INLAND WATERS BRANCH

DEPARTMENT OF ENERGY, MINES AND RESOURCES

Interlaboratory Quality Control Study No. 1

Calcium, Total Hardness, Sodium and Potassium

W.J.TRAVERSY and R.W.WALES

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Preface

This is the first of a number of reports on analytical quality control planned by the Water Chemistry Subdivision of the Water Quality Division, Inland Waters Branch. Because the Division is rapidly expanding with analytical laboratories in Ottawa and Burlington, Ontario; Moncton, New Brunswick; and Calgary, Alberta, it was considered necessary to establish a quality control program to ensure a high quality of performance in all Divisional laboratories.

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INTRODUCTION

Many laboratories operate their own in-house quality control program but the Division has taken a further step in setting up an interlaboratory program to ensure compatibility of results between the Division's laboratories and to be assured that analytical data supplied to the Division's water quality data bank is meaningful. Provincial and other agencies are welcome, and indeed are encouraged, to participate in this program.

Participating Laboratories

Department of Energy, Mines and Resources,

- West Water Quality Station (Calgary)
- East Water Quality Station (Moncton)
- Analytical Services Subsection (Burlington)
- Analytical Services Section (Ottawa)

Department of Health Services and Hospital Insurance, Vancouver, Canada.

SAMPLE PREPARATION

Experience with quality control programs has shown that duplicate analyses of a single sample usually yield results essentially identical. Youden (1959) has shown that single analyses of two different samples provide more information. With this in mind, each participating laboratory received two ranges of ten identical samples for a total of twenty samples. One analysis was done on each sample for calcium, total hardness (or magnesium), sodium and potassium. It is possible to use samples from natural sources, but because it is difficult to obtain such samples known to have minimal short-time variations in composition, artificial samples were prepared for the study. One large batch of each of the two ranges was prepared in plastic containers and stored for two weeks. After storage, one liter bottles were filled and distributed. Accompanying the samples was a Report Sheet for each parameter for entering results. Each laboratory was assigned a code number. Analytical methods were not specified although laboratories of the Water Quality Division use only those methods that have been approved by the Division.

GRAPHICAL REPRESENTATION OF RESULTS

The procedure of Youden (1959) was used with some modification to evaluate the results from each laboratory. This method permits the simultaneous evaluation of paired results and also makes it possible to identify results affected by systematic or random errors. In this procedure, samples of two different ranges are sent to participating laboratories with the request that each sample be tested once for each parameter. The pairs of results reported by the laboratories are used to prepare a graph for each parameter. The graph is prepared by drawing the X-axis at the bottom of the paper, and laying off on this axis a scale that covers the range of results obtained on one sample for a particular parameter. At the left, the Y-axis is provided with a scale that covers the range of results obtained on the other sample for the same parameter. After the points are plotted, a horizontal median line is drawn parallel to the X-axis and a second median line is drawn parallel to the Y-axis. The median values were obtained for each constitutent from the values reported by the laboratories.

In this study, the co-ordinates plotted were arbitrarily chosen from each participant's results. A co-ordinate pair is formed from the first result in the low range and the first result in the high range. Similarly, another pair is formed from the last result in the low range and the last result in the high range. The participant's results for the low and high range are the abscissa and the ordinate respectively. Thus, for each laboratory, a pair of results produces one point that is indicated by the coded number of that laboratory. Figures 1-4 show, by constituent, the results obtained on four samples by all laboratories.

