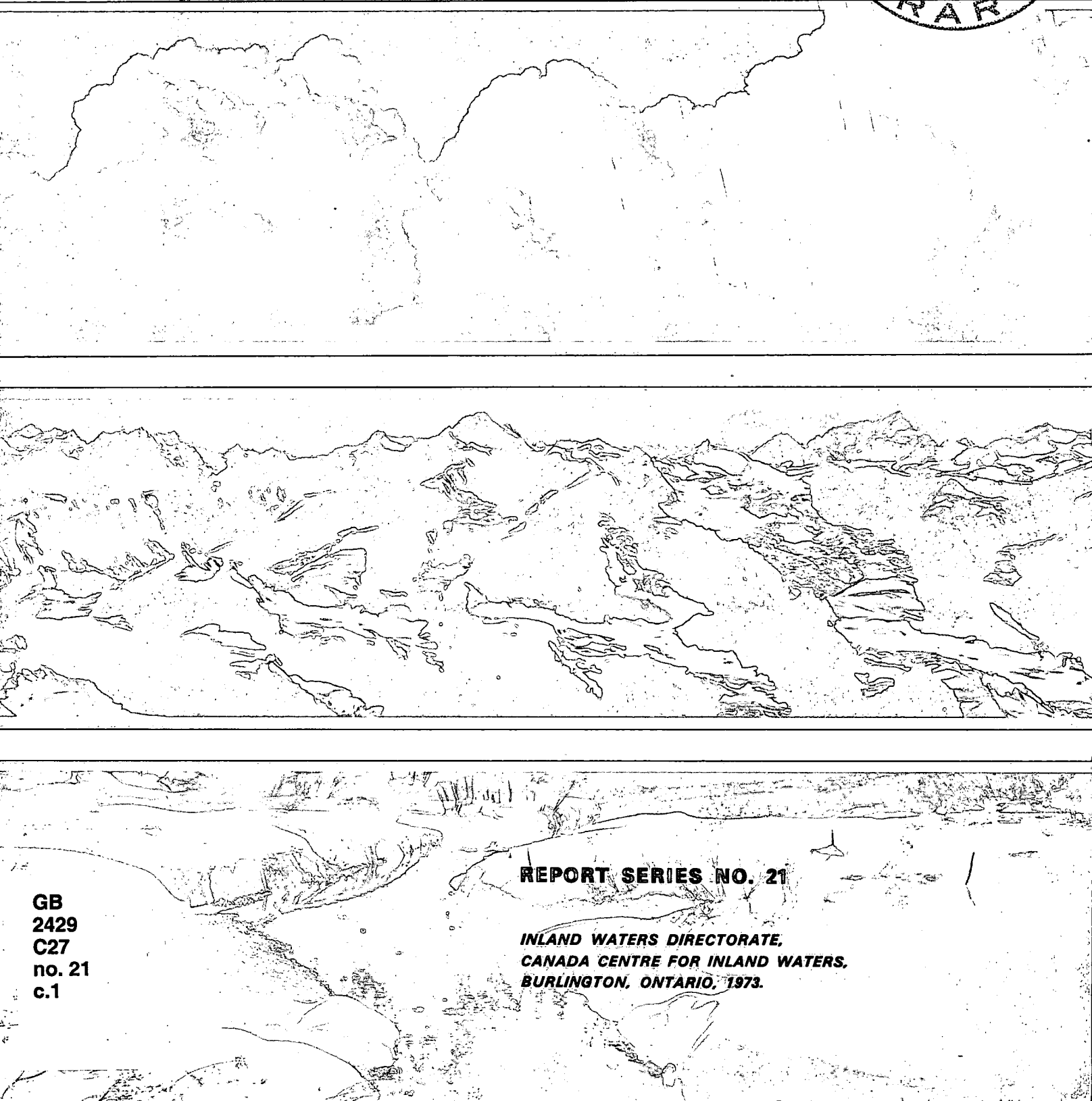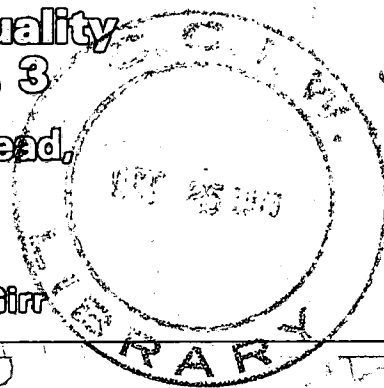Environment
Canada

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Interlaboratory Quality Control Study No. 3

Copper, Chromium, Lead, Manganese and Zinc

R. W. Wales and D. J. McGirr

REPORT SERIES NO. 21

INLAND WATERS DIRECTORATE,
CANADA CENTRE FOR INLAND WATERS,
BURLINGTON, ONTARIO, 1973.

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Contents

Appendices

Illustrations

Tables

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R.W. WALES and D.J. McGIRR

INTRODUCTION

In addition to the major metallic constituents of water such as calcium, magnesium, sodium and potassium, there is a large variety of other metals present in trace quantities of natural waters and industrial waste waters. The number of analyses requested for these trace metals has risen rapidly in recent years, particularly since the advent of atomic absorption spectroscopy. Interest in these metals has shown a parallel increase since it came to be realized that many potentially dangerous metals are much more widely distributed than had been previously realized.

Because of the large number of metals which are now commonly determined, the interlaboratory quality control study of metals has been divided into several round robins, each covering four or five metals. Chosen for the first of these round robins were copper, chromium, lead, manganese and zinc.

Five outside laboratories participated in this study in addition to the four laboratories of the Water Quality Division. The participating laboratories are listed in Appendix "A".

EXPERIMENTAL DESIGN

Seven test solutions, containing various concentrations of the five metals under test, were prepared. Each solution was used to make two duplicate samples, so that a total of 14 samples was sent out to each laboratory. The duplicate samples were 1 and 14, 2 and 8, 3 and 12, 4 and 9, 5 and 10, 6 and 13, and 7 and 11. The duplicates were used to help the laboratories in assessing the reproducibility of their results.

The concentrations of the metals in the samples are shown in Table 1. The range of concentrations used was selected with regard to both the concentrations normally found in natural waters and the concentration range to which the commonly used test methods are applicable.

The metal solutions were made in the way standard solutions normally are made in the Water Quality Division laboratories, i.e., copper was added as copper metal dissolved in 1:1 HNO_3; zinc as zinc metal dissolved in 1:1 HNO_3; chromium as potassium dichromate, $K_2Cr_2O_7$; lead as lead nitrate, $Pb(NO_3)_2$; and, manganese as manganese sulfate, $MnSO_4$.

