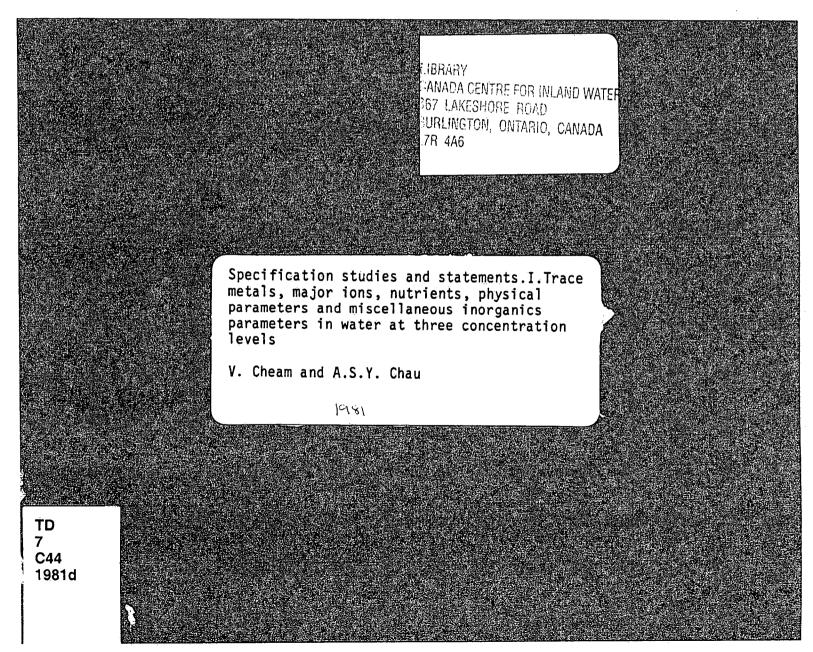




Environment Canada

Environnement Canada

National Water Research Institute Institut National de Recherche sur les Eaux



TECHNICAL REPORT 16-AMD-T-6-81-VC

Specification studies and statements.I.Trace metals, major ions, nutrients, physical parameters and miscellaneous inorganics parameters in water at three concentration levels

V. Cheam and A.S.Y. Chau

19181

Unpublished report

SPECIFICATION STUDIES AND STATEMENTS - I TRACE METALS, MAJOR IONS, NUTRIENTS, PHYSICAL PARAMETERS AND MISCELLANEOUS INORGANIC CONSTITUENTS IN WATER AT THREE CONCENTRATION LEVELS

by

V. Cheam and A.S.Y. Chau

Contents

Page

1

1

3

ABSTRACT

INTRODUCTION

HISTORICAL BACKGROUND

STUDY DESIGN AND DEFINITION FOR INORGANICS 4 Concentration levels 4 Replicate determinations 4 Detection limit 5 Precision 6 Accuracy 9 Methods 11 Background medium 12 SPECIFICATION FOR ORGANIC METHODS 12 EXPERIMENTAL 13 General 13 Trace metals 14 Major ions, nutrients, arsenic and mercury 15 Physical and miscellaneous inorganic parameters 16

DATA EVALUATION

19 **RESULTS AND SPECIFICATION STATEMENTS** Aluminum 22 Arsenic 26 Barium 28 Cadmium 30 Calcium 34 Carbon 36 Chloride 40 Chromium 44 Cobalt 48 Copper 52 Fluoride 56 Hardness 58 60 Iron Lead 64 Lithium 68 Magnesium 72 Manganese 7.4 Mercury 78 Molybdenum 80 Nickel 84 Nitrogen 88 рĤ 96

Page

18

-

•		Page
Phenols		98
Phosphorus		100
Potassium		106
Silica		108
Sodium	· · ·	110
Specific Conductance		112
Strontrium		114
Sulphate		116
Turbidity		118
Vanadium		120
Zinc		124

REFERENCES

128

ABSTRACT

Specification statements (precision, accuracy and detection limit) derived from round robin interlaboratory investigation on an analytical method are indexes of the reliability, credibility and limitation of the routine data generated, and thus form an integral and essential part of the measurement process. Since methods in the Water Quality Branch Analytical Methods Manual do not yet possess such statements, the need to generate them is urgent otherwise NAQUADAT data may not be interpreted with demonstrated levels of confidence. This report is the first (Phase I) of a series which fulfills this need and specifies interlaboratory statements of detection limit, precision and accuracy on all existing methods and the future ones used by the Water Quality Branch laboratories across Canada — Moncton, Longueuil, Burlington, Calgary and Vancouver.

Fifty three (53) analytical methods in the IWD Analytical Methods Manual have been successfully specified — 26 methods for trace methods, and 27 for major ions, nutrients, physical parameters, arsenic and mercury in various water types. Each method in this phase is specified at three different concentration levels of low, medium and high which characterize its dynamic range.

EXECUTIVE SUMMARY

Headquarters has designated the Quality Assurance and Methods Section (formely Special Services Section) to develop, design and execute a continuing program, referred to as specification program, in order to provide all existing and future analytical methods in the IWD Methods Manual with specification statements so that data stored in NAQUADAT Bank may be used or interpreted with demonstrated levels of confidence. These interlaboratory statements on detection limit, precision and accuracy for each method are indexes of reliability, credibility and limitation on the data routinely generated by using these methods.

This phase of the program, Phase I, encompasses about 2 years of continuous activities. Twelve specially designed interlaboratory studies were carried out, which resulted in fifty three analytical methods successfully specified at three concentration levels.

Specification data are realistic (not purely mathematical) functions of such variables as time, space, analyte concentration and matrix. The ultimate goal of the specification program is to provide all-reliable statements or stabilized functions derived from studies where each method has been subjected to the different variables. This entails periodical tests at more analyte levels and different matrices for both inorganic and organic analytical methods in the IWD Methods Manual.

-

ACKNOWLEDGEMENTS

0.

The authors wish to express their gratitude to Mr. J.P. Lively (former Chief, Laboratory Operations Division) and Mr. Mike Forbes, for their valuable discussions and advice on this project. Mr. M. Forbes' periodical discussion and comments during the Phase I of this project is invaluable and enlightening.

INTRODUCTION

Nearly every phase in environmental protection and pollution control depends on analytical data. Millions of dollars are involved in generating analytical data (expensive sampling trips, manpower, and equipment for analysis and for data interpretation). There are even greater financial implications when decisions such as sewage treatment process changes, plant modification or construction of new facilities, import and export of food (e.g. fish) are based on analytical data generated. Indeed, as pointed out by Uriano and Gravatt (1977) that "never before have so many critical decisions involving health, safety and economics depended on the quality of chemical analytical data". Therefore, assurance of environmental data quality is an extremely important aspect in the effort to ensure the quality of the environment and health of the public (ACS, 1980). Quality assurance must be an integral part of analytical and data intrepretation activities because questionable data result in questionable intrepretations and subsequently in questionable decisions or conclusions.

There are several key areas that could affect the quality of the analytical data generated by analytical service laboratories. One is the quality of the analytical methods used for data generation.

The methods used by WQB labs are selected, evaluated and compiled and when approved are published in the Analytical Methods

- 1 -

The data produced by these laboratories are stored in the Manual. Naquadat (National Water Quality Data Bank) (Demayo and Hunt, 1975) for immediate and future interpretation. Many of these methods have precision, accuracy and detection limit statements based on single-operator intralaboratory measurements, usually by the originator of the method, and under ideal conditions. Consequently such measurements are more precise and accurate than those generated from these regional analytical laboratories under routine operation. As an essential part of our OA program to ensure data quality and to enable data users to interpret the data generated from these methods with certain levels of confidence, it is necessary to generate interlaboratory specification statements (precision, accuracy and detection limit) under routine application for all existing and future methods used by the 5 WOB laboratories across Canada - Moncton, Longueuil, Burlington, Calgary and Vancouver. This is achieved by specially designed round robin studies which are referred to as specification studies, and the overall activity is referred to as the Specification Program.

This program has two major components: organic and inorganic method specification studies. Due to limitation of resources, the inorganic component of the program will be tackled first. This report is the first of a series and describes the results of the first phase of the specification program for inorganic methods.

- 2 -

Since for each method the specification statements wary with - analyte concentration, background matrix and time, the studies will be repeated from time to time to reflect the effect of these variables. The specification data from all the studies will be treated statistically and updated continuously until the variations become stabilized.

HISTORICAL BACKGROUND

It was realized that without interlaboratory statements on detection limit; precision, accuracy, NAQUADAT data may not be interpreted with demonstrated levels of confidence. In fact, for the interpretation to be valid, it is necessary to know the confidence with which the data may be used. This information is not specified for the methods used by WQB labs. Realizing this need, Headquarters approached our Section to design a special program (Specification Program) to provide this information. Furthermore, the program also benefits users of the TWD Analytical Methods Manual by giving them an estimate of the confidence which can be placed in the analytical methods. Several designs were proposed by Chau and Cheam on June 13, 1978 and in consultation with Headquarters, a design was chosen and approved.

- 3 -

STUDY DESIGN AND DEFINITIONS FOR INORGANICS

It was decided that the study design would require minimum amount of work from all laboratories concerned and yet give essential information on detection limit, precision, and accuracy on the whole concentration range of the method.

It should be emphasized that for specification of organics, modification of the following design will be necessary.

<u>Concentration levels</u> - For Phase I, 3 levels were agreed upon as a necessary minimum for each parameter of interest. The low level design should be near the specified single lab detection limit, in general 2 to 10 times the latter. The high level would reflect the upper concentration limit, normally 5 to 10% lower than that specified by the method. The medium level lies between the 2 extremes.

<u>Replicate determinations</u> - The minimum number of replicate analyses for each level was determined to be 2, using an arbitrary unequality proposed in an ASTM standard, D2777-77 (ASTM 1977, L. Howe personal communication). The variables taken into consideration included concentration levels, number of apparatus and operators, and seven laboratories. Thus for each level we requested each lab to do duplicate analyses on 2 different days, the second analysis being made

- 4 -

at least one day after the first was finished. At the time we formulated the program, there were seven Water Quality Branch labs providing data. Seven laboratories is the minimum number of labs required for duplicate analysis. For six labs, triplicate analysis would be desirable. However, we chose to keep the request for duplicate analysis so as to keep the criterion of minimum amount of work by each laboratory.

Detection limit - There are many definitions of limit of detection. Some agencies prefer one type of limit whereas others prefer another type. Detection limit (D.L.) can be taken to be the value of a standard deviation or several standard deviations statistically derived from a certain number of replicate blank analysis. Also it has been interpreted as the minimum analyte concentration which produces a signal distinguishable from blank signal at a certain level of significance. Yet there are other definitions. However, the thing which is common to all of these techniques is that most of the time the method originator himself defines and obtains the D.L. for his method. Naturally this limit is impressive, comparable or better than others, which is fair enough since the originator knows his method best.

When a newly developed analytical method is used in routine laboratories where real-world samples are analysed, the D.L. obtained by the originator is ,pst ;ole;u too good to be realistically applicable and useful to data users. This may also be true for precision

- 5 -

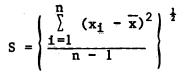
and accuracy if the one-lab data as compared to the inter-lab data

Our proposed approach to obtain detection limit, precision and accuracy reflects realistic encounter with real-world samples. Factors coming into play are many operators, many instruments, laboratories, time and locations. We define the detection limit as follows

D.L. = 2 s

where s is the interlaboratory standard deviation derived from low level sample data. A point worth noting here is that "s" should be greater than the single-lab single-operator standard deviation.

<u>Precision</u> - The precision of an analytical method refers to its capability to produce good repeatability of analytical results observed under the same conditions of procedures and sample characteristics. It thus relates to the standard deviation of the measurement and for this reason is usually indexed by the absolute value of standard deviation or relative standard deviation (% coefficient of variation, % CV). The sample standard deviation, s, is defined as follows



where x_i = each observation in the sample set of data,

- $x_1 \cdots x_n$,
- $\overline{\mathbf{x}}$ = arithmetic mean of $\mathbf{x_1}$'s
- n = number of sample observations

The sample percent coefficent of variation is expressed as

$$\% \text{ CV} = 100 \left(\frac{s}{r}\right)$$

The precision is a function of concentration and as such can be expressed as

$$S_T = a + bx + cx^2 + \dots$$
 where

 $S_{\rm T}$ = overall precision, mg/L or $\mu g/L$ or other units

of x

x =concentration of constituent, and

a,b,c = least squares coefficients

The function S_T is of vital importance owed to its best representation of data and its usefulness for the whole dynamic range of the analytical method.

Remark

The definition is simple enough but the interpretation of the precision statement could be misleading unless it accompanies the conditions (qualifying statements) under which it is obtained. Since the objective is to generate a statement on the specifications for each method in the manual for "easy interpretation of NAQUADAT data", ideally the precision statement of the data generated by the regional labs by each method is an overall precision statement. This is the "maximum precision" obtained for and from a method under all the conditions that the NAQUADAT data are generated by all the regional labs at any given time. Obviously, this statement cannot be obtained in a short time and the design and burden to us and to the regional labs would be tremendous. Therefore, the precision statement obtained from the following proposed designs would reflect only the time of participation by the laboratories and the performance of the particular analyst who will do the analysis. Longer term precision is

- 8 -

generated from repeating the quality control studies. The number of repetitions is yet to be decided upon.

The precision statements for each method in this report are based on a single round robin study and will be updated when the studies are supplemented or repeated.

<u>Accuracy</u> - In the ideal sense, the accuracy should reflect both precision and bias. But in practice, the accuracy of an analytical method refers to its ability to produce analytical results close to the true or assumed known values. In this program we choose to represent accuracy statement by the percent recovery of anayte whose concentration is assumed known by virtue of its addition to the determined background concentration. The percent recovery is defined as follows:

$$% \text{REC} = \frac{\overline{x}}{BGD + SPK} \times 100$$

where

 $\overline{\mathbf{x}}$ = arithmetic mean of observations, BGD = background concentration determined experimentally,

and

SPK = amount of analyte added.

- 9 -

Remarks

- (1) "It must be emphasized that the "spiking" approach does not reflect the true accuracy although it is a widely practised approach. Lacking SRM's and resources, the "spiking" approach due to its simplicity, is the only alternative at this time. Since the spiked compounds may not be integrated into the sample matrix and quite often the spiked recoveries are higher than those from real samples, the recovery of the spike is often not a measure of the recovery of the endogeneous compounds from the real samples (see discussions in Chau, WHO Bulletin). In the future, when suitable SRM's are developed and prepared, the accuracy data will be updated.
- (2) Similar to the precision statements for each method, the accuracy statement will be accompanied by qualifying statement as to the conditions under which those statements are generated. This is to assist users on the interpretation of the precision and accuracy statements on the data of each parameter generated by Water Quality Branch labs.

- 10 -

Also, like the precision statement, the more $t\bar{l}$ me the Q.C. studies are repeated, the closer is the accuracy statement for a particular parameter to the actual situation.

(3) In certain cases such as for some major ions, it is difficult to find natural samples containing low enough levels close to the detection limits of the methods. Spiked distilled water was chosen as a comparison to determine the precision and accuracy specification for this report.

<u>Methods</u> - In this phase of the program, most methods investigated are those which are in general routinely used by the WOB laboratories and which are subjected to monthly inter-regional quality control studies. They include methods for trace metals, major ions and nutrients, physical parameters and some miscellaneous ones for water samples.

<u>Background medium</u> - The medium is of natural source whenever possible as opposed to distilled water. As noted above, for a few parameters it is difficult to obtain natural water containing low enough concentration to be used to generate specification near the detection limits of the methods.

- 11 -

SPECIFICATION FOR ORGANIC METHODS

To generate specification for organic methods requires considerable in-house research and investigation to provide the necessary procedures and background data for the design and preparation of a study because there are a paucity of information for organic parameters in water and in sediment. The spiking technique, sample homogenization procedure, sample stability data and method of preservation must be available and suitabile for each sample and parameter before any round robin studies can be initiated.

