28				2	
29				1	
30				2	
46					1
47	2		2	2	2
47D	1		3	1	4
48			2	3	1
51B				1	
58	4	4	3		6
59			2	1	1
60	5	4	3		6
63	2	1	2	2	3
64				1	
66	2	2	2	3	3
73	2	1	3	3	3
74		2	3	2	4
80			3		3
87				1	
99	2	2	2	1	3
100				1	
107				1	
109				3	

*Laboratories Nos. 2, 3, 8, 12, 14A, 19A, 19B, 20, 21, 22, 23, 34, 51A, 52, 53, 56, 57 and 89 are unflagged, having produced no suspect results by procedures of 2S, Grubbs, standard deviation sum or ranking.

Table 22. Hardness Analytical Results*

Laboratory No.	Method	Detection limit	Sample results (mg/L $CaCO_3$) 1	2	3	4	5	6
1	Calculated	0.7	114.0	128.0	149.0	49.0 R	158.0	104.0
2	Calculated		108.0	124.0	144.0	43.0	146.0	97.0
3	Calculated		109.4	120.1	143.0	43.5	149.1	96.1
4	Calmagite	5.0	106.0	119.0	138.0	33.0 R	144.0	87.0
5	Calculated	0.02	106.0	116.0	136.0	41.5	145.0	90.9
8	Calculated	16.0	115.0	120.0	149.0	43.0	154.0	94.0
12	Calculated		112.0	124.0	146.0	45.5	155.0	96.3
13	Calculated	0.165	118.0	133.0 R	157.0	48.6	166.0 R	104.0
14	EDTA titration	5.0	111.0	124.0	143.0	42.1	152.0	95.1
15	Calculated		109.0	125.0	146.0	47.0	158.0	99.0
19A	Calculated		106.0	121.0	141.0	44.0	150.0	92.0
19B	Calculated		110.0	123.0	144.0	44.0	155.0	99.0
20	EDTA titration	10.0	113.0	124.0	146.0	43.0	156.0	94.0
21	EDTA titration		113.0	124.0	146.0	45.0	157.0	100.0
22	Calculated	1.0	116.0	126.0	149.0	46.0	157.0	95.0
23	Calculated	2.0	109.0	121.0	145.0	42.0	153.0	96.0
24	Calculated		115.0	126.0	151.0	46.0	159.0	93.0
28	Calculated	5.0	103.0	115.0 R	137.0	44.0	153.0	92.0
29A	EDTA titration		111.0	124.0	146.0	44.0	156.0	97.0
29B	Calculated		120.0	127.0	151.0	45.0	158.0	101.0
30	EDTA titration	5.0	110.0	120.0	140.0	45.0	160.0	98.0
34	EDTA titration	1.0	111.0	124.0	145.0	42.0	157.0	97.0
46	EDTA titration	4.0	104.0	120.0	142.0	38.0	148.0	88.0
47	EDTA titration	1.0	102.0 R	117.0	133.0 R	42.0	140.0	88.0
48	Calculated		121.0	131.0	152.0	47.0	164.0	117.0 R
51A	Calculated	2.0	112.0	122.0	143.5	42.0	152.5	96.5
51B	EDTA titration	1.0	114.0	118.0	142.0	48.0	152.0	97.0
52	EDTA titration	5.0	110.8	125.5	149.0	42.0	156.0	95.0
53	EDTA titration	1.0	114.4	124.9	146.6	46.2	157.4	97.4
56	Atomic absorption	1.0	111.0	123.0	143.0	44.0	152.0	95.0
57	Calculated		112.0	124.0	146.0	44.0	155.0	98.0
58	Calculated	0.1	128.8 R	139.7 R	163.2 R	50.5 R	177.6 R	110.6 R
59	Calculated		103.8	114.1 R	138.0	41.3	145.8	89.8
60	EDTA titration	1.0	113.0	121.0	141.0	45.7	150.0	96.2
63	EDTA titration	2.0	110.0	120.0	145.0	47.0	155.0	100.0
64	EDTA titration	1.0	106.0	117.0	140.0	40.0	153.0	92.0
66	EDTA titration	2.0	112.0	126.0	148.0	44.0	158.0	98.0
73	Calc./EDTA titration	1.0	117.0	132.0	156.0	47.7	166.0 R	98.8
74	EDTA titration	<1.0	113.0	126.0	148.0	49.0 R	159.0	99.0
80	Calculated		101.0 R	115.0 R	132.0 R	45.0	140.0	94.0
87	Calculated		116.0	129.0	151.0	45.6	161.0	98.5
89	EDTA titration	2.0	116.0	124.0	148.0	48.0	152.0	94.0
99	Electro titration	2.0	<2.0	<2.0	<2.0	41.0	40.0 R	26.0 R
100	Calculated		108.4	117.6	140.6	41.47	145.4	93.37
107	EDTA titration	0.1	112.2	125.0	150.8	44.6	152.0	98.5
109	Calculated		108.0	117.0	138.0	41.0	145.0	93.0
Design values (mg/L)†			111.49	123.04	145.60	44.26	158.32	97.57
Median values (mg/L)			111.5	124.0	145.0	44.0	154.0	96.2
$\bar{x}$, Mean values (mg/L)			111.00	122.19	144.66	44.36	154.18	95.77
S.D., Standard deviation (mg/L)			4.11	4.01	4.23	2.44	5.40	3.78
C.V., Coefficient of variation (%)			3.70	3.28	2.92	5.50	3.50	3.95
Mean error (mg/L)			0.49	0.85	0.94	0.1	4.14	1.8
Relative mean error (%)			0.4	0.7	0.6	0.2	2.6	1.8
Recovery (%)			100	99	99	100	97	98