In all cases after dissolution of the metal with acid and deionized water, the solutions were diluted to the desired concentrations of metal using deionized water and forwarded to participating laboratories. The concentrated samples were preserved by adding 3.5 ml of concentrated nitric acid per liter before being filled to the mark with deionized water. They were to be further diluted by a factor of 100 and represerved by the addition of nitric acid by the participating laboratories before being analyzed.

DATA EVALUATION

The first operation performed on the results received from the laboratories was the rejection of outliers. The method used was that of Dixon and Massey (1), who give tables of critical values for the ratio of the difference between the suspected outlier and the next farthest result to the range of all results. As the number of results increases above 8 the denominator of this ratio is reduced by ignoring the 1, 2 or 3 results farthest from the suspected outlier.

It should be noted that the matter of whether or not a given result was rejected depended not only on its distance from the mean or from the true value, but also on the dispersion of the other results. Thus, a result which was, say, 25% below the mean might have been rejected as an outlier among one set of data in which all the other results were clustered within 5% of the mean. The same result might not have been rejected if it had been part of another set of data in which the results were widely dispersed, or if most of the results were clustered about the mean but two or three were, say, 15% to 20% below the mean.

Although the samples were in duplicate, each sample was treated separately for purposes of rejection of outliers and subsequent calculations. Because several blanks were included and the amounts added were very low in several other samples, many answers were reported as less than a certain value. Rather than arbitrarily assigning a value of zero, or the detection limit, to these results, it was decided to disregard them as rejected outliers in the subsequent computations. It will be noted that this results in a few statistics being calculated from as few as three acceptable values, particularly where the true value is zero or 0.005.

Some laboratories assigned a value of zero instead of a "less than" value to results where no metal was detected. These results were accepted and used in the calculations, even though it might be argued that they should have been expressed as "less than". The attitude adopted is the same as in the case where an answer is out by a factor of 10 due to an apparent decimal error; the result is not corrected, but is accepted as offered and either rejected as an outlier or used in the calculations

The results as received from the laboratories are tabulated in Tables II to VI. Results rejected as outliers are shown with an "R" in these tables. They were not used in the subsequent calculations and are not plotted on any graphs.

Computer programs were written by the Water Quality Division to calculate for each metal the mean, standard deviation, relative standard deviation, mean error and relative error for all 14 samples. The *relative standard deviation*, also called the coefficient of variation, is the standard deviation expressed as a percent of the mean. The *mean error* is the difference between the mean and the true value (the amount of metal added),

and the *relative error* is the mean error expressed as a percent of the true value. These statistics are tabulated in Tables VII to XI.

Figures 1 to 5 were drawn by plotting the amount of metal added versus the amount reported, after rejection of outliers and "less thans". Since many of the results were rounded off by the laboratories to the nearest 0.005 or 0.010 ppm, there were many duplicate results. Consequently, a single point on any of these graphs may represent several results.

The theoretical 45° line is shown on each graph in addition to a linear regression line which was calculated for each metal. The latter line is the "best fit" to the points on the graph and gives some indication of the overall accuracy of the results.

In the remainder of this report, *accuracy* refers to the closeness of the mean to the true value, as indicated by the fit of the regression line to the 45° line and by the mean error and relative error in Tables VII to XI. *Precision* refers to the dispersion of results around the mean, as indicated by the scatter of points around the regression line in Figures 1 to 5 and by the standard deviation or relative standard deviation in Tables VII to XI. Precision increases as the standard deviation decreases.

RESULTS

(a) General

As was expected, the overwhelming majority of the results were obtained by atomic absorption spectrophotometry. A few colourimetric methods were used.

A variety of equipment is available for atomic absorption work and a wide variety of methods can be used. It is not practical to attempt to describe each laboratory's method for each metal in detail. Instead, only the most important characteristics of the methods are indicated at the bottom of Tables II to VI.

In the following discussions, statements pertaining to accuracy and precision refer to the overall accuracy and precision with which a given metal was analyzed and not to the accuracy of any given procedure or instrument. This permits general conclusions as to the degree of confidence that can be placed in results received for these metals from the various laboratories. In addition, a participant who finds poor results relative to the other laboratories or to his own expectations, may be able to get some idea from the data in this report as to whether the fault lies in the choice of a poor method or whether his method is not giving him the accuracy of which it is capable. However, it will usually be necessary to do further follow-up work to come to a firm conclusion.

There was a good fit of the regression line to the theoretical 45° line in all cases, indicating that the analyses for these metals were done with reasonable accuracy. The precision, however, varied from metal to metal as is discussed under the individual metals below.

(b) Copper

Eight of the laboratories determined copper by atomic absorption, and one by a spectrophotometric method in which the sample is acidified with sulfuric acid, evaporated to fumes of sulfuric acid, then extracted with amyl alcohol and bathocuproine.

3

The outliers for copper were mostly associated with the samples containing a low level of copper. Laboratory 290 used direct aspiration only and reported a result of zero for several samples which contained a low concentration of copper. Laboratory 210 tended to be high by 0.005 to 0.010 mg/l throughout. This small bias was unimportant at high levels but caused two outliers at low levels of copper. It is rare to encounter a bias which is independent of concentration in atomic absorption work, but it has been known to happen when, for example, an analyst fails to make the same baseline correction for his samples that he makes for his standards, or vice versa.

The fit of the calculated regression line to the theoretical 45° line in Figure 1 is poorer than for any of the other metals in this study, mainly because the results at higher concentrations tended to be low. It is, however, still acceptable.

The precision is acceptable, at least above the 0.010 mg/l level, as can be seen from Table VII.

(c) Chromium

Six laboratories determined chromium by atomic absorption (see Table III) and two by a commonly used colorimetric method (2) using diphenyl-carbazide. The latter method appears to be reasonably accurate, but to have sensitivity about the same as that of atomic absorption by direct aspiration. In all cases where a laboratory reported "less than" a certain limit for a sample in which chromium was actually present, the result was obtained either by direct aspiration or by the colorimetric method.

It is apparent from Figure 2 that the overall accuracy of the chromium determination was good, with no evidence of a systematic error. This same conclusion is reached if the results for the colorimetric method and for atomic absorption are considered separately.

However, the precision for chromium was the poorest of all the metals in the group, and was particularly poor at the level of 0.010 mg/l and lower. This could be partly due to the fact that the extraction procedure for chromium contains a step that the others do not. Also, since chromium is probably the least commonly determined of the metals in this study, the laboratories have less experience in its determination. In addition, there is always the possibility of occasional contamination of glassware from the chromic acid cleaning solution.