The limitation of spiking for accuracy data has been mentioned earlier for inorganics. The limitations can be as pronounced for organics because many endogeneous organics are imbedded in the sample matrix or are in complex or conjugated form. The spiked recoveries will be much better than those from naturally contaminated samples. Therefore, it is more desirable to use naturally contaminated samples whenever possible for organic studies. In particular, the application of SRM's will be invaluable here. However, due to the lack of resources to handle the complexity and tediousness of the organic specification program, it is not possible to be considered at the present time under the present resource situation.

- 12 -

EXPERIMENTAL

General

All chemicals used to prepare samples are of reagent grades or standard reference materials such as those by the National Bureau of Standards.

All containers, bottles and glassware are cleaned before use. For trace metals, we use 30% HNO₃ as cleaning reagent and after cleaning and rinsing, we store containers and bottles with 0.2% HNO₃ for a few weeks before use. For major ions, nutrients and other parameters which do not require chemical preservation, we do cleaning with chromic acid followed by rinses with hot tap water, distilled water and storage with distilled water for several weeks before use. The container types and sizes to be used are dictated by the constituents and analytical methods (Analytical Methods Manual, 1979).

All water samples are first prepared in bulk, preserved if necessary, homogenized and subsampled into appropriate bottles. Pre-distribution analyses are then made to confirm the added analyte concentration; these confirmatory analyses are often kindly provided by the Analytical Services Section of WQB laboratories in Burlington. If the added amount is not confirmed, new batches have to be prepared all over again. Some constituents have to be distributed as solid samples to avoid unstability problems. In these instances, each sample contains a carefully weighted solid substance with dissolution instructions.

Having weighted, prepared and confirmed the samples, we packaged them in carton boxes filled with foam peanuts in such a way as to avoid breakage or leakage during shipment to various regions across Canada. Each box would contain the same types of samples and instructions specific to each study.

<u>Trace Metals (IR51-54)</u> - Twenty six trace metal methods were investigated - Al (13305, 13302), V (23302, 23301), Cr (24303, 24302), Mn (25306, 25304), Fe (26305, 26304), Co (27302, 27301), Ni (28302, 28301), Cu (29305, 29306), Zn (30305, 30304), Mo (42302, 42301), Cd (48302, 48301), Pb (82302, 82301), Sr (38301) and Ba (56301).

Lake Ontario water was judged suitable for the study. All chemicals were of Fisher Standard Reference solutions (Fisher Scientific Co. Ltd.), polyethylene containers of 500 mL size for direct aspiration methods, D/A, and 2 L size for solvent extraction methods, S/E. Nitric acid was used as preservative (0.2% HNO₃) for all S/E samples and the low level D/A sample. The other D/A samples are readily preserved by the acids originally present in reference solutions and contain higher percentage of various acids.

- 14 -

<u>Major ions, nutrients, arsenic and mercury (IR55-56, 60-61)</u> Twenty nine methods were investigated - Hardness (10602, 1060 $\overline{3}$), sodium (11103), Magnesium (12102), silica (14102), potassium (19103), Calcium (20103), arsenic (33304), selenium (34102), total P (15403), Fluoride (09106), sulfate (16306), chloride (17203, 17206), TKN (07010), total organic N (07401), Ammonia (07552), NO₃ and NO₂ (07106, 07110), total nitrogen (07601), total inorganic carbon (06051), DOC (06101, 06104), DIC (06151, 06152), total alkalinity (10101, 10106), P. alkalinity (10151), and mercury (80301).

As some background constituents significantly exceed the anticipated detection limits of the corresponding methods, such as calcium for example, distilled water had to be used in low level samples so that the criterion of low level - detection limit correspondence may be satisfied. At medium and high levels, natural waters from Lake Superior and a rain sampler were used. In certain cases such as alkalinity and carbon determinations, it was advantageous to use distilled water in all levels.

Reagent grade or better chemicals were used for all samples. They were purchased from NBS, Alfa Products or Fisher Scientific Company: Nacl (NBS - SRM919, stock 2010.01 ppm Na and 3099.66 Cl); MgSO₄ (Fisher Lot 774820, stock 2004.7 ppm Mg and 7922.9 SO_4); Na₂S₁O₃ • 9H₂O (Fisher Lot 780440 with 1000 ppm S₁, 2139.45 ppm S₁O₂ and 1637.22 ppm Na); Kcl (NBS - SRM918, stock

- 15 -

2205.86K and 2000.39 Cl); $CaCl_2 \cdot 6H_2O$ (Fisher Lot 781990-12, stock 1993.1 ppm Ca and 3525.8 Cl); As_2O_3 (Fisher Lot 780440); and Na_2 SeO₄ (Alfa Lot 110376, stock 999.75 ppm Se and 582.17 ppm Na); KH₂PO₄ (NBS - SRM200, stock 2535.12 ppm K and 2008.33 ppm P); HgCl₂ (Fisher M-114, standard 1000 ppm Hg); NaF (Fisher S-299, stock 2423.15 ppm Na and 2002.48 ppm F); Na₂ SO₄ (Baker chemicals, stock 2001.46 ppm Na and 4181.30 ppm SO₄); NH₂ CO NH₂ (ANALAR R, stock 4675.9 ppm N and 2004.8 ppm C); NH₄ Cl (Fisher, S-299, Lot 775722, stock 2006.8 ppm N and 5079.4 ppm Cl); KNO₃ (NBS - SRM193, stock 2002.21 ppm N and 5588.85 ppm K); KHC₈H₄O₄ (Fisher, Lot 760168, stock 2012.5 ppm C and 818.9 ppm C).

Container types, sizes and preservatives were specified in each study distribution (IR 55-56, 60-61).

Physical and Miscellaneous Inorganic Parameters (IRQC studies No. 62 to 63, 68 to 69) - Eighteen methods were investigated -Iodide (53201), NTA (10711), turbidity (02073), pH (10301), specific conductance (02041), COD (08301), color (02011), cyanide (06601), sugar (06541), phenol (06531), Be (04002), Sb (51002), Li (03001), Be (04001), Sb (51001), B (05105), Ag (47302 and 47301).

The following background waters were used: Lake Ontario water for iodide, NTA and ortho-inorganic P; Hamilton Harbor water for Li, Be, Sb, B and Ag, deionized distilled water for the rest of constituents. To minimize bacterial activities and to ensure stability of samples, we sterilized spiked and unspiked water samples for ortho- and inorganic P analysis; we distributed the samples in duplicate bottles with instructions to make the first analysis on one bottle for day 1 and the second analysis on the other bottle for day 2.

Solid samples for cyanide (KCN), sugar (D-xylose) and phenol (C₆H₅OH) had to be distributed with appropriate dissolution instructions, since these constituents are too unstable in solutions. For NTA, iodide and P, the chemicals used were NTA, KI and KH₂PO₄. Other chemials used are: Potassium chloroplatinate (K₂PlCl₆) and cobaltous chloride (CoCl₂*6H₂O) for color; sodium borate decahydrate (borax = Na₂B₄O₇*10H₂O) for pH 9.180; Potassium dihydrogen phosphate and disodium hydrogen phosphate (KH₂ PO₄ + Na₂ H PO₄) for pH 6.865; Potassium hydrogen phthalate (KHC₈H₄O₄) for pH 4.008 (Standard Methods, 1975); Potassium hydrogen phthalate (KHC₈H₄O₄) for specific conductance and chemical oxygen demand COD (Smith, 1978); Hydrazine sulphate (N₂H₄H₂SO₄) and hexamethylenetetramine ((CH₂)₆N₄) for turbidity.

Fisher certified stocks of 1000 ppm Sb, Li, B and Ag (amber bottle) were used to prepare test samples. For Be, the salt

- 17 -

 $Be(NO_3)_2 \cdot 3H_2O$ was used to prepare 1000 ppm stock and subsequent solutions.

Test sample containers used were: 125 mL glass bottles for iodide, turbidity and color samples which were to be kept at 4°C until analysis; 125 mL polyethylene bottles for NTA samples (preserved with formaldehyde and at 4°C) and for pH samples; 250 mL polyethylene bottles for specific conductance and COD samples; 250 mL glass bottles for P samples; 500 mL clear polyethylene bottles for Li, Be and Se samples which were preserved in 0.2% HNO₃; 125 mL clear polyethylene bottles for B samples to be stored at 4°C until analysis; 500 mL and 100 mL amber polyethylene bottles for Ag samples which were preserved with 0.4% EDTA.

DATA EVALUATION

Before the data are used to calculate the mean, standard deviation, coefficient of variation and % recovery, anomalous results were examined using Grubbs rules to determine statistically whether or not they are outliers (Grubbs 1969, Grubbs Personal Communication, 1979). The outliers are flagged with the letter "R" and automatically omitted by the computer during the calculation of statistics.

When dealing with background samples, there are often many less than values and if some are positive, they are far apart from each other. As the rejection criteria can not be effectively applied in such instances, some of the results were flagged on simple judgement.

In this phase, most parameters have three concentration levels and three corresponding standard deviation values. Least square fit on 3 points sometimes does not tell the true behavior of a function, in this case precision function. In such cases, the choice of the best fit among those derived from a linear function and a polynomial one is sometimes not the best choice simply because it seems too mathematical to reflect the real-world situation; the fit with realistic behavior of the function would be preferred. On the other hand, had we been armed with many more points, the best fit would probably be the choice always. Phase II and the future ones of the program will provide more points, which along with present points should always give realistic fits and thus permit ready selection of the best fit.

RESULTS AND SPECIFICATION STATEMENTS

Each analytical method used by WQB laboratories is briefly described and coded in the NAQUADAT Dictionary of Parameter Codes (1981). Detailed procedures are found in the Analytical Methods Manual (1979). For convenience, each method will be referred to in the statements below by the constituent name and its associated code, such as Al-13305.

The statements are arranged alphabetically according to the names of constituents. Each presents data on precision and accuracy at all concentration levels studied so far, along with a detection limit, a graph and a representative equation of the precision function.

Fifty three (53) analytical methods have been successfully specified, of which there are 26 trace metal methods and 27 methods for major ions, nutrients, physical and miscellaneous parameters, arsenic and mercury in water. Other methods attempted in this phase are not yet specified here because either they are no longer in routine use by the labs (therefore we have no data at all) or we do not have enough data for all 3 concentration levels.

Specification statements have been derived for the following methods.

Aluminum -	13302	Manganese -	25304
Aluminum -	13305	Manganese -	25305
Arsenic -	33304	Mercury -	80301
Barium -	56301	Molybdenum -	42301
Cadmium -	48301	Molybdenum -	42302

Cadmium -	48302	Nickel -	28301
- Calcium -	20103	Nickel -	28302
Carbon, DOC -	06104	Nitrogen, NO ₃ & NO ₂ -	07106
Carbon, DIC -	06152	Nitrogen, NO ₃ & NO ₂ -	07110
Chloride -	17203	Nitrogen, Ammonia —	07552
Chloride -	17206	Nitrogen, total -	076 01
Chromium -	24302	рН —	10301
Chromium -	24303	Phenols -	06531
Cobalt -	27301	Phosphorus, Diss. ortho -	- 15254
Cobalt -	27302	Potassium -	19103
Copper -	29305	Silica -	14102
Copper -	29306	Sodium -	11103
Fluoride -	09106	Specific conductance -	02041
Hardness total -	10602	Strontium -	38301
Iron -	26304	Sulphate -	16306
Iron -	26305	Turbidity -	02073
Lead -	82301	Vanadium -	23301
Lithium -	03001	Vanadium -	23302
Lithium -	03301	Zinc -	30304
Magnesium -	12102	Zinc -	30305

ALUMINUM - 13302

- 10. Precision and Accuracy
 - 10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .3 , 23.0 and 45. mg Al/L to be respectively .0096, 1.41 and .82 mg/L, and may be expressed as follows:

 $S_{T} = 0.3305 + 0.0183 X$

where S_T = overall precision, mg/L and

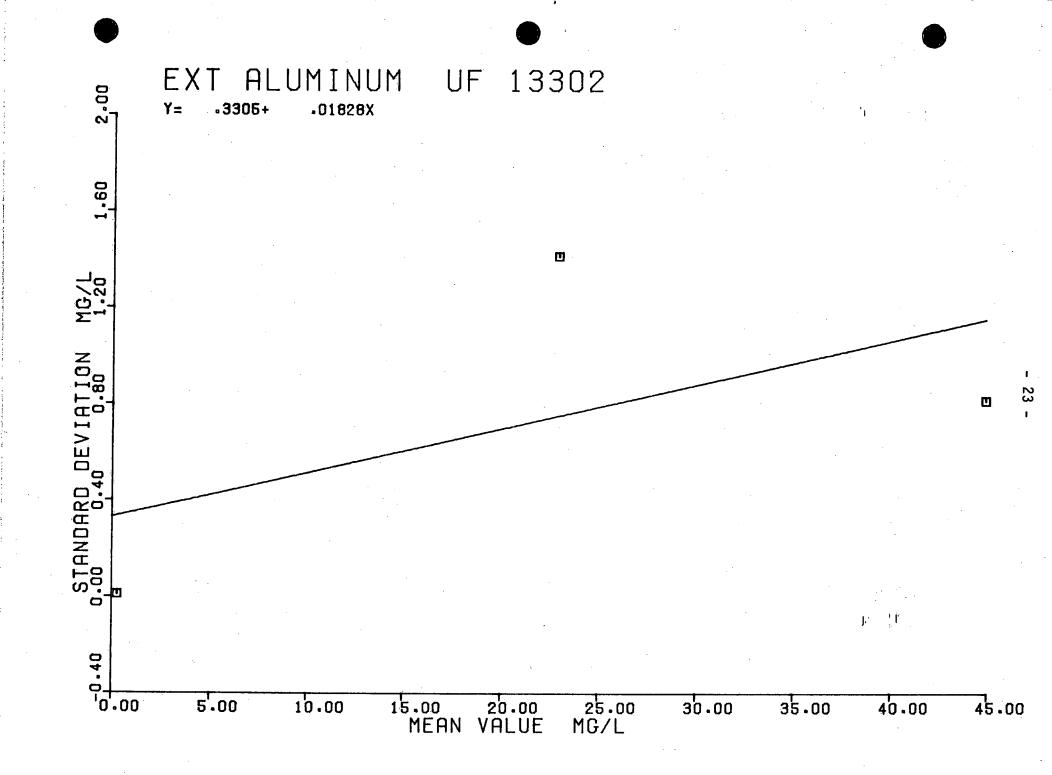
X = concentration of Aluminum , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
2	.3	3
2	23.0	6
2	45.0	2

10.3 The percent recoveries are 96%, 102%, and 100% at concentration levels of .3 , 23 , and 45 mgA1/L respectively.

10.4 Detection Limit = 0.02 mg A1/L



ALUMINUM - 13305

10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on spiked and unspiked Lake Ontario waters at levels of .0055, .0098 , .075, and .15 mg Al/L to be respectively .0006, .0017 , .0057, and .0058 mg/L, and may be expressed as follows:

 $S_{T} = 0.0014 + 0.0338 X$

where S_T = overall precision, mg/L and

X = concentration of Aluminum , mg/L

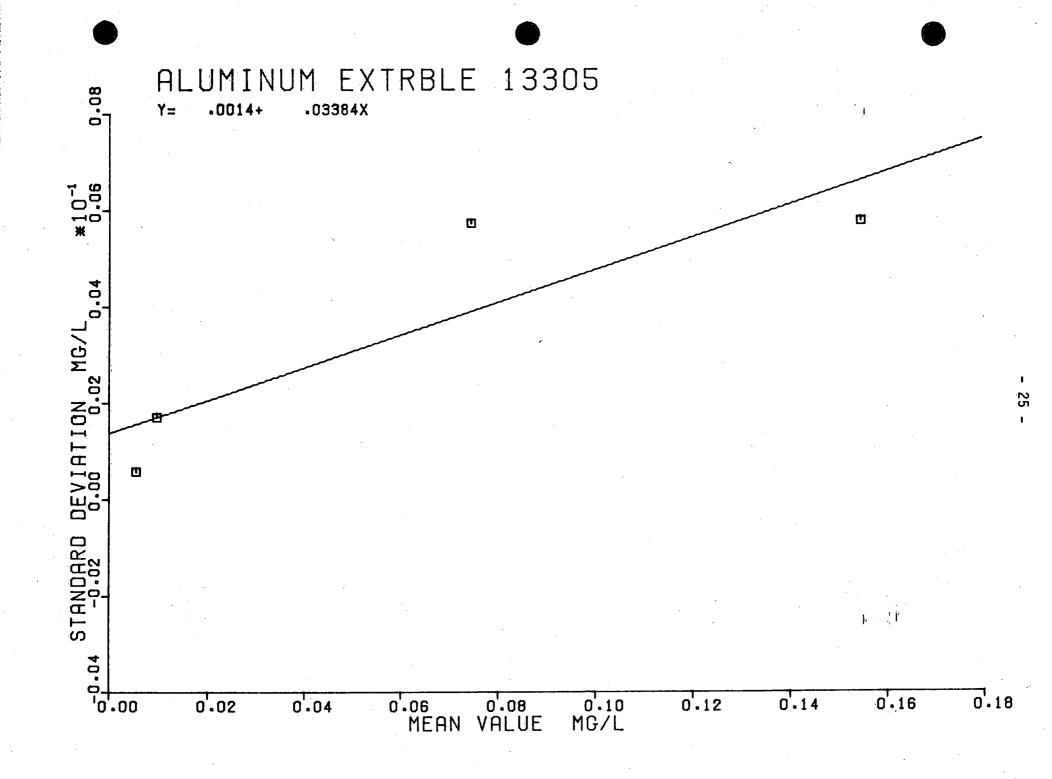
10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, Mg/L	Coefficient of Variation, percent
2	.0055	11
2	.0098	17
2	.075	8
2	.15	4

10.3 The percent recoveries are 95%, 98%, and 104 % at concentration levels of .01, .076, and .15 mg Al/L respectively.

10.4 Detection Limit = 0.003 mg A1/L

- 24 -



ARSENIC 33304

10. Precision and Accuracy

10.1 The precision of this method was determined on synthetic,
spiked and unspiked Lake Superior waters at levels of .0005,
.0004, .0017 and 0028mg As/L to be respectively .0001, .0001
.0001 and .0003mg/L and may be expressed as follows:

 $S_{\tau} = 0.00059 + 0.06787 X$

where $S_T = overall precision, mg/L and$

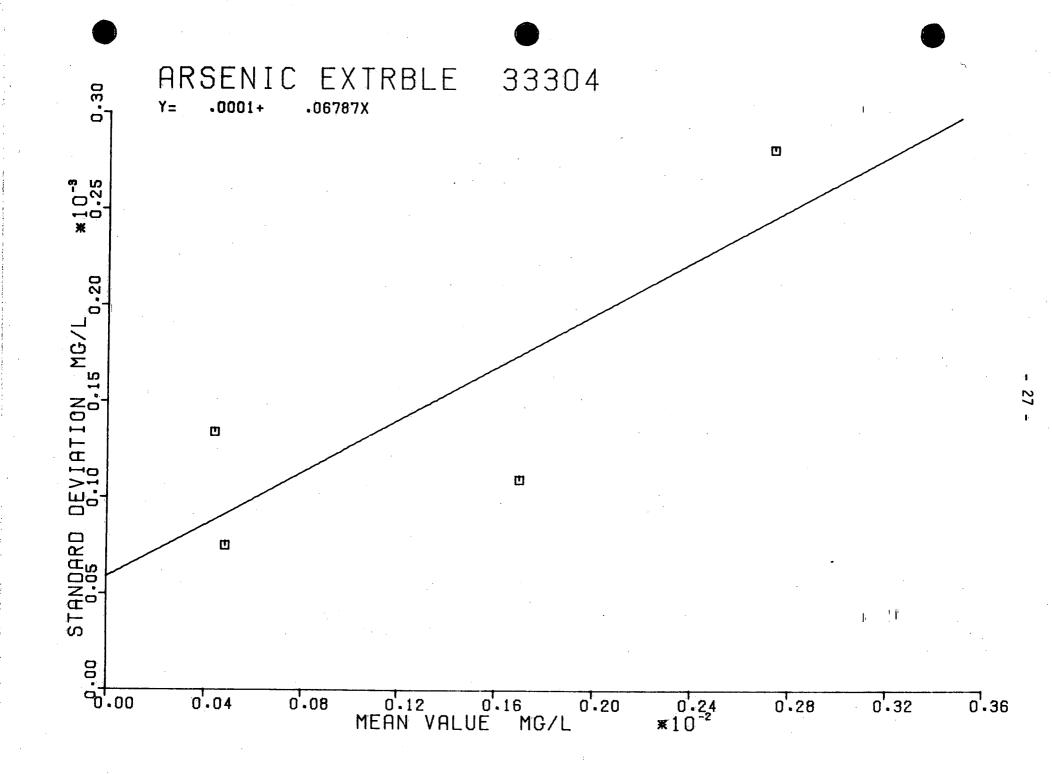
X = concentration of As , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
3	0.0005	15.6
3	0.0004	30.5
3	0.0017	6.4
3	0.0028	10.2
The procent roce	voning and 07 4	

10.3 The precent recoveries are 97%, 94%, and 92% at concentration levels of 0005, 0018 and 003 mg As/L respectively.

10.4 Detection Limit = 0.0002 mg As/L



BARIUM - 56301

10. Precision and Accuracy

10.1 The precision of this method was determined on

spiked Lake Ontario water at levels of .3 , 11 and 22 mg Ba/L to be respectively .02 , .45 and 1.6 mg/L, and may be expressed as follows:

 $S_{T} = 0.0219 - 0.00096 X + 0.00348 X^{2}$

where $S_T = overall precision, mg/L and$

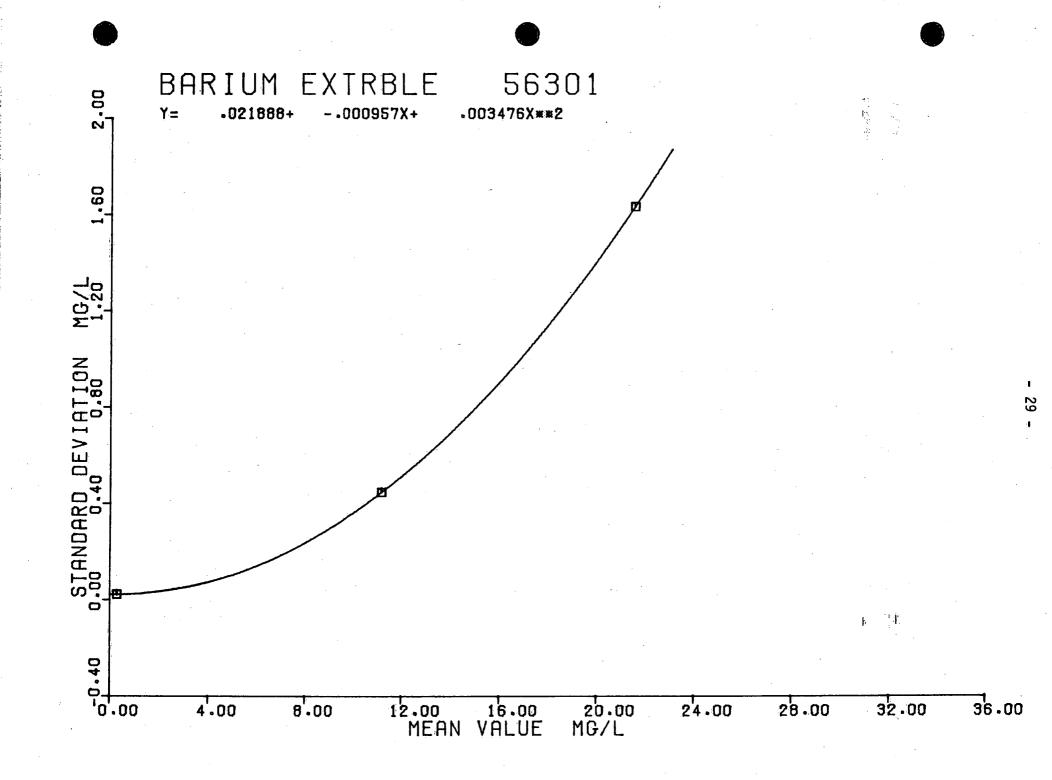
X = concentration of Barium, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	<u>Mean, mg/L</u>	Coefficient of Variation, percent
3	.3	7
3	11	4
3	22	7

10.3 The percent recoveries are⁹⁹ %, 102%, and 98 % at concentration levels of .3 , 11 , and ₂₂ mgBa/L respectively.

10.4 Detection Limit = 0.04 mg Ba/L



CADMIUM - 48301

- 10. Precision and Accuracy
 - 10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .05, -.9 and 1.8 mg Cd/L to be respectively .005, .03 and .08 mg/L, and may be expressed as follows:

$$S_{T} = 0.00417 + 0.021 X + 0.011 X^{2}$$

where S_T = overall precision, mg/L and

X = concentration of Cadmium , mg/L

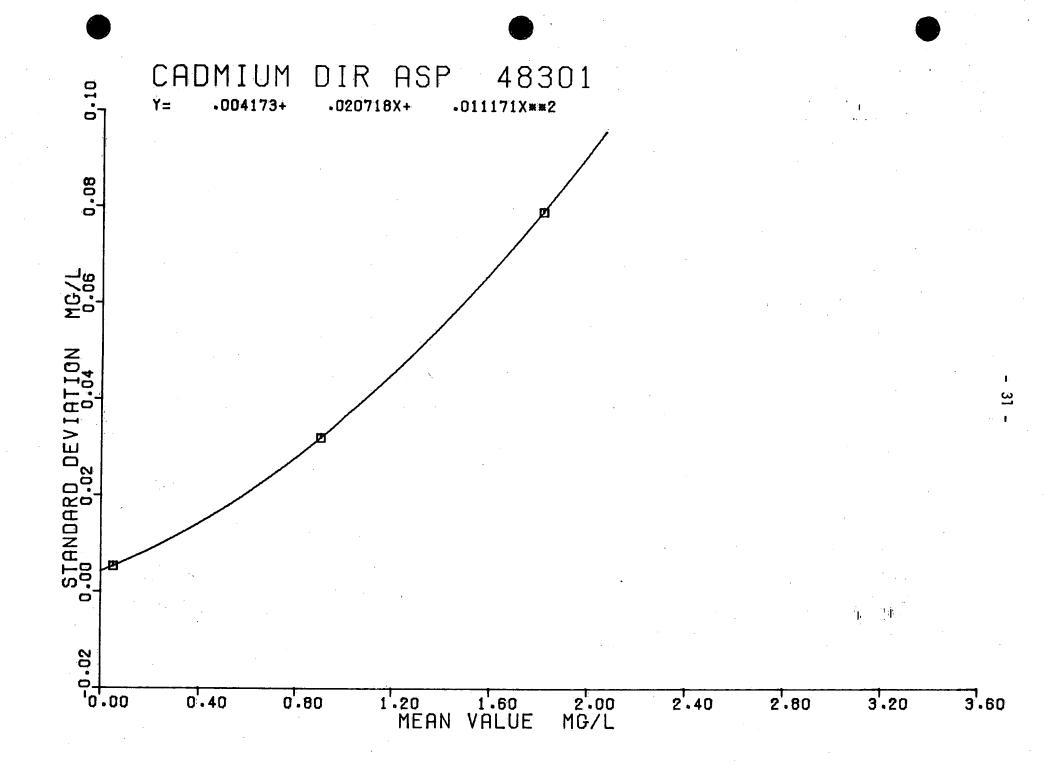
10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
5	.05	. 10
5	.9	4
5	1.8	4

10.3 The percent recoveries are 103%, 99 %, and 101% at concentration levels of .05 , .9 , and 1.8 mgCd/L respectively.

10.4 Detection Limit = . 01 mg Cd/L

- 30 -



CADMIUM - 48302

10. Precision and Accuracy

- 10.1 The precision of this method was determined on
 - spiked Lake Ontario water at levels of .002 ,...03 and .05mg Cd/L to be respectively .0005, .0022, and .006 mg/L, and may be expressed as follows:

 $S_{T} = 0.00048 + 0.0153 X + 1.82 X^{2}$

where $S_T = overall precision, mg/L and$

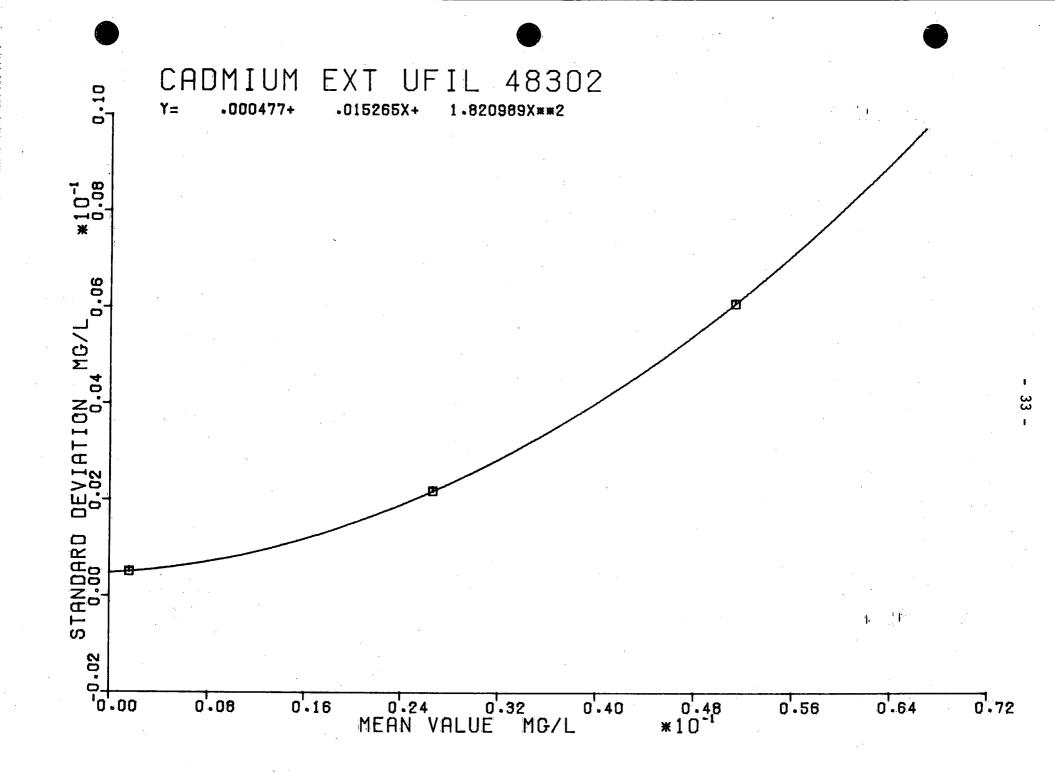
X = concentration of Cadmium , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Variation, percent
5	.002	31
5	.03	8
5	.05	12

10.3 The percent recoveries are 87%, 92 %, and 90 % at concentration levels of .002 , .03 , and .06 mgCd/L respectively.

10.4 Detection Limit = 0.001 mg Cd/L



CALCIUM 20103

10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of .275, 13.16,44.46 and 64.2mg /L to be respectively.045, .456,

1.14 and 1.05 mg/L and may be expressed as follows:

 $S_{T} = 0.0067 + 0.0431 X - 0.000414 X 2$

where S_T = overall precision, mg/L and

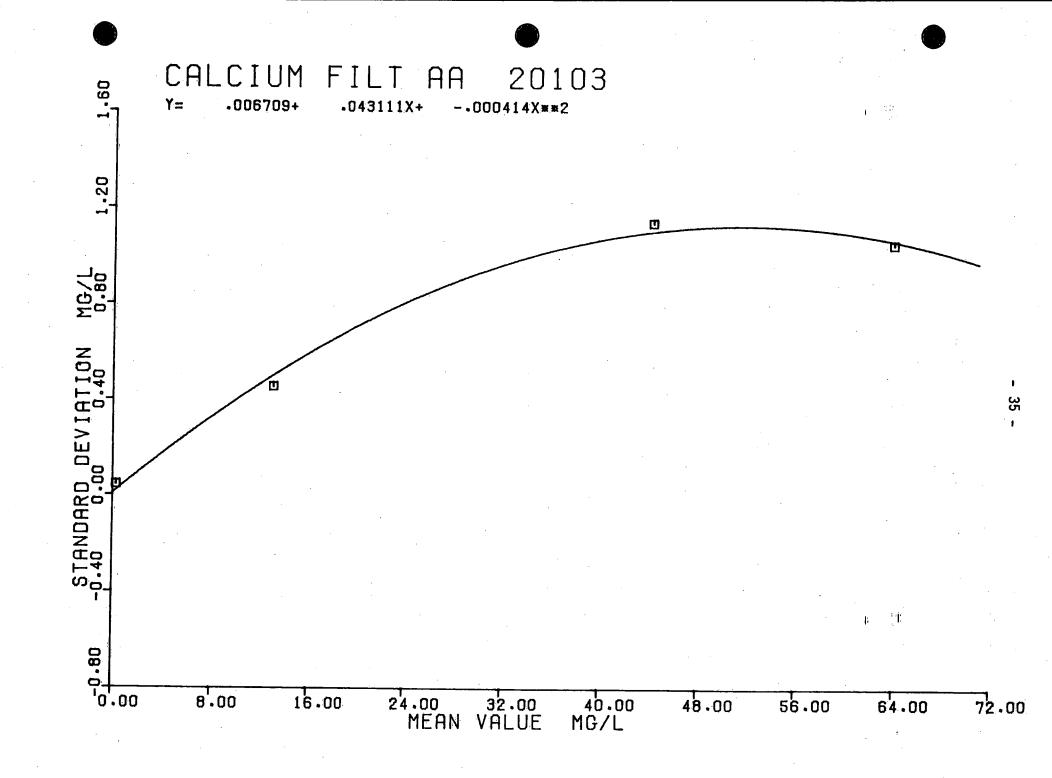
X = concentration of Ca , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
4	.275	16.3
4	13.16	3.5
4 >	44.5	2.6
4	64.2	1.6

10.3 The precent recoveries are 93%, 102 %, and 86 % at concentration levels of .296, 43.8, and 74.4mg Ca/L respectively.

10.4 Detection Limit = 0.1 mg Ca/L



10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on synthetic 20.5, and 44 mg C/L to be respectively .07, 2.1, and 5.7 mg/L and may be expressed as follows: $S_T = -0.107 + 0.089X + 0.00095X^2$

where $S_T = overall precision, mg/L and$

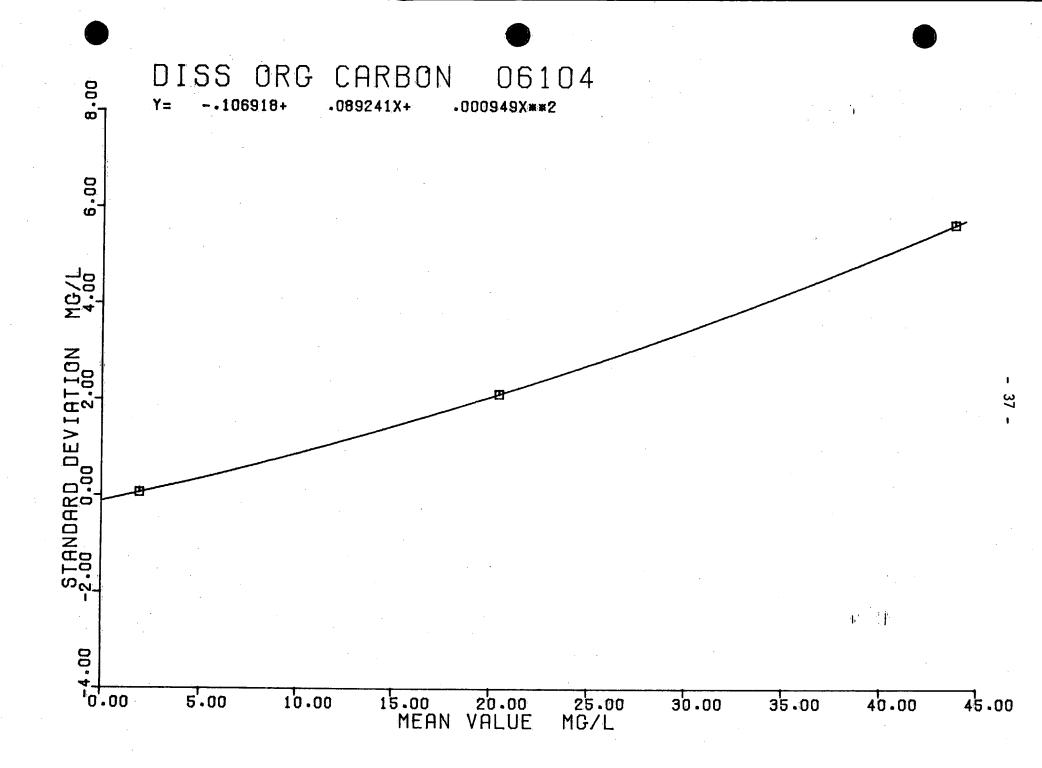
X = concentration of DOC , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
2	1.95	3.6
2	20.5	10.3
2	44	12.9

10.3 The precent recoveries are 97%, 86 %, and 92 % at concentration levels of 2.0, 24 , and 48 mg C/L respectively.

10.4 Detection Limit = 0.2 mg DOC/L



10. Precision and Accuracy

10.1 The precision of this method was determined on synthetic waters at levels of 2.5,

24 , and 49 mg C/L to be respectively 7 , 1.4,

and 1.4 mg/L and may be expressed as follows:

 $S_{T} = 0.806 + 0.0148X$

where $S_T = overall precision, mg/L and$

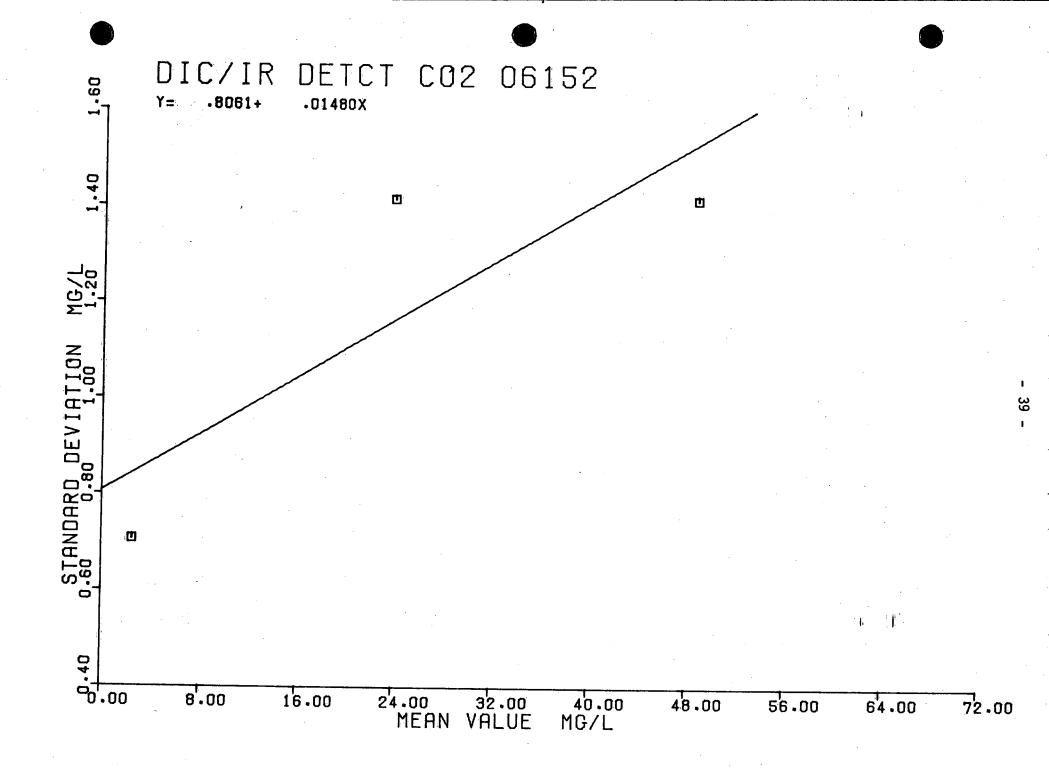
X = concentration of DIC , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
2	2.5	28.3
2	24	5.9
2	49	2.9

10.3 The precent recoveries are 124%,100 %, and102 % at concentration levels of 2.01, 24 , and 48 mg C/L respectively.

10.4 Detection Limit = 2 mg DIC/L



10. Precision and Accuracy

10-1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of .89,

1.1, 44, and 91 mgcl/L to be respectively .18, .22, 3.6,

and 3.2 mg/L and may be expressed as follows:

 $S_{T} = 0.082 + 0.122X - 0.00096X^{2}$

where S_T = overall precision, mg/L and

X = concentration of cl , mg/L

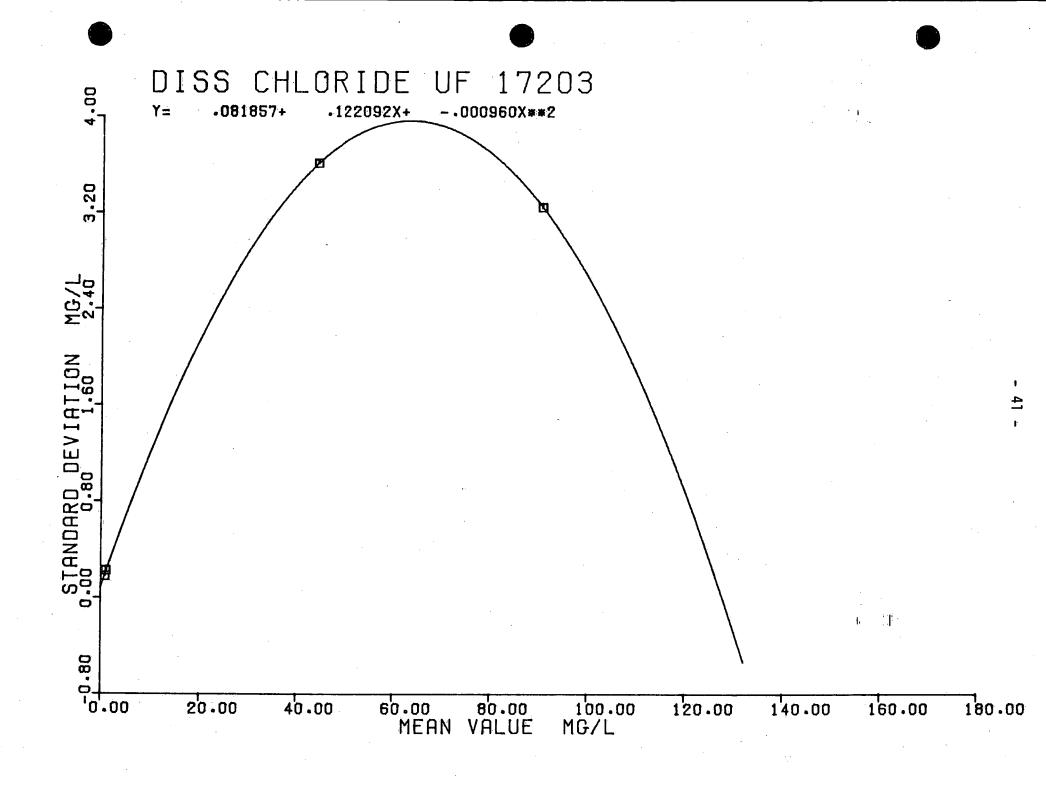
10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
3	. 89	20.1
3	1.1	20.6
3	44	8.1
3	91	3.6

10.3 The precent recoveries are 88%, 96 %, and 99% at concentration levels of 1.02,46.5, and 92 mgcl/L respectively.

10.4 Detection Limit = 0.4 mg cl/L

- 40 -



CHLORIDE - 17206

10. Precision and Accuracy

- 10.1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of \cdot ⁹³,
 - 1.2,48, and 94 mgcl/L to be respectively.06, .0,1.5,

and 5.3 mg/L and may be expressed as follows:

 $S_{\tau} = 0.02155 + 0.0064X + 0.000528X^2$

where S_T = overall precision, mg/L and

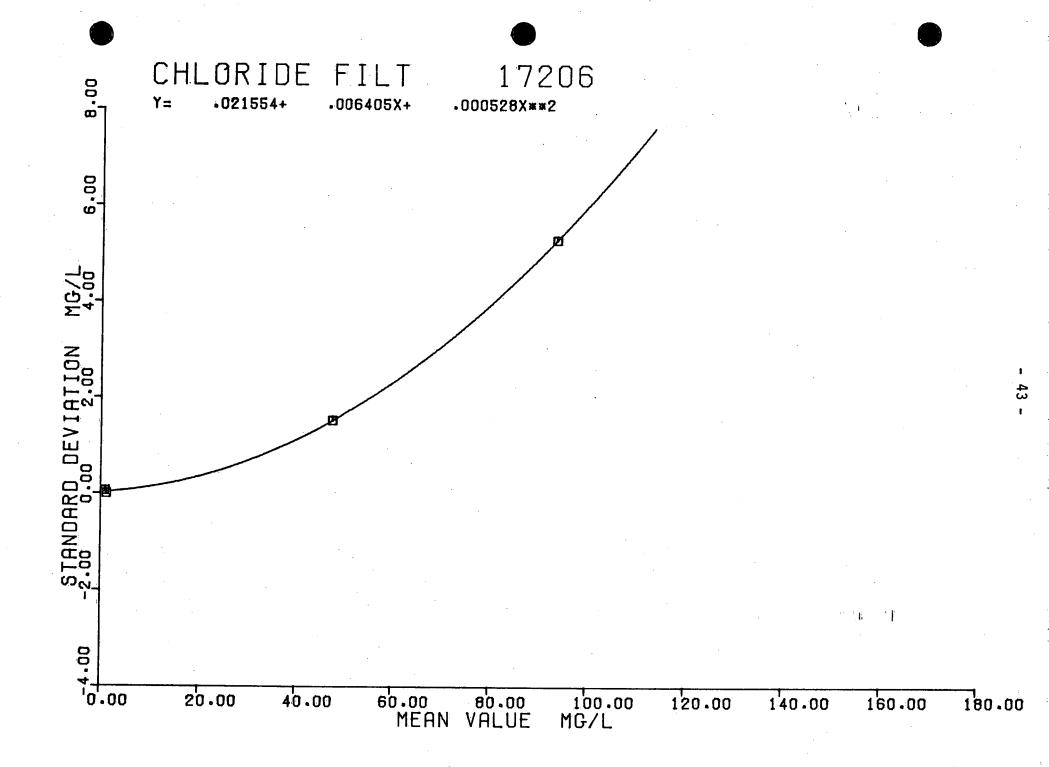
X = concentration of cl , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
2	.93	6.2
2	1.2	0.0
2	48	3.2
2	94	5.6