The data, when represented graphically, permit considerable interpretation both as to overall performance of a laboratory and types of errors that may account for poor performance. The relationship between a laboratory's results and the intersection of the two median lines is the basis for interpretation. In general, results lying close to the intersection represent a high degree of accuracy, whereas distant points represent poor accuracy. Co-ordinates lying close to one median but distant from the other indicate an inconsistent performance. When a result is far from the intersection of the medians, further interpretation is possible. The median line divides the graph into four quadrants. In the situation where only random or chance errors affect laboratory results, the points would be expected to be equally dispersed in all quadrants. This follows because plus and minus errors are equally probable. This is rarely seen, however; instead, most charts show the majority of points falling in the upper right (+,+) and lower left (-,-) quadrants. This means that systematic errors tend to produce results that are either high or low. Points lying in the other two quadrants are affected inconsistently, since they represent results high on one sample and low on the other. Each quadrant indicates different effects influencing a laboratory's results on the two samples and, in general, the following interpretations can be given:

1. Results in the upper right and lower left quadrants are systematically affected and are usually indicative of one or more of the following: poor instrument adjustment or calibration, inaccurate standards, or improper techniques;

2. Results in the upper left or lower right quadrants are inconsistently and less predictably affected and may be due to human errors introduced when calculating, graph reading or reporting results.

Using this type of graph, acceptability of any laboratory's results can be defined following criteria by Greenberg (1961):

1. Results falling between the mean and ±1 standard deviation are acceptable;

2. Results between ±1 and ±2 standard deviations are acceptable but questionable;

3. Results outside the limits of ±2 standard deviations are unacceptable.

The standard deviation limits are represented as ellipses drawn on the graph. The inner ellipse on each graph defines the ±1 standard deviation area and the outer ellipse, the ±2 standard deviation area.

Ideally, standard deviation limits are represented by a circle where the standard deviation is the same value along both axes. In this study, the standard deviation along the ordinate is normally greater than that along the abscissa. For this reason, the limits are drawn as ellipses of the general form

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1$$

where a and b are functions of the standard deviations on ordinate and abscissa respectively.

DISCUSSION OF RESULTS

Tables I - IV list all the results reported by the participating laboratories and for each parameter in each range show the mean result, the standard deviation and the coefficient of variation (%) for each laboratory. The coefficient of variation (v) is defined as the standard deviation (σ) expressed as a percentage of the mean result x, i.e. $v = \frac{100\sigma}{x}$

Calcium

Precision: Two laboratories obtained high coefficients of variation in determining calcium at the 13 mg/l level. It is to be noted that both these laboratories determined calcium by Atomic Absorption Spectrophotometry. Because of the poor results, it is recommended that the precision at this level be checked.

All laboratories had good precision at the 45 mg/l level.

Overall Performance: A laboratory's overall performance is determined by its position on the graphs relative to the median lines. From the calcium graph (Fig. 1) it is noted that one laboratory has points quite distant from the median lines (outside the ±2 standard deviation limit) showing that they obtained high results in both ranges. This is a systematic error possibly caused by an incorrect stock solution or error in noting sample size. The results fall outside the ±2 standard deviation and are unacceptable.

Total Hardness

Precision: From Table I, it is noted that the two laboratories with high coefficients of variation for calcium also show similar high values for total hardness. This is because their total hardness results are calculated from calcium and magnesium results determined by atomic absorption and the poor precision of the calcium analyses is reflected in the total hardness figures. The precision at the total hardness level of 180 mg/l $CaCO_3$ was good for all laboratories.

Overall Performance: From Figure 2 it can be seen that the points of laboratory 102 occupy approximately the same position as their points on the calcium graph, again because the total hardness values were calculated from the calcium and magnesium results. The points for laboratory 101 are quite distant from those of the other laboratories. Their points while close to the verticle median are far off the horizontal median. Often points falling in this manner are due to a mistake in calculation, dilution, typing, or graph reading. In this case it was discovered that the error was in the determination of magnesium and was due to a mistake in applying a dilution correction; the magnesium results were about one half of the values reported by the other laboratories. The points for laboratory 104, while close to the ±2 standard deviation limit, show a slight systematic bias.

Sodium

Precision: The coefficients of variation were below two per cent for four of the five laboratories. Laboratory 101 had coefficients of 3.4% and 6.9% respectively. The wide scatter may have been due to random errors occurring in measuring the peak heights and in reading the results from the calibration curve.