(d) Lead

Eight laboratories determined lead, seven by atomic absorption and one by a colorimetric method using dithizone and carbon tetrachloride (3).

Laboratory 240 obtained very low results throughout. Since this laboratory obtained satisfactory results on other metals, the problem must lie with some factor specific to lead, such as incorrect standards. Laboratory 210 obtained very slightly high results throughout, similar to that laboratory's results for copper.

Both precision and accuracy were very good for lead, as can be seen from Figure 3 and Table IX. The results obtained using both the photometric method and the Sampling Boat technique were at least as good as the overall

results. (One should guard against concluding that the methods are superior on these grounds, however, since only one laboratory used each method).

(e) Manganese

Eight laboratories determined manganese, all by atomic absorption. Accuracy and precision were both very good as can be seen from Tables V and X and Figure 4, and there were only a few scattered outliers. It appears that manganese can be measured more precisely at lower levels than most other metals, since the relative standard deviation was low even at the 0.010 mg/l level.

(f) Zinc

All nine laboratories determined zinc and all used atomic absorption. Accuracy was reasonable but precision was only fair throughout the range shown in Figure 5. (The precision was better for the 0.250 mg/l sample which is not shown on the graph).

There was a liberal sprinkling of outliers. Several were attributed to Laboratory 290, and at least some of these were due to that laboratory using direct aspiration only. More laboratories than usual reported zinc in samples which contained none; this contributed to the calculated line on Figure 5 lying above the theoretical 45° line throughout the range, unlike the other metals. The fit of the regression line to the theoretical 45° line is acceptable however.

CONCLUSION

In this study, unlike the previous studies in this series, outliers seemed to be associated with certain laboratories rather than with any other factor. One probable reason for this is the amount of experience an individual laboratory has gained in determining the metals under study. Obviously, a laboratory that determines these metals routinely will likely have greater precision than a laboratory that determines them only rarely. The same may be said of the individual technicians who did the tests. There were some special cases such as the problem that laboratory 240 had with lead. Also, the laboratories that used only direct aspiration were not, in general, able to get accurate results at the lowest levels.

It is interesting to note that the relative standard deviation for most of the metals in this group, considered as a function of decreasing metal concentration, seems to reach a peak in the range of 0.010 to 0.050 mg/l, then decrease toward the lower levels of 0.010 mg/l to 0.005 mg/l. A good example of this is manganese (see Table X). The standard deviation for manganese falls from a range of 10.3% - 12.2% at 0.040 mg/l to 3.6% at 0.010 mg/l. It is normal for the standard deviation to increase slowly with decreasing concentration, and to turn up sharply as the detection limit is approached. The presence of an extra peak in the range of 0.010 to 0.050 mg/l may be because the results were obtained by a mixture of methods (direct aspiration, some photometric methods) having a detection limit of about 0.010 mg/l and methods (solvent extraction) having a detection limit below 0.005 mg/l. Unfortunately, enough data are not available to calculate separate standard deviations for the different procedures.

The data in Tables II to XI show that, with the possible exception of chromium at low levels, the analytical data obtained from the participating laboratories can be considered comparable.

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2. American Public Health Association, 1971. Standard Methods for the Examination of Water and Wastewater, 13th edition, p. 157.

3. Ibid, p. 196.

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2. Wales, R.W. and W.J. Traversy. Interlaboratory Quality Control Study No. 2; Total Phosphate, Organic Nitrogen, Nitrate Nitrogen and Organic Carbon. Report Series No. 19, Inland Waters Directorate, Department of the Environment, Ottawa.

Appendices

APPENDIX A

Participating Laboratories

Environment Canada

West Water Quality Subdivision (Calgary)

East Water Quality Subdivision (Moncton)

Analytical Services Section (Ottawa)

Analytical Services Subsection (Burlington)

Alberta Department of the Environment

Edmonton, Alberta

Water Resources Service, B.C. Department of Lands, Forests and Water Resources

Vancouver, British Columbia

Cominco Ltd.