10.3 The precent recoveries are 92%,102 %, and 102% at concentration levels of 1.02, 47 , and 92 mgcl/L respectively.

10.4 Detection Limit = 0.2 mg cl/L



CHROMIUM - 24302

- 10. Precision and Accuracy
 - 10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .05,_2.2 and 4.3 mg Cr/L to be respectively .01 , .175 and .45 mg/L, and may be expressed as follows:

$$S_{\tau} = 0.0085 + 0.045 X + 0.013 X^2$$

where S_T = overall precision, mg/L and

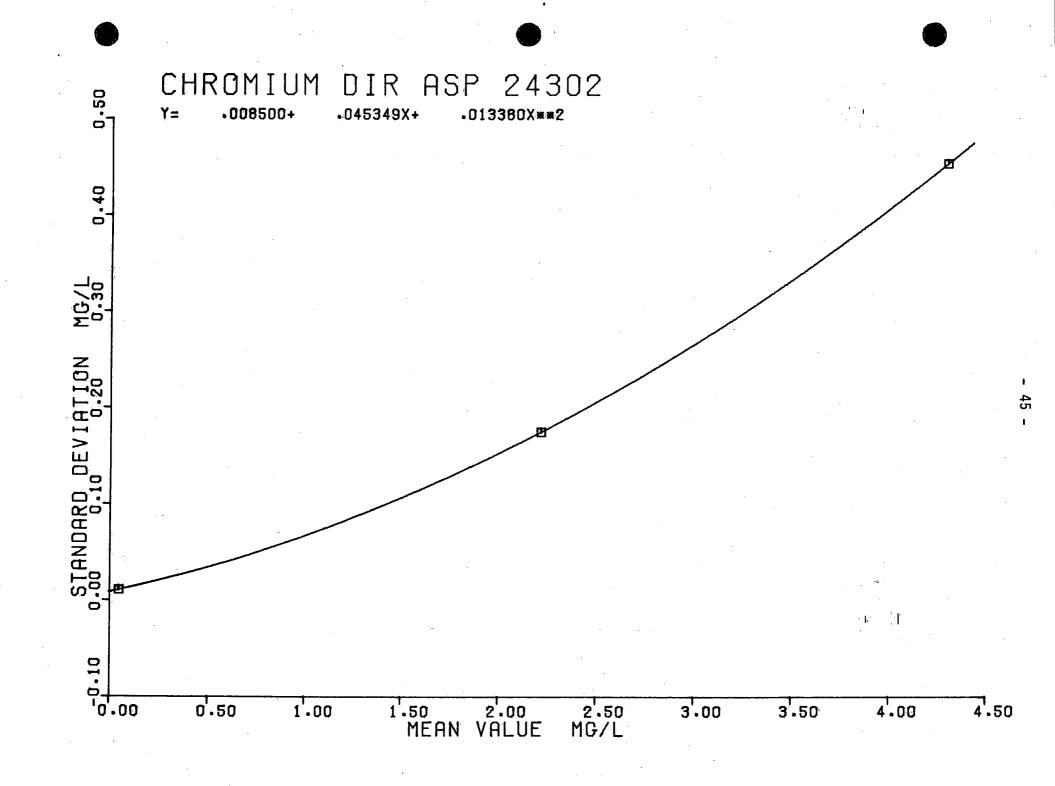
X = concentration of Chromium, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
5	.05	21
5	2.2	8
5	4.3	10

10.3 The percent recoveries are100%, 99 %, and 96 % at concentration levels of .05, 2.2, and 4.5 mgCr/L respectively.

10.4 Detection Limit = 0.02 mg Cr/L



CHROMIUM - 24303

- 10. Precision and Accuracy
 - 10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .002,-.047 and .1 mg Cr/L to be respectively .001 , .017, and .033 mg/L, and may be expressed as follows:

 $S_{\tau} = 0.00078 + 0.318 X$

where S_{T} = overall precision, mg/L and

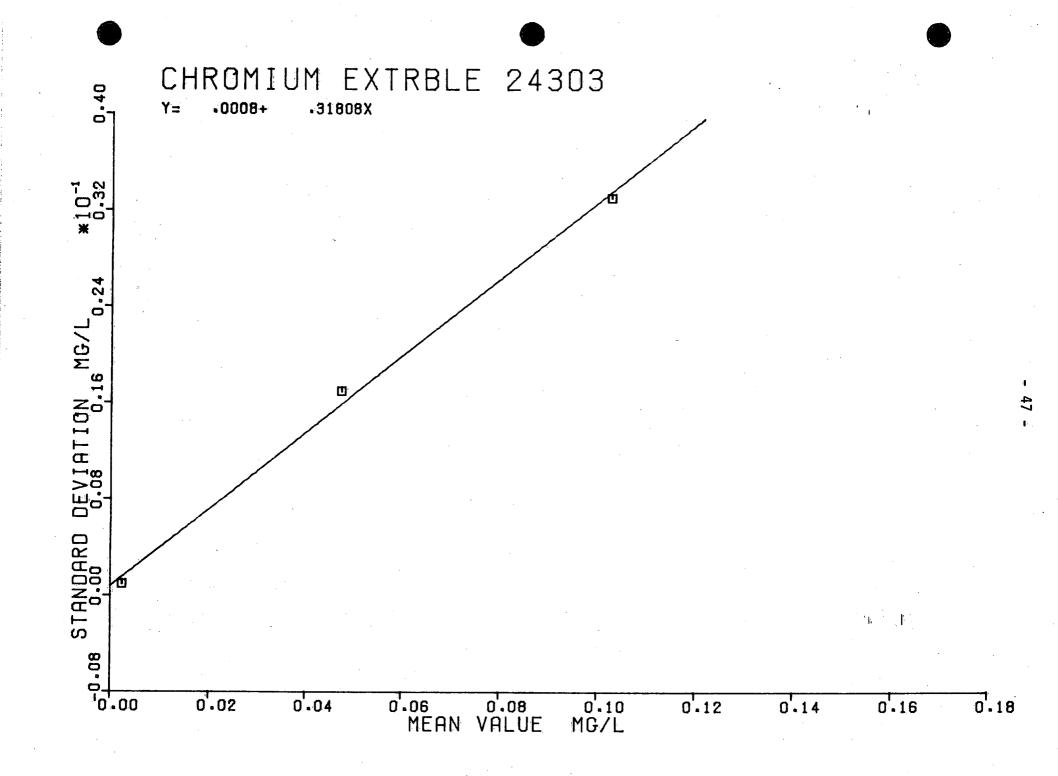
X = concentration of Cr , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
4	.002	39
4	.047	36
4	.1	32

10.3 The percent recoveries are 74%, 95 %, and 103% at concentration levels of .003 , .05 , and .1 mgCr/L respectively.

10.4 Detection Limit = 0.002 mg Cr/L



COBALT - 27301

10. Precision and Accuracy

10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .11, =2.3 and 4.5mg Co/L to be respectively .018, .22 and .45 mg/L, and may be expressed as follows:

$$S_{-} = 0.0085 + 0.0845 X + 0.0031 X^{2}$$

where $S_T = overall precision, mg/L and$

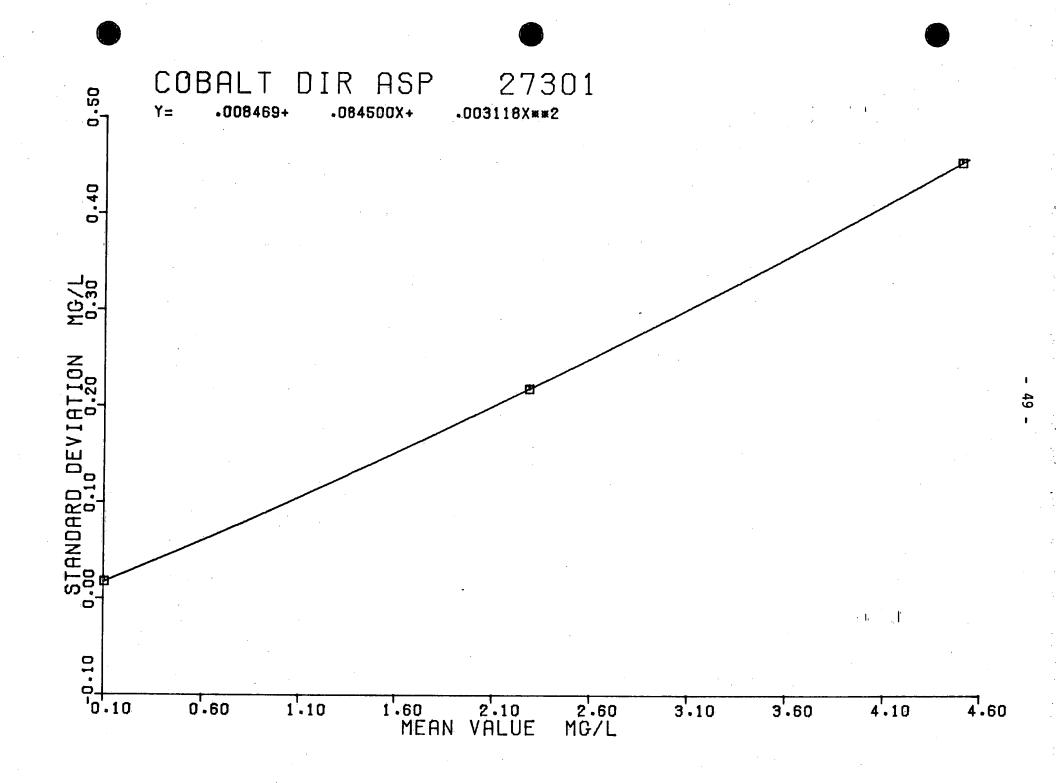
X = concentration of Cobalt , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	<u>Mean, mg/L</u>	Coefficient of Variation, percent
5	.11	16
5	2.3	9
5	4.5	10

10.3 The percent recoveries are 106%, 102 %, and 100 % at concentration levels of .1 , 2.3 , and 45 mgCo/L respectively.

10.4 Detection Limit = 0.03 mg Co/L



COBALT - 27302

- 10. Precision and Accuracy
 - 10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .003, .05 and .1 mg Co/L to be respectively .0009, .0048, and .0035 mg/L, and may be expressed as follows:

 $S_{T} = 0.00177 + 0.0267 X$

where S_T = overall precision, mg/L and

X = concentration of Co, mg/L

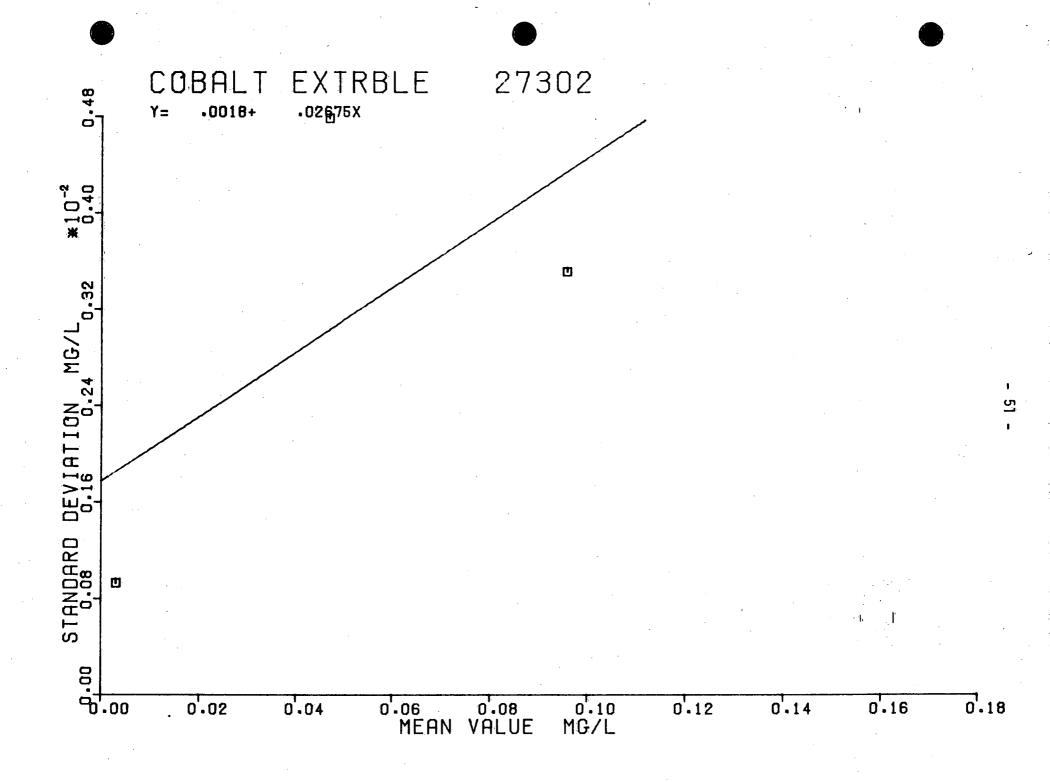
10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
5	.003	30
5	.005	10
5	.096	4

10.3 The percent recoveries are 94%, 94%, and 95% at concentration levels of .003, .05, and .1 mg_{CO}/L respectively.

10.4 Detection Limit = 0.002 mg Co/L

- 50 -



COPPER - 29305

10. Precision and Accuracy

10.1 The precision of this method was determined on spiked and unspiked Lake Ontario waters at levels of .0015, .0027, .0275 and .056 mg Cu/L to be respectively .0005, .0004, .0025, and .004 mg/L, and may be expressed as follows:

 $S_{T} = 0.000244 + 0.097 X - 0.546 X^{2}$

where $S_T = overall precision, mg/L and$

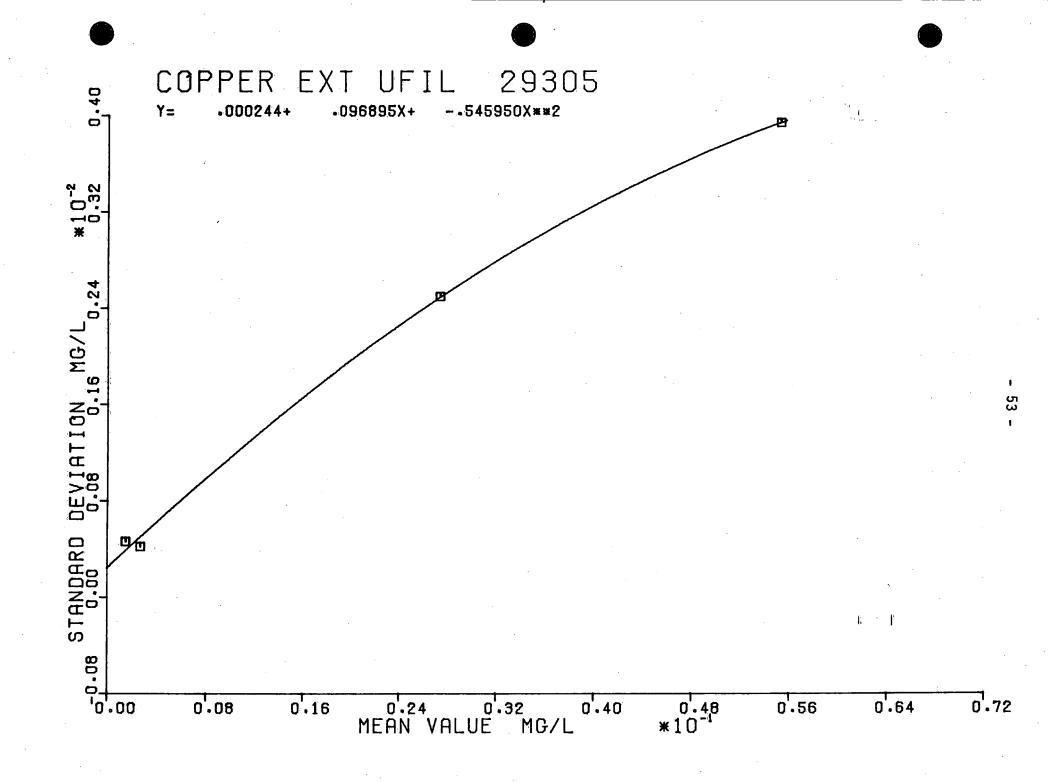
X = concentration of Copper , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, Mg/L	Coefficient of Variation, percent
5	.0015	30
5	.0027	16
5	.0275	9
5	.056	7