Overall Performance: From Figure 3 it can be seen that three of the five laboratories fell within the ±2 standard deviation limit of acceptability. Laboratory 101 has one point high in the upper right and the other mid-way in the lower left quadrant. On the verticle axis this represents a spread of 12 mg/l. It is impossible to draw any statistical conclusions from such data except to say that they are an example of inconsistent performance.

The points for laboratory 104 fell in the lower left quadrant outside the ±2 standard deviation limit. This is possibly caused by a slight standardization bias.

Potassium

Precision: All laboratories obtained acceptable coefficients of variation in the low range. In the high range, laboratory 101 had a high coefficient of variation. This was caused by changing the method of analysis from emission to absorption half-way through the series of replicates. The change introduced a bias of 3 mg/l into the results.

Overall Performance: Four of the five laboratories fell within the limits of acceptability (Fig. 4). The points for laboratory 101 are beyond these limits.

SUMMARY

The use of results obtained on two water samples analysed for the same constituents permits the application of an effective analytical technique. The data, when presented graphically, enable each laboratory to readily interpret its own results. It is expected that after studying its own results relative to that of other laboratories, each laboratory will carry out an appropriate follow-up procedure if the precision of its methods do not fall within acceptable limits.

REFERENCES

1. Greenberg, A.E. 1961. Use of Reference Samples in Evaluating Water Laboratories. Public Health Reports, 76:783.

2. Greenberg, A.E. *et al*, 1969. Chemical Reference Samples in Water Laboratories. Jour. AWWA, Nov.

3. Youden, W.J. 1959. Graphical Diagnosis of Interlaboratory Test Results. Industrial Quality Control, 15:24.

TABLE I

CALCIUM, MG/L Ca

LABORATORY	101	102	103	104	105
Calcium (low range)	13.0	14.0	13.2	13.3	13.0
	13.0	15.0	12.8	13.3	13.2
	13.0	14.0	13.2	13.0	13.0
	13.5	13.5	12.8	13.3	13.2
	15.0	13.0	13.0	13.7	13.3
	15.0	14.0	13.0	13.6	13.2
	12.7	13.0	13.8	13.8	13.0
	12.7	13.5	13.8	13.8	13.0
	12.7	13.5	13.6	13.6	13.0
	12.7	14.0	13.0	13.5	13.3
mean	13.3	13.8	13.2	13.5	13.1
standard deviation	0.914	0.589	0.383	0.261	0.132
coefficient of variation (%)	6.86	4.29	2.89	1.93	1.00
Calcium (high range)	44.0	49.0	44.3	46.2	44.4
	44.5	50.0	44.3	46.2	44.4
	44.5	50.0	44.3	46.4	44.4
	45.0	50.5	44.3	46.2	44.9
	44.5	50.0	44.7	46.2	44.4
	44.5	50.0	44.3	46.2	44.4
	44.5	50.0	44.3	46.4	44.9
	44.5	50.0	44.7	46.4	44.4
	44.5	50.0	44.7	46.2	44.9
mean	44.6	50.0	44.5	46.3	44.6
standard deviation	0.369	0.369	0.209	0.146	0.262
coefficient of variation (%)	0.89	0.74	0.47	0.31	0.59

TABLE II

TOTAL HARDNESS, MG/L $CaCO_3$

LABORATORY	101	102	103	104	105
Total Hardness (low range)	51.0	55.5	52.5	50.3	52.5
	51.0	58.0	52.1	49.6	52.5
	51.8	53.4	53.0	50.3	52.5
	53.1	53.9	52.5	51.2	52.5
	56.8	50.6	52.3	50.9	52.5
	56.8	55.1	52.0	50.9	52.5
	51.1	52.6	52.0	50.3	52.5
	51.1	53.9	52.0	50.5	52.5
	51.1	53.9	52.0	50.3	52.5
	51.1	55.1	52.0	50.3	52.5
mean	52.5	54.2	52.2	50.5	52.5
standard deviation	2.361	1.949	0.340	0.448	0.000
coefficient of variation (%)	4.50	3.60	0.65	0.89	0.00
Total Hardness (high range)	144	184	182	175	177
	145	185	181	175	178
	145	187	181	175	177
	147	188	182	175	180
	144	187	179	175	178
	146	187	182	176	179
	145	187	179	175	178
	147	187	181	175	180
	145	187	180	176	178
	145	187	182	175	180
mean	145	187	181	175	179
standard deviation	1.061	1.176	1.199	0.425	1.179
coefficient of variation (%)	0.73	0.63	0.66	0.24	0.66