Trail, British Columbia

Department of Chemical Engineering, University of Ottawa

Ottawa, Ontario

Department of Chemistry, University of Saskatchewan, Regina Campus

Regina, Saskatchewan
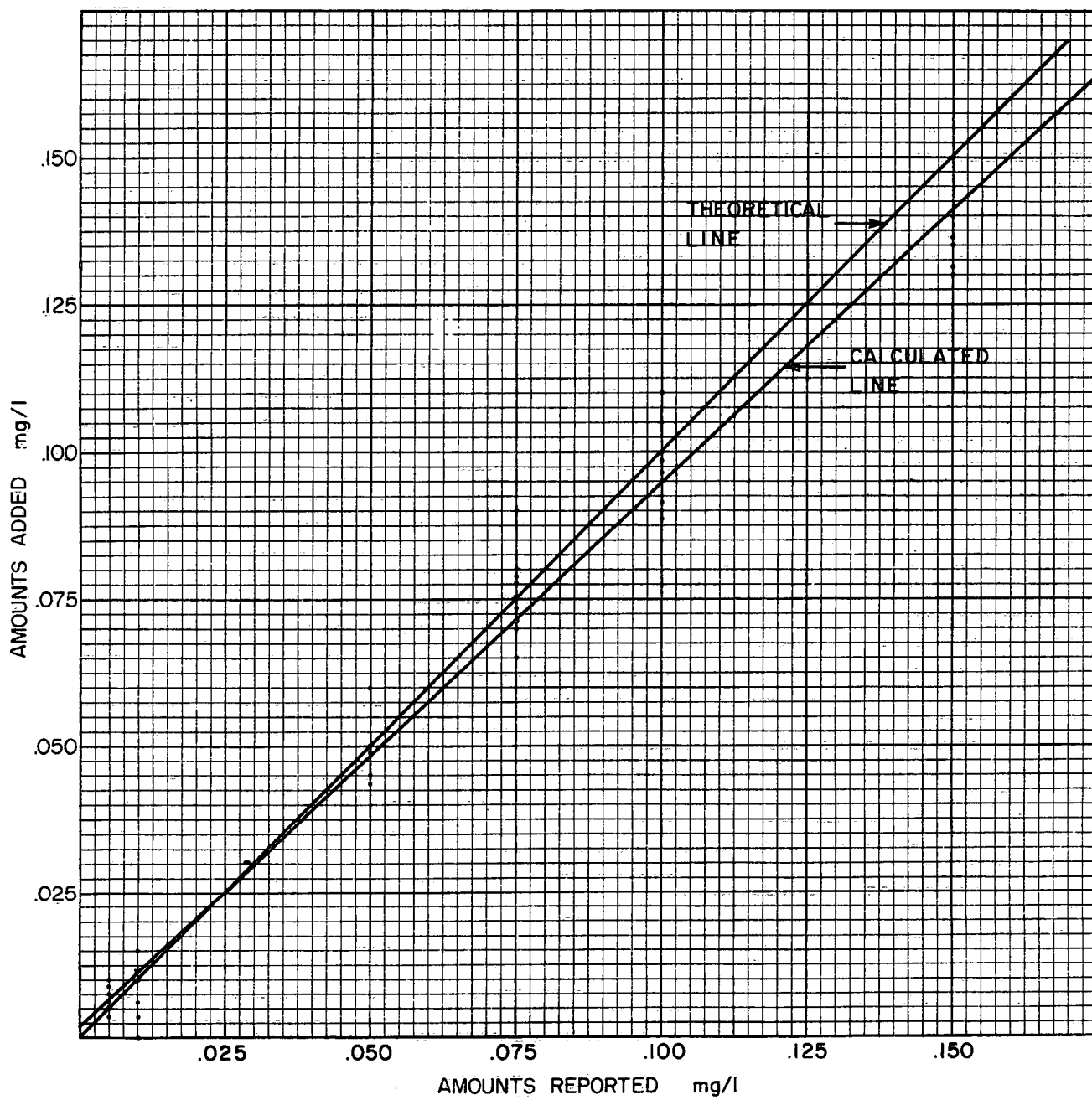
Figure 1. Regression line for copper.
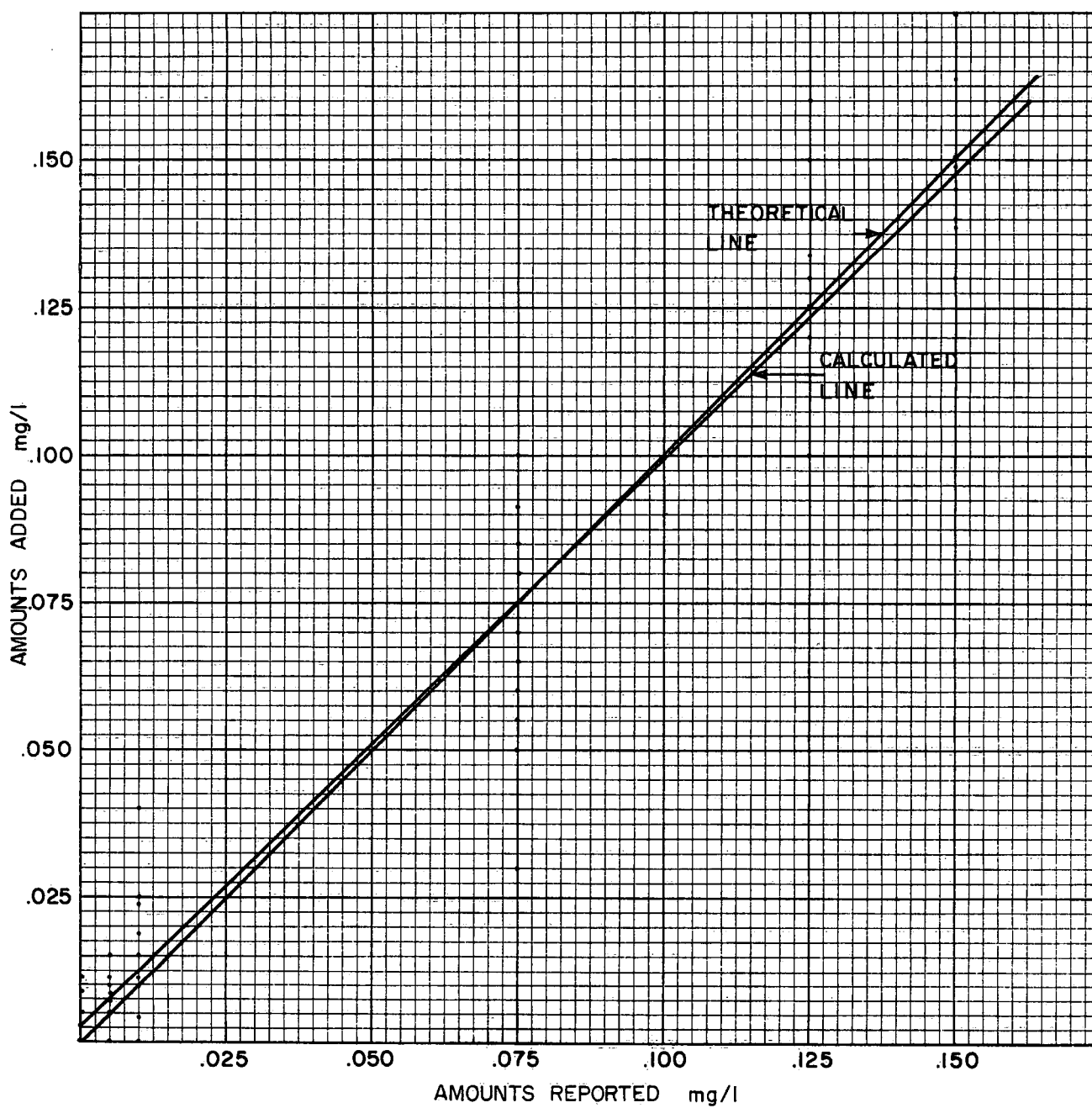
Figure 2. Regression line for chromium.