10.3 The percent recoveries are 79%, 90 %, and 95 % at concentration levels of .003, .03 , and .07 mg Cu/L respectively.

10.4 Detection Limit = 0.001 mg Cu/L



4. 17

- 10. Precision and Accuracy
 - 10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .05 ,= 2.4 and 4.7 mg Cu/L to be respectively .005, .15 and
 - .41 mg/L, and may be expressed as follows:

 $S_{T} = 0.00258 + 0.04 X + 0.0094 X^{2}$

where S_{T} = overall precision, mg/L and

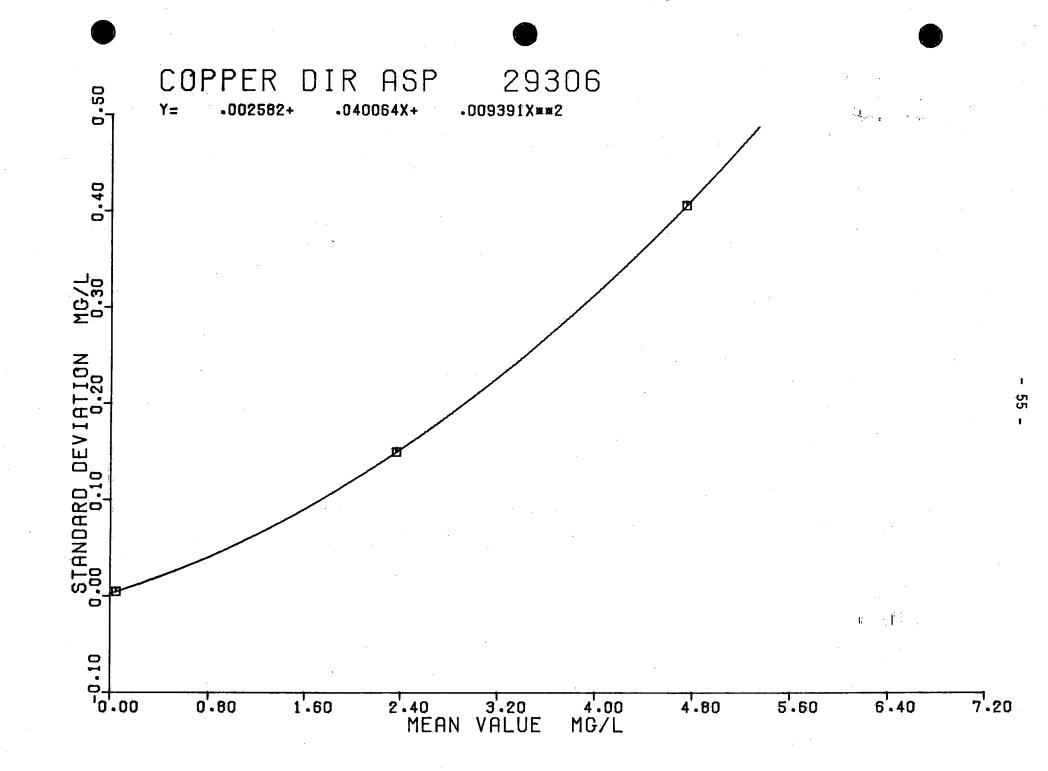
X = concentration of Copper , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	<u>Mean, mg/L</u>	Coefficient of Variation, percent
5	.05	9
5	2.4	6
5	4.7	8

10.3 The percent recoveries are 101%, 105%, and 105 % at concentration levels of .05 , 2.3 , and 4.5 mgCu/L respectively.

10.4 Detection Limit = 0.01 mg Cu/L



10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of .047, .136,.91, and 1.83mg F/L to be respectively.014, .01, .04,

and .068 mg/L and may be expressed as follows:

 $S_{T} = 0.0098 + 0.0317X$

where S_T = overall precision, mg/L and

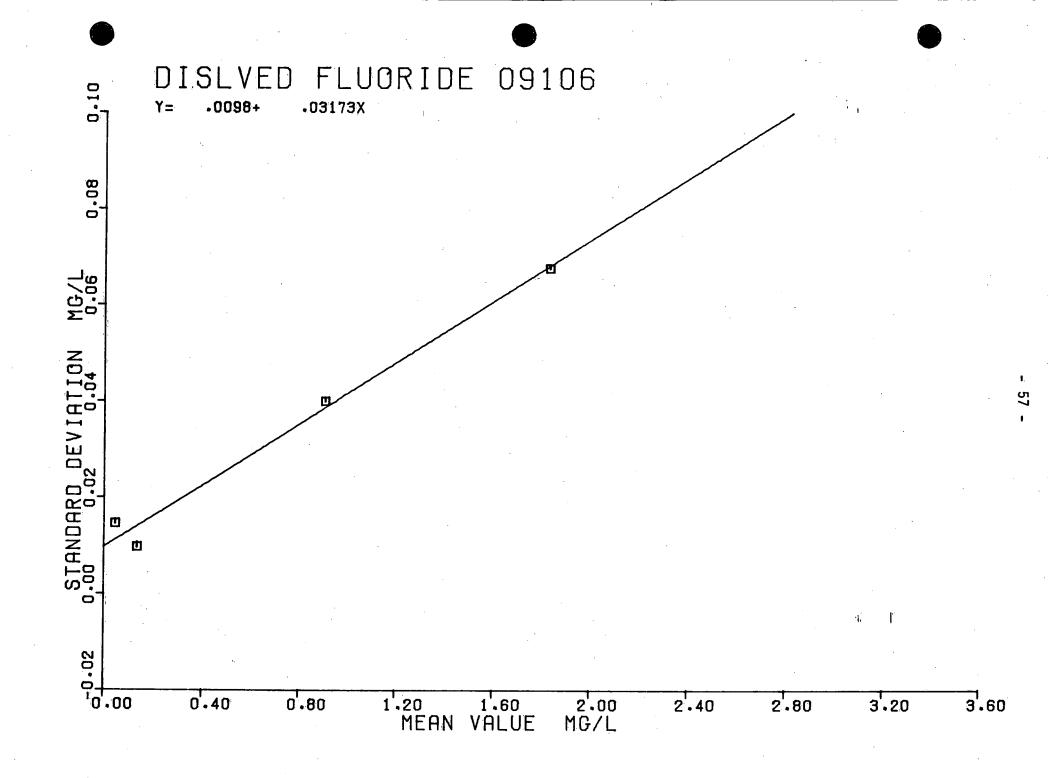
X = concentration of F , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Nu	mber of Labs	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
,	4	.047	31.3
	4	.136	7.2
	4	.91	4.4
	4	1.83	3.7

10.3 The precent recoveries are 97%, 95 %, and 99 % at concentration levels of.136,.91 , and1.83mg F/L respectively.

10.4 Detection Limit = 0.02 mg F/L



TOTAL HARDNESS 10602

10.1

10. <u>Precision and Accuracy</u>

The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of 0.96, $CaCO_3$ 44.3,159.0, and 244 mg /L to be respectively 0.1,1.5 ,4.6 ,

and 4.2 mg/L and may be expressed as follows:

 $S_{T} = 0.59 + 0.018 X$

where S_T = overall precision, mg/L and

X = total hardness in mg CaCO3/L

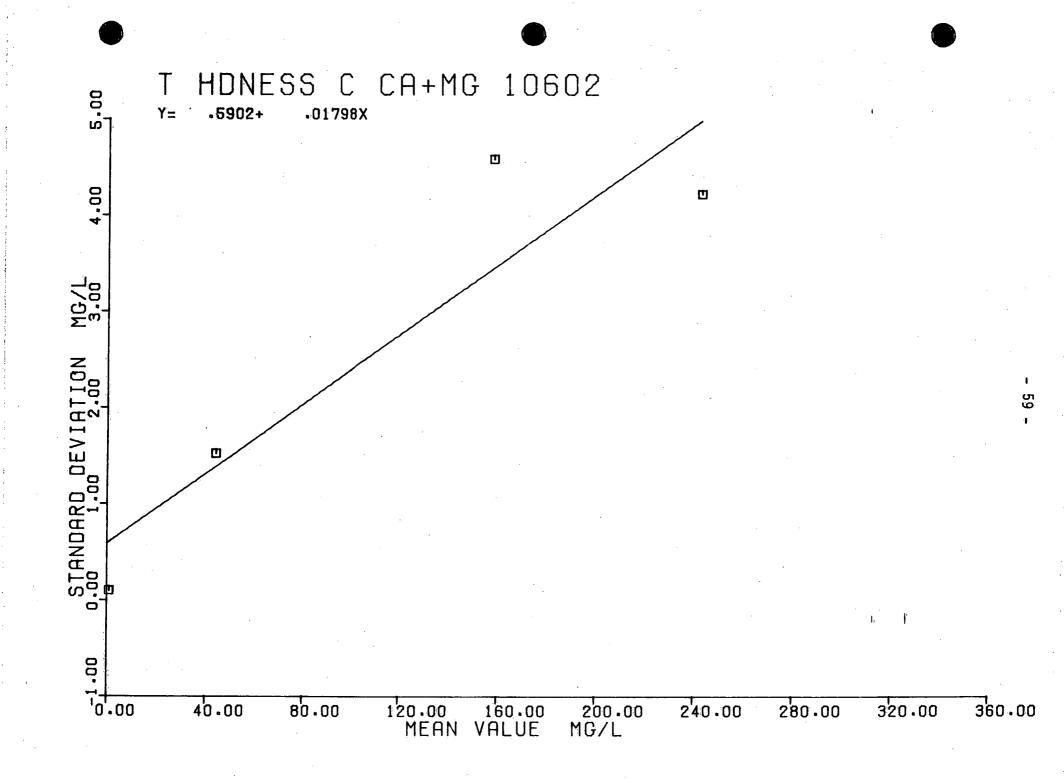
10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
4	0.96	10.3
4	44.3	3.4
4	159.0	2.9
4	244.2	1.7

10.3 The precent recoveries are 96 %, 101 %, and 91 % at CaCO₃ concentration levels of 0.96, 159, and 244 mg /L respectively.

10.4 Detection Limit = $0.2 \text{ mg } \text{CaCO}_3/\text{L}$

- 58 -



- 10. Precision and Accuracy
 - 10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .15,_4.35 and 8.9 mg Fe/L to be respectively .009 , .15 and .25 mg/L, and may be expressed as follows:

 $S_{T} = 0.0126 + 0.028 X$

where S_T = overall precision, mg/L and

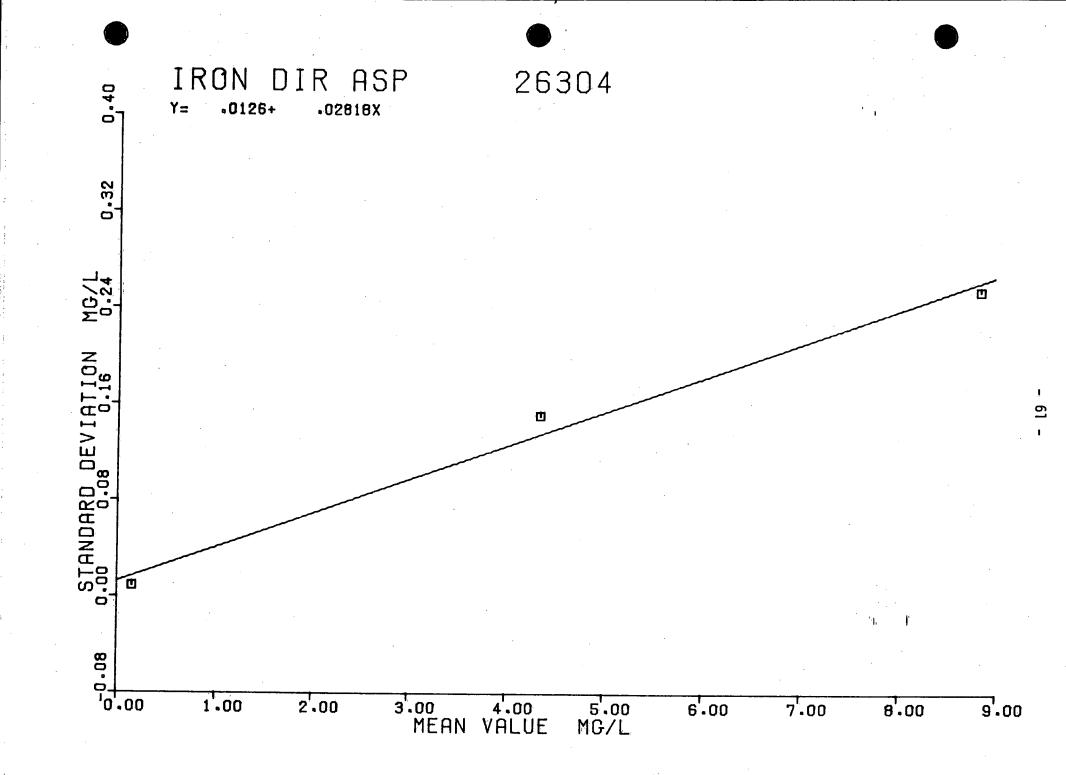
X = concentration of Iron , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	<u>Mean, mg/L</u>	Coefficient of Variation, percent
5	.15	6
5	4.35	3
5	8.9	3

10.3 The percent recoveries are100%, 97%, and 98% at concentration levels of .15 , 4.5 , and 9.0 mgFe/L respectively.

10.4 Detection Limit = 0.02 mg Fe/L



IRON - 26305

10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on spiked and unspiked Lake Ontario waters at levels of .0036, .0069 .0516, and .09 mg Fe/L to be respectively .0012, .0009 , .0038, and .0117 mg/L, and may be expressed as follows:

 $S_{T} = 0.0012 - 0.0352 X + 1.6705 X^{2}$

where S_T = overall precision, mg/L and

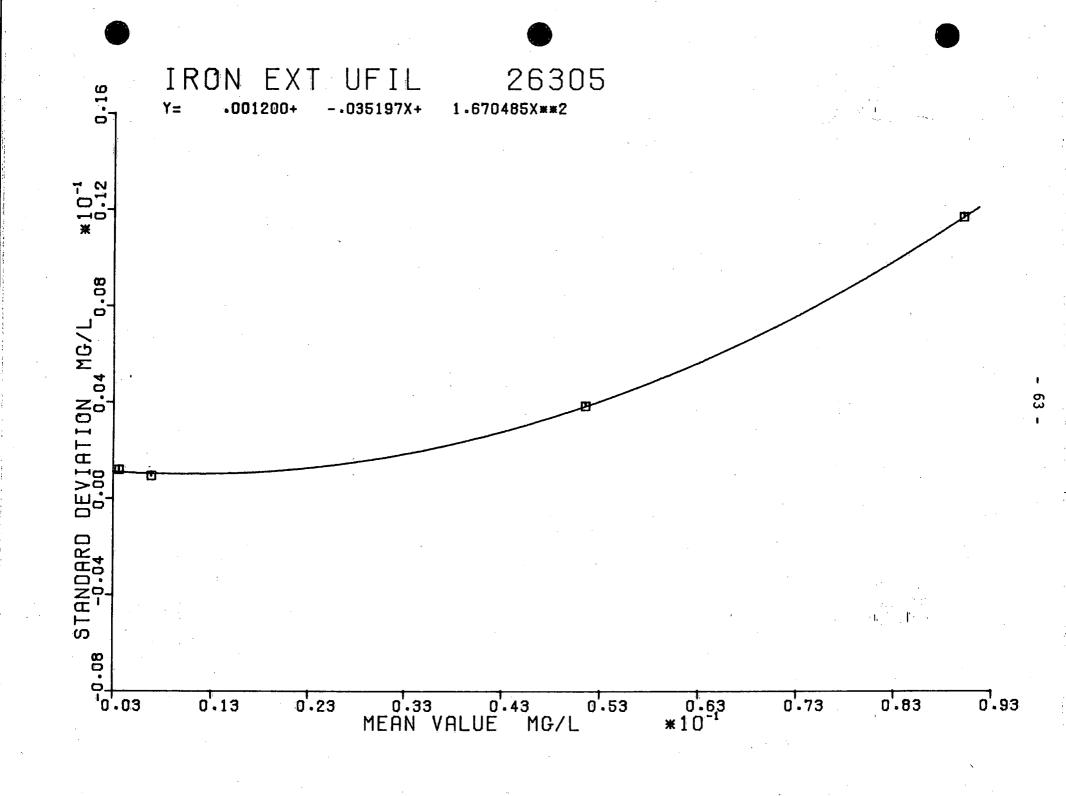
X = concentration of Iron , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, Mg/L	Coefficient of Variation, percent
4	.0036	32
4	.0069	13
4	.0516	8
4	.09	13