TABLE III

SODIUM, MG/L Na

LABORATORY	101	102	103	104	105
Sodium (low range)	11.6	11.9	11.3	11.0	12.0
	11.5	11.9	11.2	11.4	12.2
	11.5	11.9	11.2	11.4	12.2
	11.3	11.8	11.4	11.4	12.2
	11.2	11.9	11.4	11.3	12.2
	12.5	11.9	11.3	11.4	11.8
	11.2	12.0	11.4	11.4	11.8
	11.5	11.8	11.3	11.3	11.8
	11.5	12.0	11.4	11.6	11.8
	11.2	11.9	11.4	11.8	12.2
	11.2	11.9	11.4	11.2	11.8
mean	11.5	11.9	11.4	11.4	12.0
standard deviation	0.395	0.067	0.072	0.215	0.199
coefficient of variation (%)	3.44	0.57	0.67	1.89	1.66
Sodium (high range)	75.0	66.2	65.5	61.2	67
	72.0	66.0	66.0	63.8	68
	62.5	66.0	66.2	63.8	68
	65.0	66.2	66.1	63.0	68
	66.0	66.0	66.0	63.7	68
	69.0	66.0	67.8	63.0	68
	62.5	66.0	66.4	64.5	68
	62.0	66.2	66.0	63.0	68
	63.0	66.0	67.7	63.0	68
	63.0	66.2	67.7	63.0	68
mean	66.0	66.1	66.5	63.2	67.9
standard deviation	4.54	0.114	0.855	0.875	0.317
coefficient of variation (%)	6.88	0.17	1.29	1.38	0.47

TABLE IV

POTASSIUM, MG/L K

LABORATORY	101	102	103	104	105
Potassium (low range)	7.0	6.3	6.4	5.8	6.0
	7.0	6.3	6.3	5.9	6.0
	6.8	6.3	6.5	5.9	6.1
	6.8	6.3	6.4	5.9	6.0
	6.8	6.2	6.5	6.0	5.9
	6.8	6.3	6.5	6.0	5.8
	7.0	6.2	6.5	5.9	5.8
	7.0	6.3	6.4	6.1	5.9
	6.5	6.3	6.4	5.9	5.8
mean	6.8	6.3	6.4	5.9	5.9
standard deviation	0.193	0.042	0.070	0.084	0.106
coefficient of variation (%)	2.83	0.67	1.09	1.42	1.79
Potassium (high range)	38.4	34.0	35.0	35.0	35
	38.4	33.8	36.0	35.7	35
	38.1	33.8	36.0	35.7	35
	38.1	33.8	36.0	35.2	35
	38.1	33.8	36.0	35.1	35
	38.1	33.7	37.0	35.1	35
	42.3	33.7	36.5	35.9	35
	41.2	33.8	37.0	35.0	35
	41.2	33.6	37.0	34.9	35
	42.3	33.8	36.8	35.0	35
mean	39.6	33.8	36.3	35.3	35.0
standard deviation	1.874	0.113	0.650	0.364	0.000
coefficient of variation (%)	4.73	0.34	1.79	1.03	0.00