11
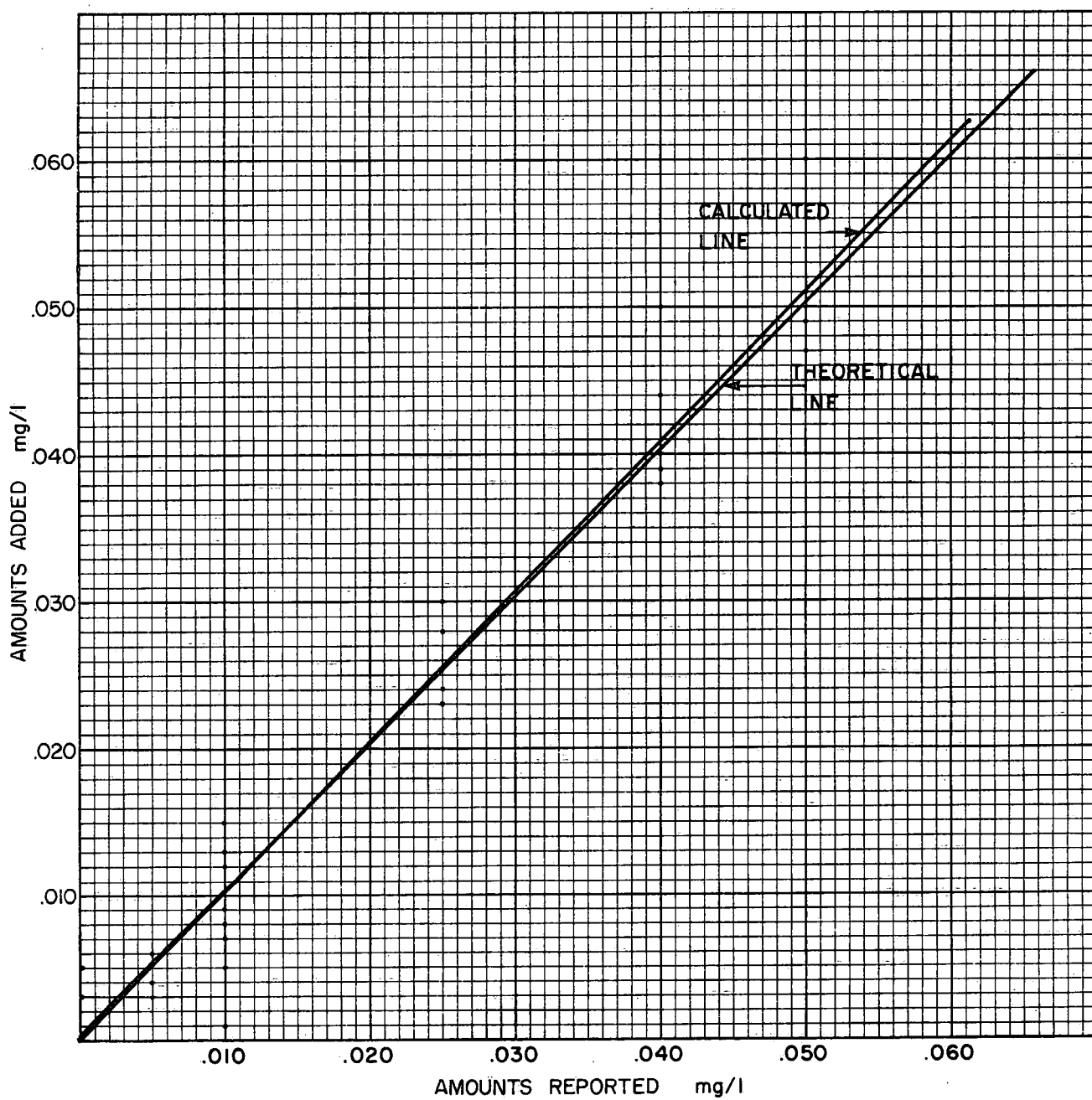
Figure 3. Regression line for lead.
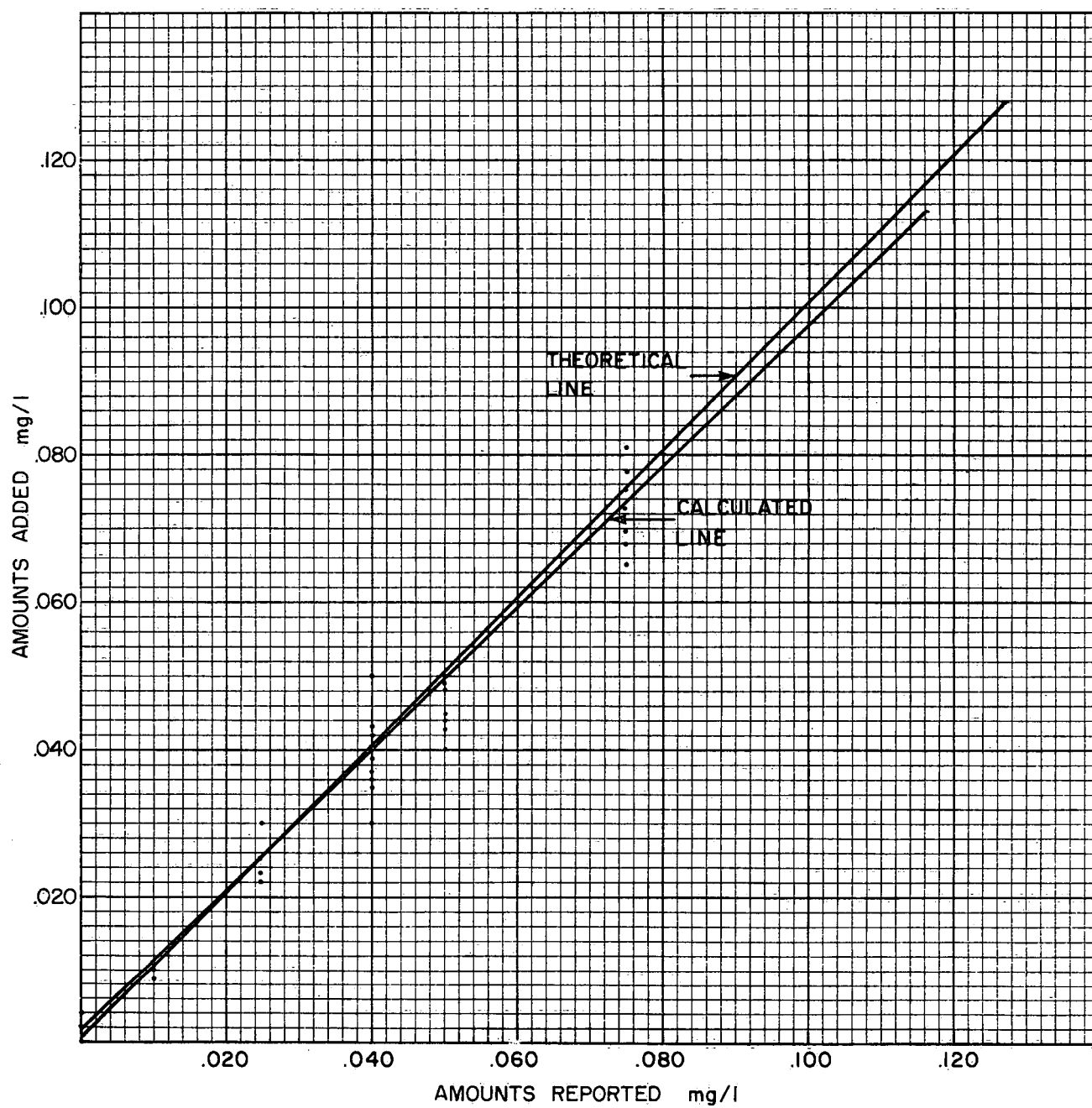
Figure 4. Regression line for manganese.
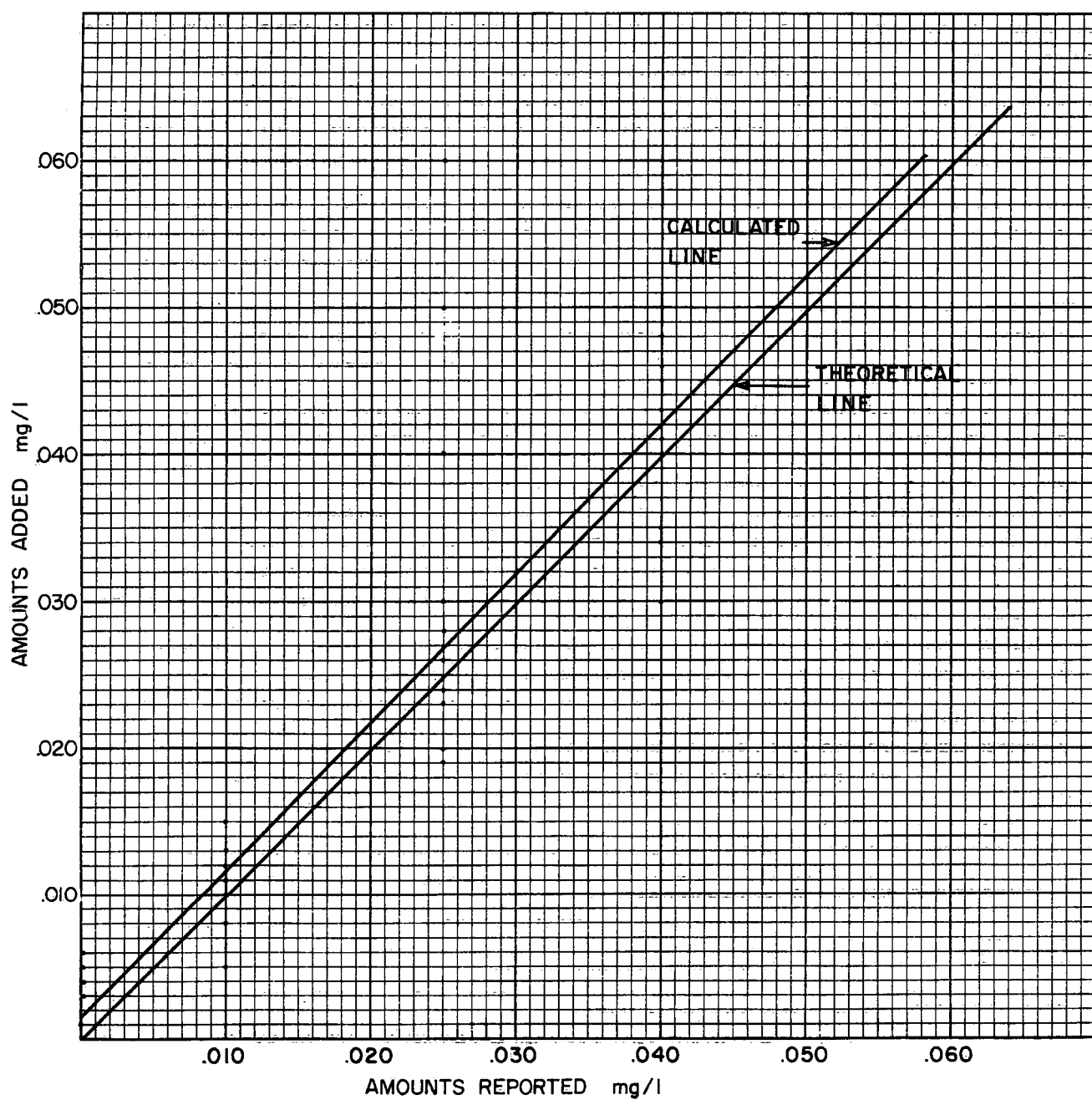
Figure 5. Regression line for zinc.