10.3 The percent recoveries are 100%, 96%, and 87% at concentration levels of .007, .05, and .1 mg Fe/L respectively.

10.4 Detection Limit = 0.002 mg Fe/L



<u>LEAD - 82301</u>

10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on

spiked Lake Ontario water at levels of .14 , 9.0 and 19 mg Pb/L to be respectively .02 , .2 and 1.5 mg/L, and may be expressed as follows:

 $\dot{s}_{T} = 0.0254 - 0.034 x + 0.006 x^{2}$

where S_{T} = overall precision, mg/L and

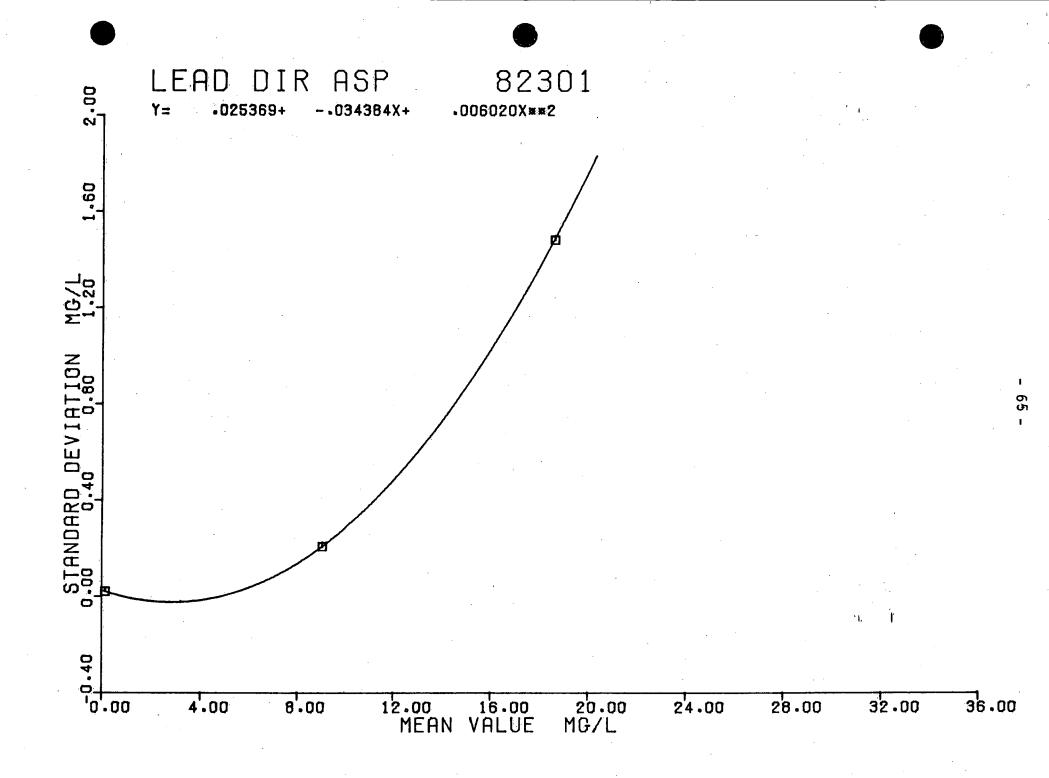
X = concentration of Lead, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
5	.14	14
5	9.0	2
5	19.	8

10.3 The percent recoveries are ⁹⁵ %, ¹⁰⁰%, and ¹⁰⁴ % at concentration levels of .15 , 9.0 , and 18 mg ^{Pb}/L respectively.

10.4 Detection Limit = 0.04 mg Pb/L



10. Precision and Accuracy

10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .003 ,- .05 and .1 mg Pb/L to be respectively .0009, .0038 and .007 mg/L, and may be expressed as follows:

$$S_{T} = 0.00067 + 0.061 X + 0.061 X^{2}$$

where S_T = overall precision, mg/L and

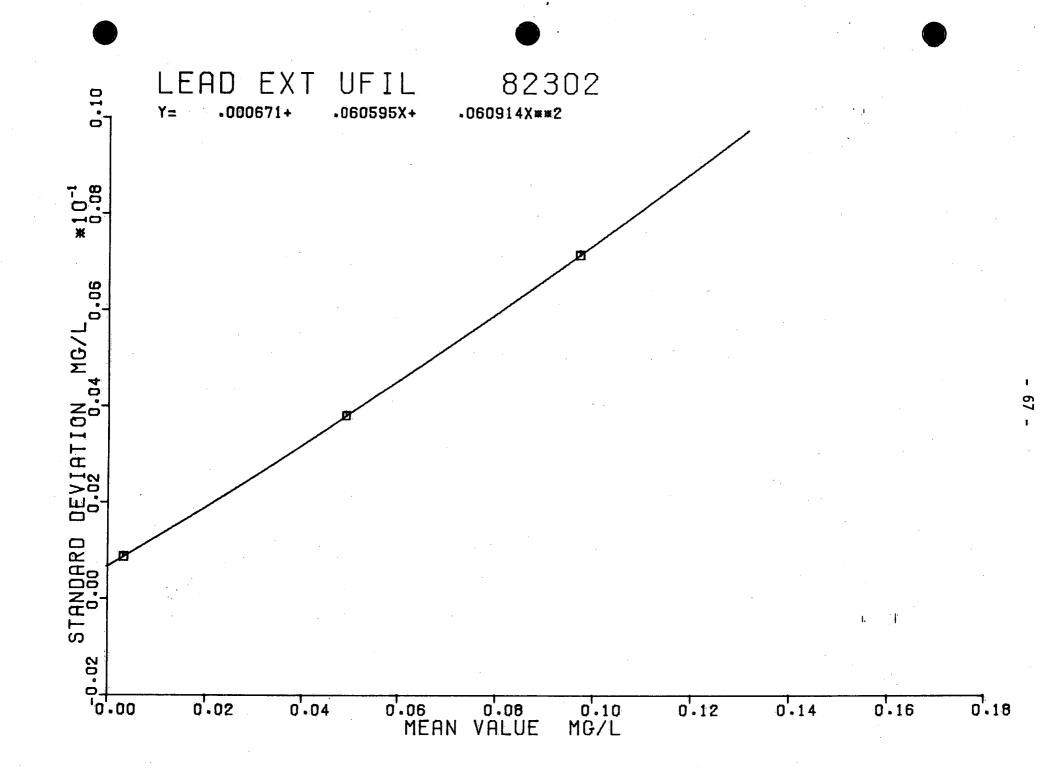
X = concentration of Lead , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

<u>Number of Labs</u> .	Mean, mg/L	Coefficient of <u>Variation, percent</u>
5	.003	26
5	.05	8
5	.1	7

10.3 The percent recoveries are102%, 99 %, and 97 % at concentration levels of .003 , .05 , and .1 mgPb/L respectively.

10.4 Detection Limit = 0.002 mg Pb/L



LITHIUM - 03001

10. Precision and Accuracy

10.1 The precision of this method was determined on spiked and unspiked Hamilton Harbor waters at levels of .008, .05, 1.15, and 2.3 mg Li/L to be respectively .001, .002, .079, and .062 mg/L and may be expressed as follows: S_T = 0.0097 + 0.0303 X

where S_T = overall precision, mg/L and

X = concentration of Li, mg/L

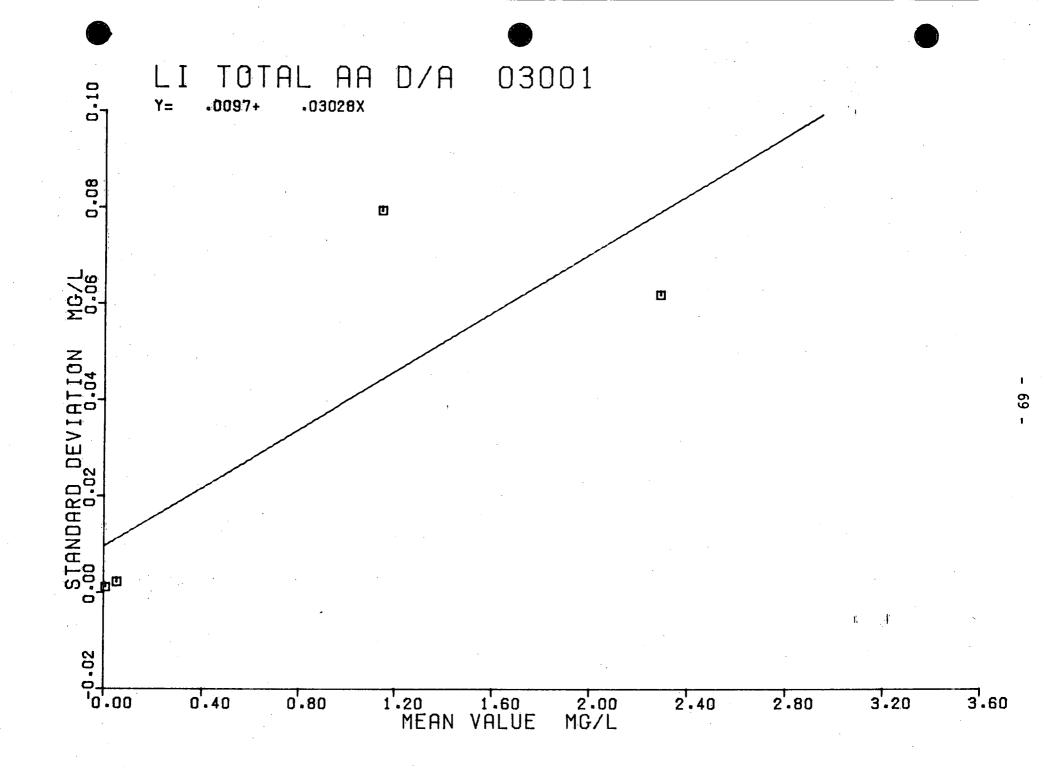
10.2

The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
3	.0082	14.3
3	.0535	4.2
3	1.147	6.9
3	2.295	2.7

10.3 The percent recoveries are 104%, 103%, and 104% at concentration levels of .052, 1.112, and 2.22 mg Li/L respectively.

10.4 Detection Limit = 0.004 mg Li/L



LITHIUM - 03301

10. Precision and Accuracy

10.1 The precision of this method was determined on spiked and unspiked Hamilton Harbour waters at levels of .0075, .05, 1.15, and 2.3 mg Li/L to be respectively .0006, .002 .102 and .078 mg/L and may be expressed as follows: $S_T = 0.0118 + 0.0388 X$

where $S_T = overall precision, mg/L and$

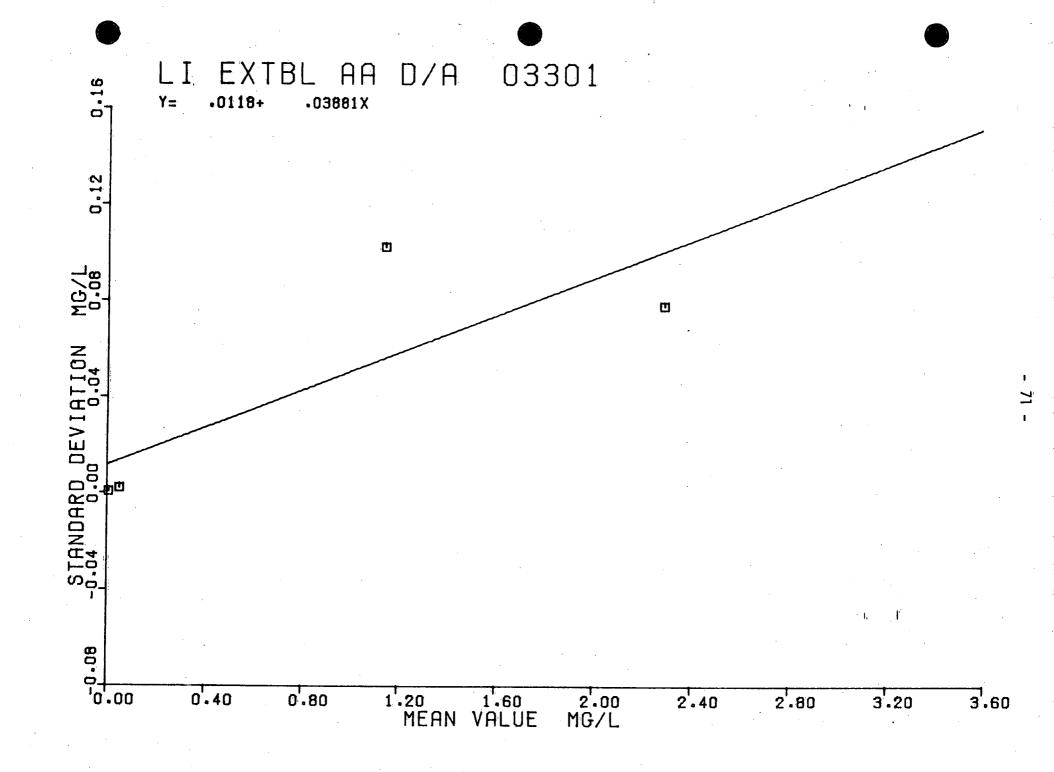
 $X = concentration of Li_mg/L$

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
2	.0075	7.7
2	.0525	4.0
2	1.1475	8.9
2	2.2925	3.4

10.3 The percent recoveries are 102%, 103% and 103% at concentration levels of .052, 1.112, and 2.22 mg Li/L respectively.