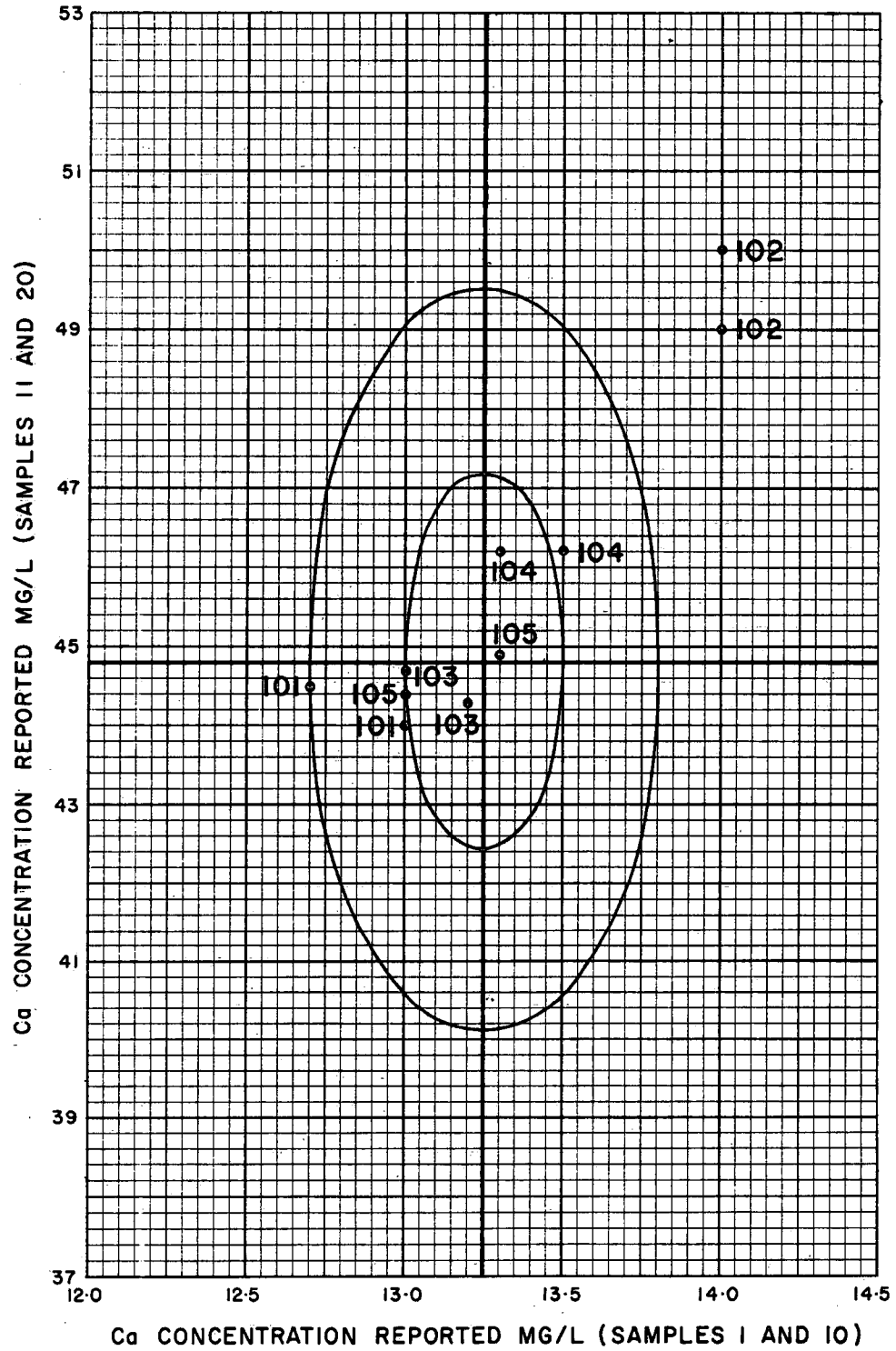

Figure 1. Relative performance of five laboratories in the analysis for Calcium.