APPENDIX C

TABLE I

Actual Concentrations of Metals in Samples

SAMPLE NUMBER	COPPER (mg/1)	CHROMIUM (mg/1)	LEAD (mg/1)	MANGANESE (mg/1)	ZINC (mg/1)
1	0.005	0.150	0.010	0.010	0.025
2	0.075	0.125	0.010	0.000	0.040
3	0.010	0.075	0.025	0.000	0.025
4	0.050	0.005	0.050	0.025	0.000
5	0.100	0.010	0.000	0.040	0.010
6	0.010	0.075	0.005	0.075	0.250
7	0.150	0.000	0.040	0.050	0.005
8	0.075	0.125	0.010	0.000	0.040
9	0.050	0.005	0.050	0.025	0.000
10	0.100	0.010	0.000	0.040	0.010
11	0.150	0.000	0.040	0.050	0.005
12	0.010	0.075	0.025	0.000	0.025
13	0.010	0.075	0.005	0.075	0.250
14	0.005	0.150	0.010	0.010	0.025

ABBREVIATIONS FOR TABLES II TO VI

AA   - atomic absorption

D   - direct aspiration of all samples

E   - all samples extracted [with ammonium pyrrolidine dithiocarbamate (APDC) and MIBK unless otherwise indicated, except for manganese which is extracted with 8-hydroxy-quinoline (oxine) and MIBK].

D-E   - direct aspiration for higher concentrations and extraction for lower concentrations

DEDC   - indicates complex was formed using diethyldithiocarbamate instead of APDC with subsequent extraction by MIBK

Total   - indicates sample was evaporated to dryness, and redissolved in acid, then determined by direct aspiration.