*Results with a flag R and underlined were determined to be suspect by Grubbs and 2S procedures, respectively.

†Values for samples 1, 2, 3, 5 and 6 were calculated from estimated volume and amounts of chemicals added. The value for sample 4 is an average value of several in-house analyses.

Table 23. Summary of Suspect Hardness Results by Single Sample Treatment

Laboratory No.	Sample	Value	Rejection
1	4	49.0	−, Grubbs
4	4	33.0	2S, Grubbs
13	2	133.0	2S, Grubbs
13	3	157.0	2S, −
13	5	166.0	−, Grubbs
28	2	115.0	−, Grubbs
46	4	38.0	2S, −
47	1	102.0	−, Grubbs
47	3	133.0	2S, Grubbs
47	5	140.0	2S, −
48	1	121.0	2S, −
48	6	117.0	2S, Grubbs
58	1	128.8	2S, Grubbs
58	2	139.7	2S, Grubbs
58	3	163.2	2S, Grubbs
58	4	50.5	2S, Grubbs
58	5	177.6	2S, Grubbs
58	6	110.6	2S, Grubbs
59	2	114.1	−, Grubbs
73	2	132.0	2S, −
73	3	156.0	2S, −
73	5	166.0	−, Grubbs
74	4	49.0	−, Grubbs
80	1	101.0	2S, Grubbs
80	2	115.0	−, Grubbs
80	3	132.0	2S, Grubbs
80	5	140.0	2S, −
99	5	40.0	2S, Grubbs
99	6	26.0	2S, Grubbs

Table 24. Summary of Suspect Hardness Results by Paired Sample Treatment

	Number of paired results outside the circles	
Laboratory No.	Greenberg *et al.* (5)*	S.D. sum (8)
1	3 out of 3	0 out of 3
3	2	0
4	3	0
5	3	2
8	3	0
13	3	3
19A	3	0
22	3	0
24	2	0
28	3	3
29B	3	2
30	3	0
46	3	0
47	3	3
48	3	3
51A	1	0
51B	2	0
52	2	0
58	3	3
59	3	3
60	2	0
63	2	0
64	3	0
66	1	0
73	3	3
74	1	0
80	3	3
87	3	1
89	2	0
100	3	0
107	2	0
109	3	1

*Throughout the study, circles of radius are considered 2 Sg rather than 2.448 Sg.