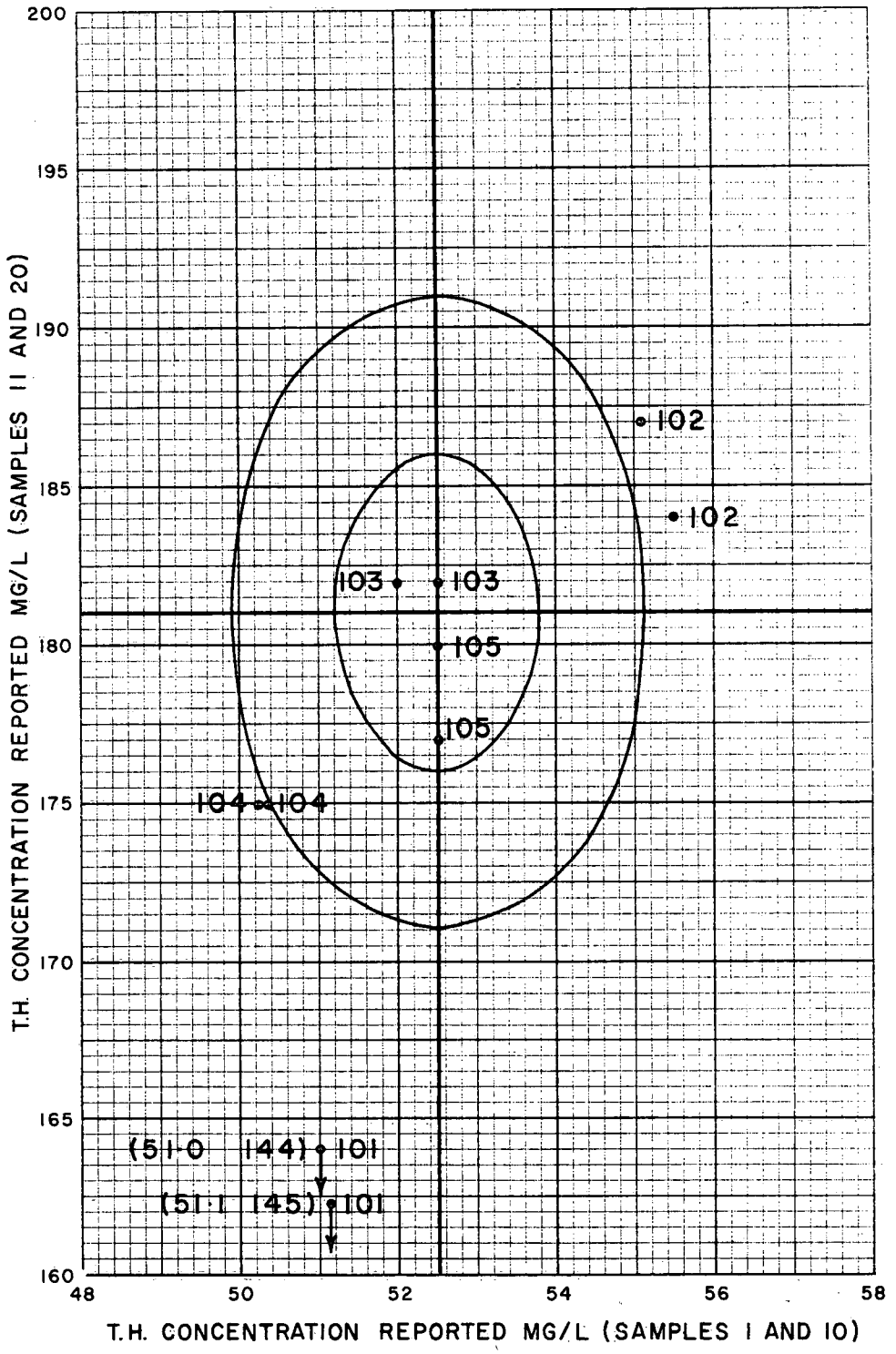

Figure 2. Relative performance of five laboratories in the analysis for Total Hardness.