Sample Boat - indicates the Sampling Boat technique was used

Conc   - concentration of a 200-ml sample before aspiration

Color   - colorimetric methods, which are described in the section for the metal concerned

TABLE II

Copper Results

SAMPLE NUMBER	AMT. ADDED	210	220	230	240	250	260	270	280	290
1	.005	.014R	.005	.005	.004	.004	.005	.005	.005	.0R
2	.075	.04 R	.075	.070	.065	.075	.070	.080	.070	.078
3	.010	.02R	.010	.010	.003	.010	.010	.010	.010	.0
4	.050	.06	.125R	.045	.043	.050	.045	.050	.050	.052
5	.100	.10	:10	.090	.092	.096	.095	.100	.10	.130R
6	.010	.015	.010	.010	.007	.010	.010	.010	.015	.0
7	.150	.15	.13	.135	.131	.14	.135	.140	.15	.200R
8	.075	.09	.079	.070	.072	.074	.070	.080	.075	.078
9	.050	.05	.049	.045	.050	.050	.045	.050	.050	.052
10	.100	.11	.10	.090	.088	.098	.095	.100	.10	.105
11	.150	.15	.13	.135	.136	.14	.140	.140	.14	.200R
12	.010	.015	.012	.010	.010	.010	.010	.010	.010	.0R
13	.010	.012	.012	.010	.010	.010	.010	.010	.015	.0R
14	.005	.010	.006	.005	.007	.005	.008	.005	.005	.0R
METHOD (SEE PAGE 16)		AA E-D	AA E-D	AA E	AA E	AA E-D	AA Total	AA E DEDC	Color	AA D

TABLE III

Chromium Results

SAMPLE NUMBER	AMT. ADDED LAB	210	220	230	240	250	260	270	280	290
1	.150	.13	.15	.150	-	.15	.138	.145	.14	.149
2	.125	.16	.15	.125	-	.12	.120	.125	.10	.100
3	.075	.08	.10	.075	-	.07	.080	.080	.070	.050R
4	.005	.01	.010	.005	-	<.010	.008	.005	<.005	.0
5	.010	.04	.025	.010	-	<.010	.015	.010	.005	.0
6	.075	.12R	.075	.075	-	.07	.080	.080	.075	.050R
7	.000	<.01	.037R	.00	-	<.010	.008	<.005	<.005	.0
8	.125	.12	.13	.125	-	.12	.133	.125	.10	.0R
9	.005	<.01	.012	.005	-	<.010	.015	.006	<.005	.0
10	.010	<.01	.019	.010	-	<.010	.023	.011	.005	.0
11	.000	<.01	.005	.00	-	<.010	.011	<.005	<.005	.0
12	.075	.03	.10	.075	-	.07	.092	.080	.070	.055
13	.075	.06	.10	.075	-	.06	.085	.085	.065	.050
14	.150	.11R	.15	.150	-	.15	.163	.145	.15	.177
METHOD (SEE PAGE 16)		Phot.	AA D-E	AA E	-	AA D	AA Total	AA E DEDC	Color	AA E

18

TABLE IV

Lead Results

SAMPLE NUMBER	AMT. ADDED \ LAB	210	220	230	240	250	260	270	280	290
1	.010	.015	.007	.010	.001	.008	.009	.010	.005	-
2	.010	.015	.009	.010	.001	.009	.013	.010	.010	-
3	.025	<.002	.025	.025	.003R	.024	.025	.024	.025	-
4	.050	.06	.051	.050	.006R	.047	.047	.050	.050	-
5	.000	.004R	.000	.00	*	<.006	.000	<.001	<.005	-
6	.005	.005	.004	.005	.003	<.006	.000R	.005	.005	-
7	.040	.05	.044	.040	.009R	.038	.039	.040	.040	-
8	.010	.012	.010	.010	.003R	.008	.010	.010	.015	-
9	.050	.07 R	.051	.050	.009R	.049	.050	.050	.050	-
10	.000	.005	.000	.00	.003	<.006	.003	<.001	<.005	-
11	.040	.05R	.040	.040	.010R	.038	.038	.040	.040	-
12	.025	.03	.023	.025	.050R	.025	.028	.024	.025	-
13	.005	.009R	.005	.005	.004	.006	.005	.006	.005	-
14	.010	.016R	.010	.010	.004R	.012	.010	.010	.010	-
METHOD (SEE PAGE 16)		AA D-E	AA D-E	AA E	AA D-E	AA E	AA Total	AA Sample Boat	Color	-

* Not detectable.

TABLE V

Manganese Results

SAMPLE NUMBER	AMT. ADDED	210	220	230	240	250	260	270	280	290
1	.010	.01	.010	.010	.010	.009	.010	.010	.010	–
2	.000	.01^R	.004	.00	*	<.001	.000	<.001	<.005	–
3	.000	<.01	.000	.00	.002	<.001	.000	<.001	<.005	–
4	.025	<.01	.025	.025	.020^R	.023	.025	.025	.025	–
5	.040	.05	.039	.040	.043	.036	.040	.040	.050	–
6	.075	.05^R	.073	.075	.081	.97	.072	.070	.075	–
7	.050	.05	.048	.050	.049	.044	.050	.045	.060^R	–
8	.000	<.01	.000	.00	*	<.001	.000	<.001	<.005	–
9	.025	.03	.023	.025	.040^R	.022	.025	.025	.025	–
10	.040	.04	.035	.040	.037	.036	.040	.042	.030	–
11	.050	.04	.043	.050	.044	.044	.050	.050	.040	–
12	.000	<.01	.000	.00	*	<.001	.000	<.001	<.005	–
13	.075	.07	.070	.075	.068	.078	.073	.070	.065	–
14	.010	.01	.010	.010	*	.009	.010	.010	.010	–
METHOD (SEE PAGE 16)		AA D	AA D-E	AA E	AA E	AA D-E DEDC	AA Total	AA E DEDC	AA Conc.	–

* Not detectable.

TABLE VI

Zinc Results

SAMPLE NUMBER	AMT. ADDED \ LAB	210	220	230	240	250	260	270	280	290
1	.025	.05	.027	.025	.025	.026	.020	.030	.025	.040
2	.040	.07R	.043	.040	.048	.041	.034	.040	.035	.050
3	.025	.02	.026	.025	.027	.025	.019	.026	.025	.040R
4	.000	<.002	.001	.00	.004	<.001	.001	.006	<.005	.048R
5	.010	.012	.010	.010	.012	.012	.010	.011	.010	.015R
6	.250	.26	.25	.250	.161R	.26	.156R	.250	.24	.270
7	.005	.006	.005	.005	.007	.005	.005	.005	.015R	.0R
8	.040	.05	.046	.040	.041	.040	.030	.045	.030	.050
9	.000	<.002	.005	.00	.003	<.001	.005	<.005	.025R	.0
10	.010	.015	.012	.010	.013	.012	.008	.010	.005	.015
11	.005	.008	.006	.005	.007	.008	.005	.005	.005	.0R
12	.025	.03	.027	.025	.027	.024	.020	.025	.020	.030
13	.250	.28	.25	.250	.150R	.26	.158R	.250	.24	.250
14	.025	.06	.028	.025	.025	.023	.019	.025	.020	.040
METHOD (SEE PAGE 16)		AA D-E	AA D-E	AA E	AA E	AA D-E	AA Total	AA Sample Boat	AA Conc.	AA D