Table 25. Hardness Ranking Results

Laboratory No.	Total rank	Average rank	No. of samples ranked	Summary of flagging*	Bias	Method
99	9.50	1.583	6	VLVLVLLVLVL	Insufficient data	Electro titration
47	30.00	5.000	6	LLLVLL	Low	EDTA titration
59	33.00	5.500	6	LLLL	Low	Calculated
4	33.50	5.583	6	VLLVL	Low	Calmagite
5	37.00	6.167	6	LLL	Low	Calculated
109	46.00	7.667	6	LLL		Calculated
46	49.50	8.250	6	LVLL		EDTA titration
80	53.00	8.833	6	VLLVLVL		Calculated
64	57.00	9.500	6	LL		EDTA titration
100	59.00	9.833	6	L		Calculated
28	63.50	10.583	6	LL		Calculated
19A	81.50	13.583	6			Calculated
3	100.00	16.667	6			Calculated
23	108.50	18.083	6			Calculated
2	111.50	18.583	6	L		Calculated
14	116.50	19.417	6			EDTA titration
56	117.00	19.500	6			Atomic absorption
51A	120.50	20.083	6			Calculated
60	130.50	21.750	6			EDTA titration
8	141.00	23.500	6			Calculated
30	142.50	23.750	6			EDTA titration
34	143.00	23.833	6			EDTA titration
51B	144.00	24.000	6	H		EDTA titration
19B	145.50	24.250	6			Calculated
20	145.50	24.250	6			EDTA titration
52	149.50	24.917	6			EDTA titration
29A	155.50	25.917	6			EDTA titration
63	158.50	26.417	6	H		EDTA titration
57	160.50	26.750	6			Calculated
12	161.50	26.917	6			Calculated
89	172.00	28.667	6	H		EDTA titration
107	178.00	29.667	6			EDTA titration
21	187.00	31.167	6			EDTA titration
66	187.50	31.250	6			EDTA titration
15	188.00	31.333	6	H		Calculated
22	198.50	33.083	6			Calculated
53	199.00	33.167	6			EDTA titration
24	200.50	33.417	6			Calculated
74	224.00	37.333	6	VH		EDTA titration
87	231.50	38.583	6			Calculated
29B	232.00	38.667	6	H		Calculated
1	236.50	39.417	6	VHH		Cadmium red
73	250.50	41.750	6	HHHH	High	Calc./EDTA titration
48	258.00	43.000	6	VHHHHVH	High	Calculated
13	264.00	44.000	6	HHHVHHH	High	Calculated
58	275.00	45.833	6	VHVHVHVHVHVH	High	Calculated

*L – One low result; VL – One very low result; H – One high result; VH – One very high result.

Note: Overall average rank is 23.500.

Table 26. Evaluation Summary of Total Hardness Results*

Laboratory No.	2S	Grubbs	Paired results S.D. sum	Rank L/H	Rank VL/VH
1		1		1	1
2				1	
4	1	1		1	2
5			2	3	
13	2	2	3	5	1
15				1	
28		1	3	2	
29B			2	1	
46	1			2	1
47	2	2	3	4	1
48	2	1	3	3	2
51B				1	
58	6	6	3		6
59		1	3	4	
63				1	
64				2	
73	2	1	3	4	
74		1			1
80	3	3	3	1	3
87			1		
89				1	
99	2	2		1	5
100				1	
109			1	3	

*Laboratories Nos. 3, 8, 12, 14, 19A, 19B, 20, 21, 22, 23, 24, 29A, 30, 34, 51A, 52, 53, 56, 57, 60, 66 and 107 are unflagged, having produced no suspect results by procedures of 2S, Grubbs, standard deviation sum or ranking.

Appendix
List of Participants

List of Participants

Environment Canada, Environmental Conservation Service
- Atlantic Region, Water Quality Branch Laboratory (Moncton)
- Ontario Region, Water Quality Branch, Inorganic Laboratory (Burlington)
- Pacific and Yukon Region, Water Quality Branch Laboratory (Vancouver)
- Western Region, Water Quality Branch Laboratory (Calgary)

Environment Canada, Environmental Protection Service
- Air Pollution Technology Centre (Ottawa)
- Atlantic Region, Environmental Services Branch (Halifax)
- Northwest Region, Environmental Services Branch (Edmonton)

Health and Welfare Canada, Medical Services Branch
- Occupational Health Unit (Ottawa)

Provincial Government Laboratories
- Alberta Department of the Environment, Pollution Control Laboratory (Edmonton)
- British Columbia Research Council, Division of Applied Biology (Vancouver)
- Manitoba Department of Mines, Resources and Environmental Management, Environmental Protection Branch (Winnipeg)
- Ontario Ministry of the Environment, Thunder Bay Regional Laboratory (Thunder Bay)
- Ontario Ministry of the Environment, Inorganic Trace Contaminants Section (Rexdale)
- Ontario Ministry of Natural Resources, Geoscience Laboratories (Toronto)
- Saskatchewan Department of Public Health, Provincial Laboratories (Regina)
- Service de la protection de l'environnement, Complexe scientifique (Sainte-Foy)

Industrial and Consulting Laboratories
- Acres Consulting Services (Niagara Falls, Ontario)
- Beak Consultants Ltd. (Mississauga, Ontario)
- CAN TEST Ltd. (Vancouver, British Columbia)
- Chemex Labs Ltd. (Calgary, Alberta)
- Chemical and Geological Laboratories (Edmonton, Alberta)
- Domtar Ltd. (Senneville, Quebec)
- Enviroclean Ltd. (London, Ontario)
- Noranda Mines Ltd. (Noranda, Quebec)
- Powell Analytical Consulting & Services (Calgary, Alberta)
- Shell Canada Resources Ltd. (Calgary, Alberta)