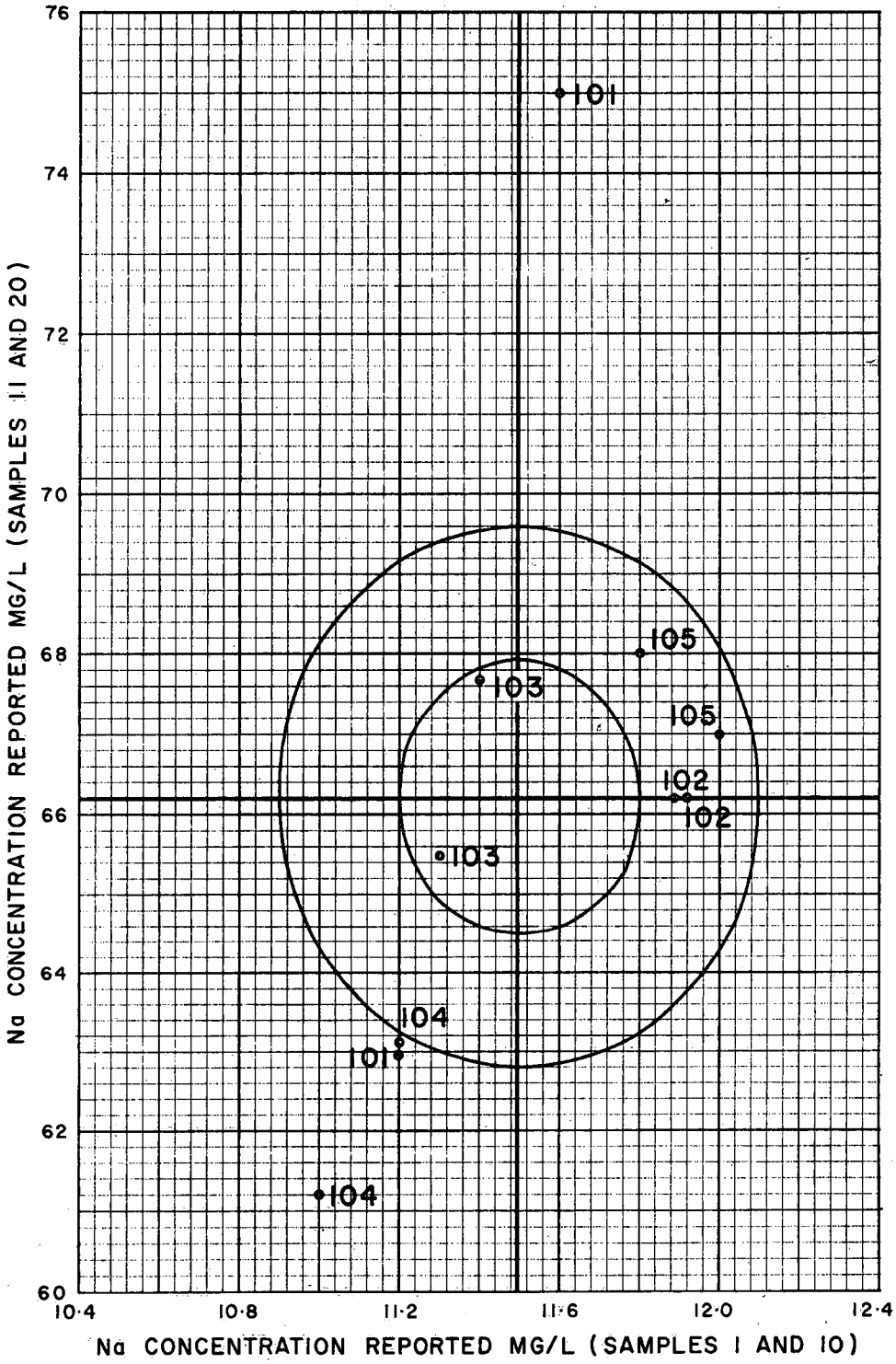

Figure 3. Relative performance of five laboratories in the analysis for Sodium.