TABLE VII

Copper: Statistical Data

SAMPLE NUMBER	AMOUNT ADDED (mg/1)	MEAN (mg/1)	STANDARD DEVIATION (mg/1)	RELATIVE STANDARD DEVIATION (%)	MEAN ERROR (mg/1)	RELATIVE ERROR (%)
1	.005	.0047	.0005	10.4	-.0003	- 5.7
14	.005	.0064	.0019	29.0	.0014	27.5
3	.010	.0079	.0040	51.0	-.0021	-21.3
6	.010	.0097	.0045	46.0	-.0003	- 3.3
12	.010	.0109	.0018	16.6	.0009	8.8
13	.010	.0111	.0018	16.3	.0011	11.3
4	.050	.0494	.0054	10.8	-.0006	- 1.3
9	.050	.0490	.0024	4.9	-.0010	- 2.0
2	.075	.0729	.0050	6.8	-.0021	- 2.8
8	.075	.0765	.0063	8.2	.0015	1.9
5	.100	.0966	.0040	4.2	-.0034	- 3.4
10	.100	.0985	.0069	7.0	-.0016	- 1.6
7	.150	.1389	.0078	5.6	-.0111	- 7.4
11	.150	.1389	.0058	4.1	-.0111	- 7.4

TABLE VIII

Chromium: Statistical Data

SAMPLE NUMBER	AMOUNT ADDED (mg/1)	MEAN (mg/1)	STANDARD DEVIATION (mg/1)	RELATIVE STANDARD DEVIATION (%)	MEAN ERROR (mg/1)	RELATIVE ERROR (%)
7	.000	.0027	.0046	-	.0027	-
11	.000	.0040	.0052	-	.0040	-
4	.005	.0063	.0038	60.5	.0013	26.7
9	.005	.0076	.0060	78.2	.0026	52.0
5	.010	.0150	.0136	90.3	.0050	50.0
10	.010	.0113	.0086	75.4	.0013	13.3
3	.075	.0793	.0102	12.8	.0043	5.7
6	.075	.0758	.0038	5.0	.0008	1.1
12	.075	.0715	.0218	30.4	-.0035	- 4.7
13	.075	.0725	.0167	23.0	-.0025	- 3.3
2	.125	.1250	.0212	17.0	.0000	0.0
8	.125	.1219	.0108	8.8	-.0032	- 2.5
1	.150	.1440	.0074	5.1	-.0060	- 4.0
14	.150	.1550	.0112	7.2	.0050	3.3

TABLE IX

Lead: Statistical Data

SAMPLE NUMBER	AMOUNT ADDED (mg/1)	MEAN (mg/1)	STANDARD DEVIATION (mg/1)	RELATIVE STANDARD DEVIATION (%)	MEAN ERROR (mg/1)	RELATIVE ERROR (%)
5	.000	.0000	.0000	-	.0000	-
10	.000	.0022	.0022	-	.0022	-
6	.005	.0045	.0008	18.6	-.0005	-10.0
13	.005	.0052	.0007	13.4	.0002	2.9
1	.010	.0081	.0041	50.3	-.0019	-18.8
2	.010	.0096	.0041	42.3	-.0004	- 3.8
8	.010	.0107	.0022	20.7	.0007	7.1
14	.010	.0103	.0008	7.9	.0003	3.3
3	.025	.0247	.0005	2.1	-.0003	- 1.3
12	.025	.0257	.0024	9.5	.0007	2.9
7	.040	.0416	.0042	10.0	.0016	3.9
11	.040	.0393	.0010	2.6	-.0007	- 1.7
4	.050	.0507	.0044	8.6	.0007	1.4
9	.050	.0500	.0006	1.3	.0000	0.0

TABLE X

Manganese: Statistical Data

SAMPLE NUMBER	AMOUNT ADDED (mg/1)	MEAN (mg/1)	STANDARD DEVIATION (mg/1)	RELATIVE STANDARD DEVIATION (%)	MEAN ERROR (mg/1)	RELATIVE ERROR (%)
2	.000	.0013	.0023	-	.0013	-
3	.000	.0005	.0010	-	.0005	-
8	.000	.0000	.0000	-	.0000	-
12	.000	.0000	.0000	-	.0000	-
1	.010	.0099	.0004	3.6	-.0001	-1.3
14	.010	.0099	.0004	3.8	-.0002	-1.4
4	.025	.0247	.0008	3.3	-.0003	-1.3
9	.025	.0250	.0025	10.1	.0000	0.0
5	.040	.0423	.0052	12.2	.0023	5.6
10	.040	.0375	.0039	10.3	-.0025	-6.3
7	.050	.0480	.0025	5.2	-.0020	-4.0
11	.050	.0451	.0043	9.6	-.0049	-9.8
6	.075	.0737	.0038	5.2	-.0013	-1.7
13	.075	.0711	.0041	5.7	-.0039	-5.2

TABLE XI

Zinc: Statistical Data

SAMPLE NUMBER	AMOUNT ADDED (mg/1)	MEAN (mg/1)	STANDARD DEVIATION (mg/1)	RELATIVE STANDARD DEVIATION (%)	MEAN ERROR (mg/1)	RELATIVE ERROR (%)
4	.000	.0024	.0025	–	.0024	–
9	.000	.0026	.0025	–	.0026	–
7	.005	.0054	.0008	14.5	.0004	8.6
11	.005	.0061	.0014	22.1	.0011	22.5
5	.010	.0109	.0010	9.1	.0009	8.8
10	.010	.0111	.0033	29.3	.0011	11.1
1	.025	.0298	.0094	31.4	.0048	19.1
3	.025	.0241	.0030	12.2	-.0009	- 3.5
12	.025	.0253	.0037	14.5	.0003	1.3
14	.025	.0295	.0130	44.1	.0045	17.8
2	.040	.0414	.0056	13.5	.0014	3.4
8	.040	.0413	.0075	18.1	.0013	3.3
6	.250	.2543	.0098	3.8	.0043	1.7
13	.250	.2543	.0127	5.0	.0043	1.7

9371