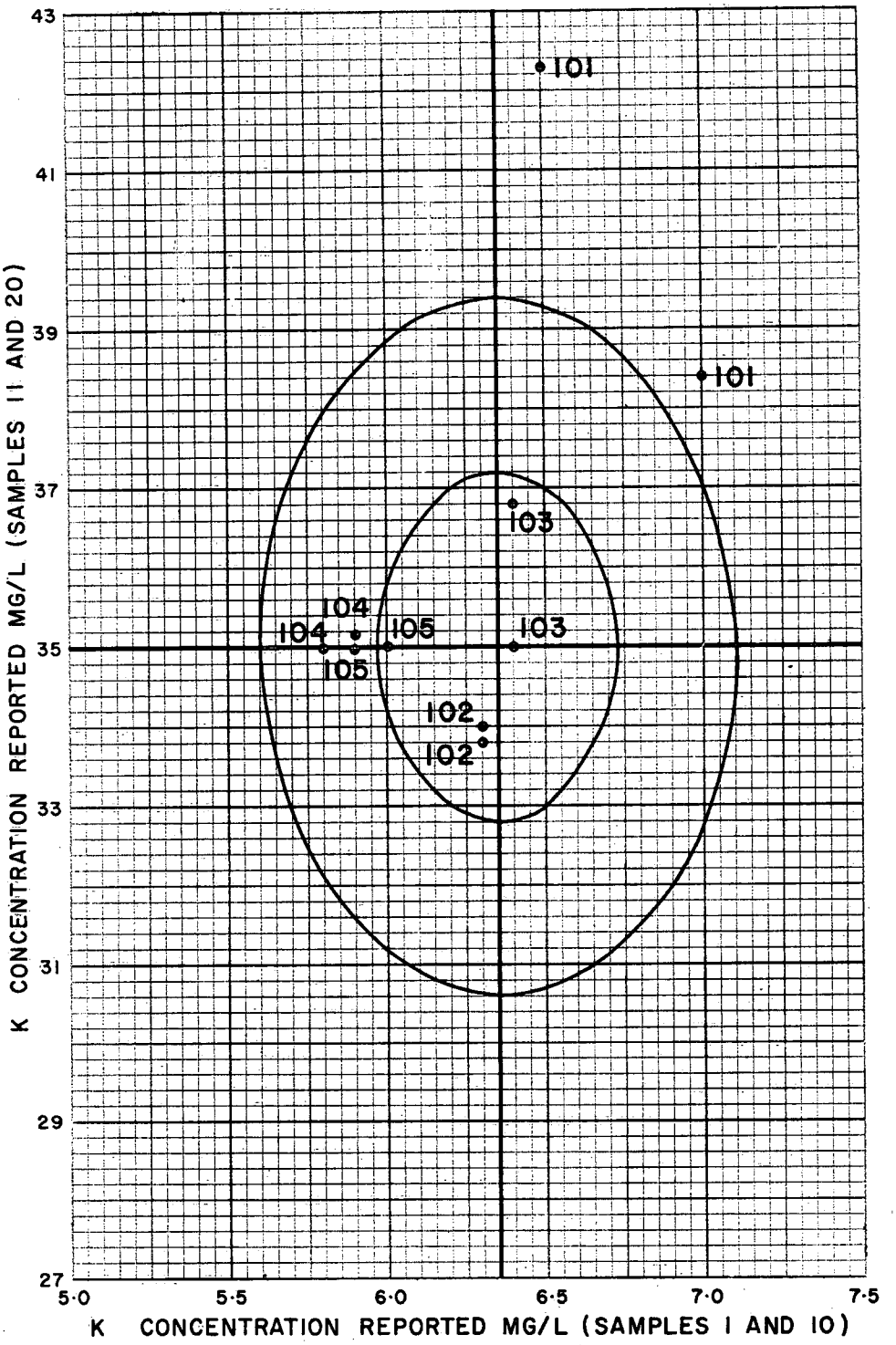

Figure 4. Relative performance of five laboratories in the analysis for Potassium.

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