10.4 Detection Limit = 0.004 mg Li/L



10. Precision and Accuracy

- 10.1 The precision of this method was determined on synthetic,
 - spiked and unspiked Lake Superior waters at levels of.056,
 - 2.78,11.68 and 20.4 mgMg/L to be respectively.005,.113,.51 ,

and .64 mg/L and may be expressed as follows:

 $S_{T} = 0.034 + 0.0324X$

where S_T = overall precision, mg/L and

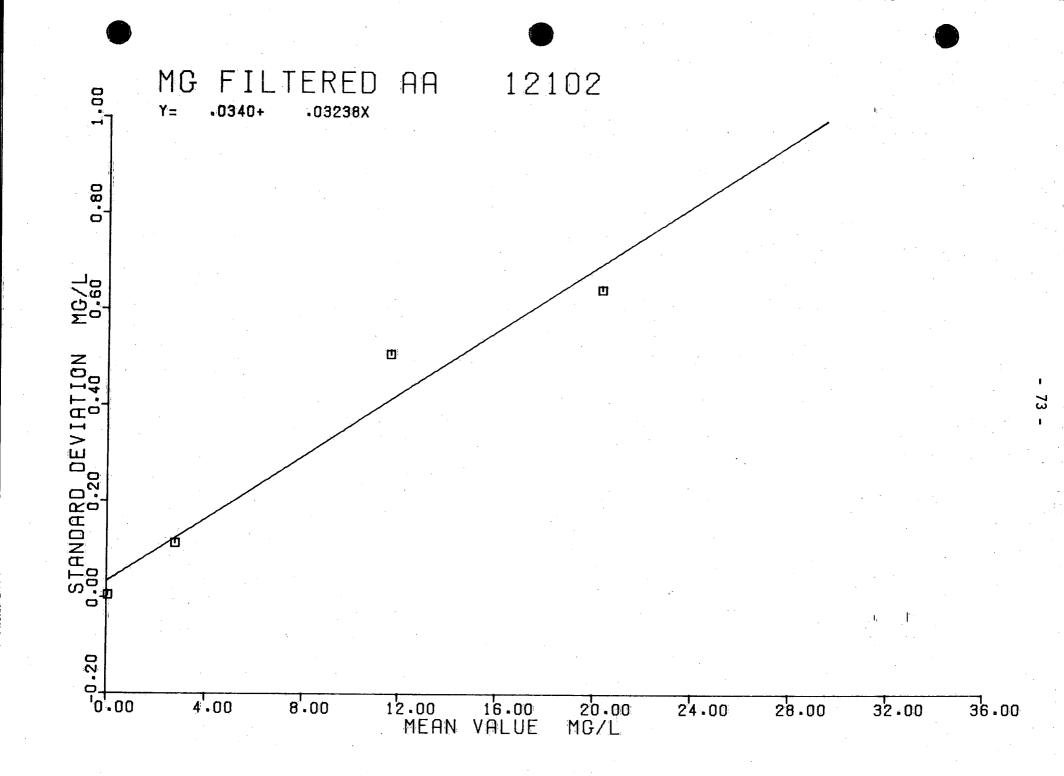
X = concentration of Mg , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
4	.056	8.5
4	2.78	4.1
4	11.7	4.3
4	20.4	3.1

10.3 The precent recoveries are94 %,100 %, and 99 % at concentration levels of .06,11.6, and20.5mgMg/L respectively.

10.4 Detection Limit = 0.01 mg Mg/L



MANGANESE - 25304

10. Precision and Accuracy

10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .05 .1.4 and 2.8 mg Mn/L to be respectively .001 , .07 and .13 mg/L, and may be expressed as follows:

 $S_{T} = 0.0026 + 0.046 X$

where $S_T = overall precision, mg/L and$

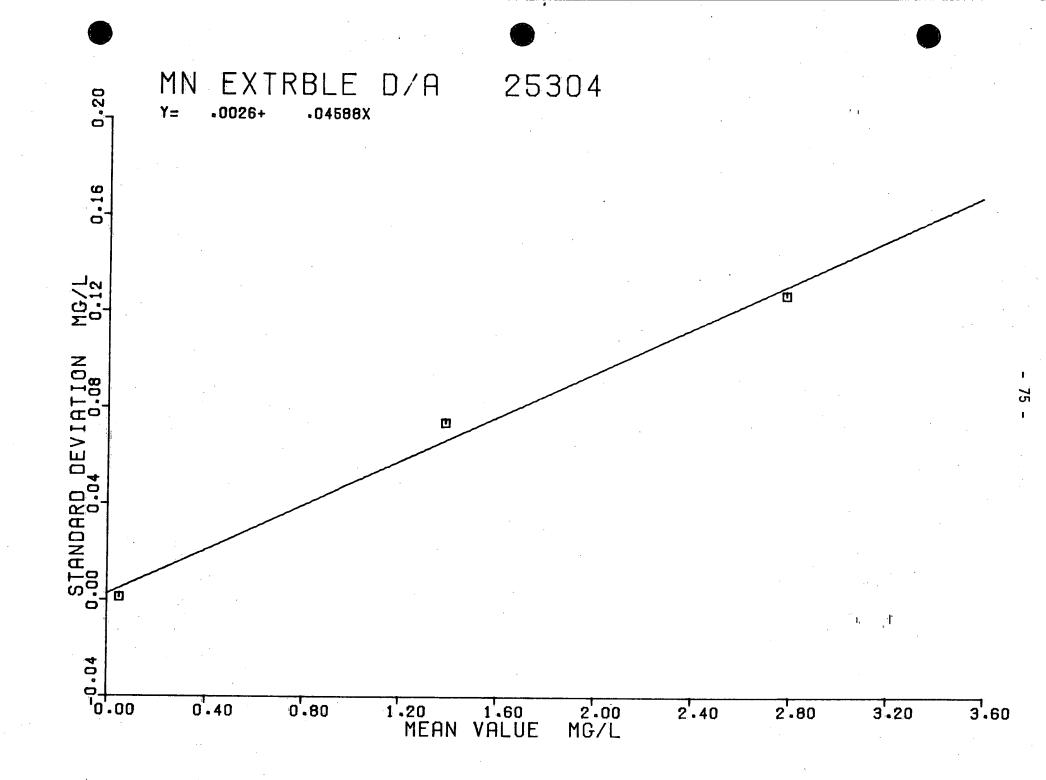
X = concentration of Manganese , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
5	.05	2
5	1.4	5
5	2.8	5

10.3 The percent recoveries are 95%, 103%, and 104 % at concentration levels of .05, 1.3, and 2.7 mg Mn/L respectively.

10.4 Detection Limit = 0.002 mg Mn/L



MANGANESE - 25305

10. Precision and Accuracy

10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .0055,_.0367 and .06 mg Mn/L to be respectively .0007,.0059, and .0017 mg/L, and may be expressed as follows:

 $S_{T} = 0.00235 + 0.0164 X$

where S_{T} = overall precision, mg/L and

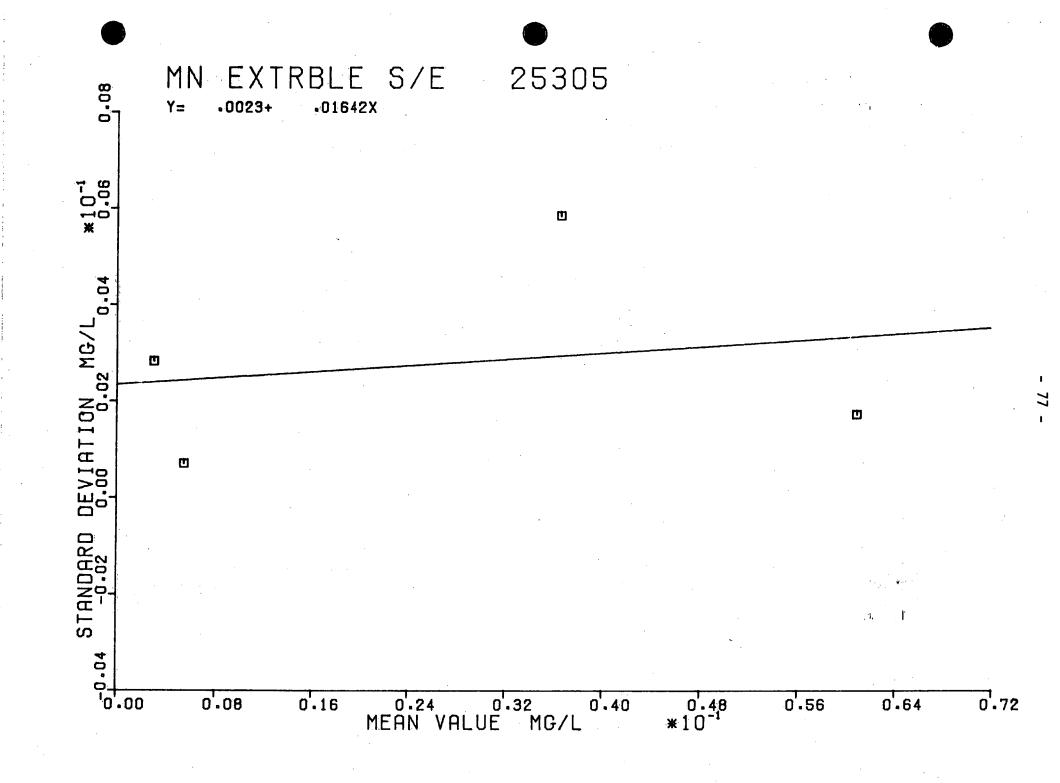
X = concentration of Mn , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
2	.0055	13
2	.0367	16
2	.06	3

10.3 The percent recoveries arel12%, 115%, and 102% at concentration levels of .005, .03, and .06 mgMn/L respectively.

10.4 Detection Limit = 0.002 mg Mn/L



MERCURY 80301

10. Precision and Accuracy

10.1 The precision of this method was determined on spiked rain waters at levels of .18, 41, and 82 µg Hg/L to be respectively .016, 2.1, and 4.6 µg/L and may be expressed as follows:

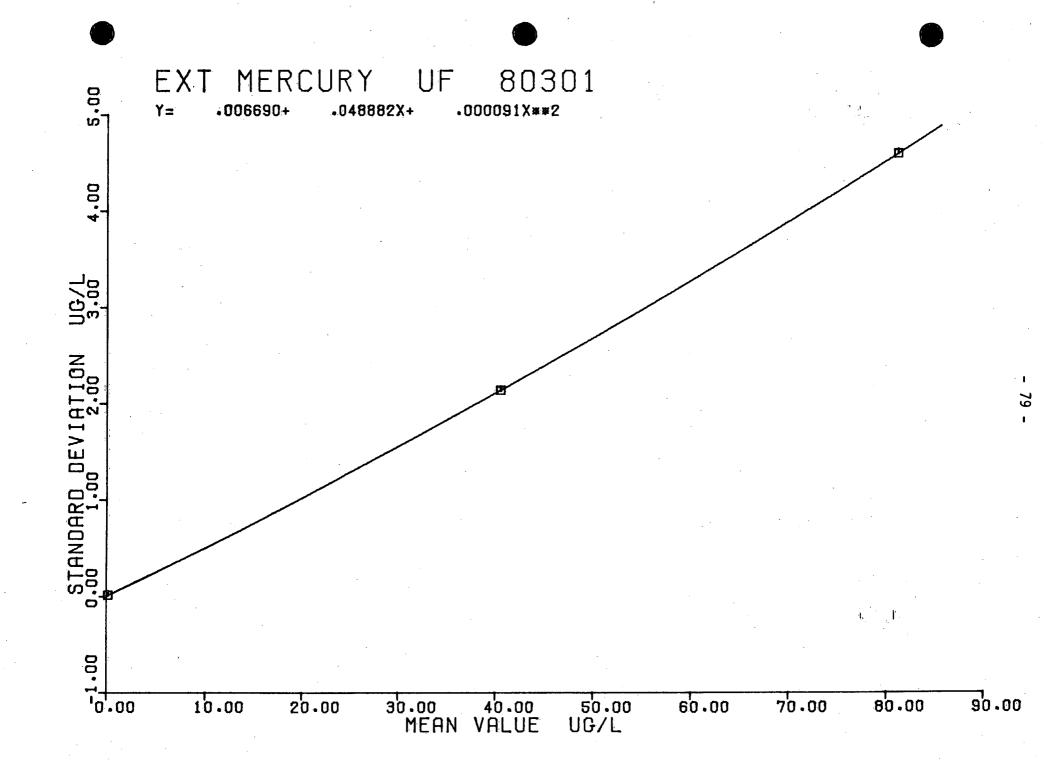
> $S_T = 0.00669 + 0.0489 X + 0.00009 X ^2$ where $S_T =$ overall precision, μ g/L and X = concentration of HG, μ g/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, µg/l	Coefficient of Variation, percent
3	.18	8.6
3	40.6	5.3
3	81.5	5.6

10.3 The percent recoveries are 105%, 95% and 95% at concentration levels of .17, 43, and 86 μg HG/L respectively.

10.4 Detection Limit = 0.04 μ g Hg/L



MOLYBDENUM - 42301

10. Precision and Accuracy

10.1 The precision of this method was determined on

spiked Lake Ontario water at levels of .34,-27.0 and 59 mg Mo/L to be respectively .11 , 4.5 and 13.5 mg/L, and may be expressed as follows:

$$S_{T} = 0.0709 + 0.113 X + 0.0019 X^{2}$$

where $S_T = overall precision, mg/L and$

X = concentration of Molybdenum, mg/L

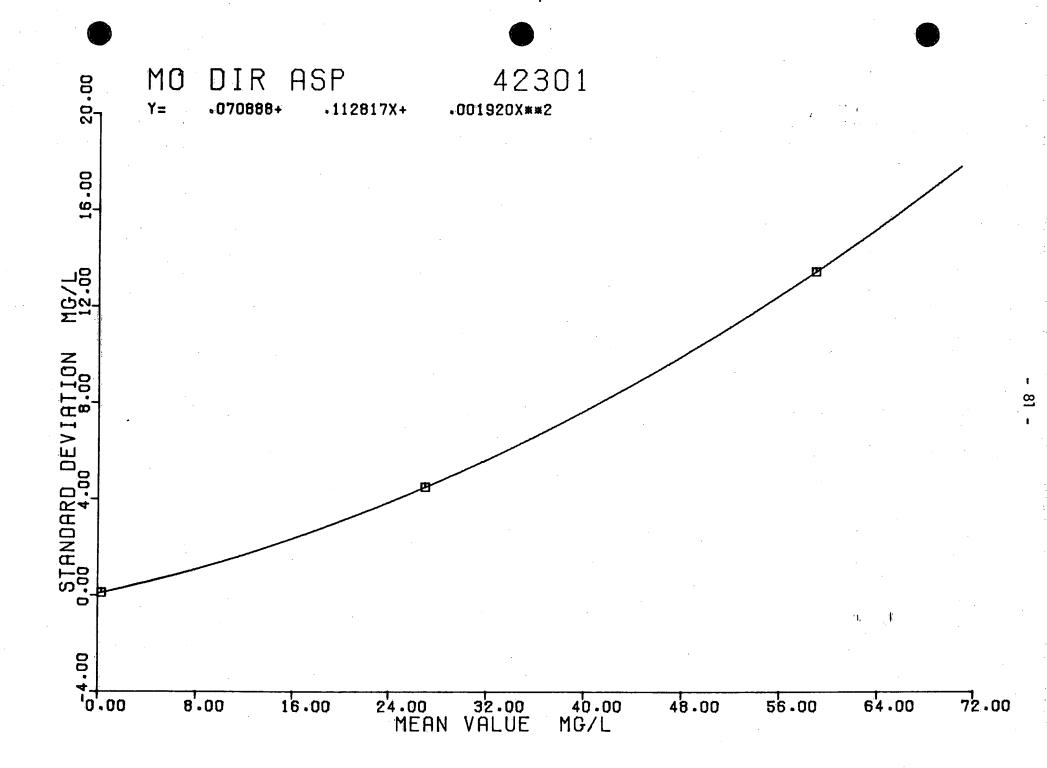
10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	<u>Mean, mg/L</u>	Coefficient of Variation, percent
3	.34	32
3	27.0	16
3	59.	23

10.3 The percent recoveries arel14%, 98 %, and 108 % at concentration levels of .3 , 27 , and 55 mg Mo/L respectively.

10.4 Detection Limit = 0.2 mg Mo/L

- 80 -



MOLYBDENUM - 42302

10. Precision and Accuracy

10.1 The precision of this method was determined on spiked and unspiked Lake Ontario waters at levels of .0015, .005 , .06, and .1 mg Mo/L to be respectively .0007, .0008 , .0038, and .016 mg/L, and may be expressed as follows:

 $S_T = 0.0009 - 0.054 X + 1.82 X^2$

where S_{τ} = overall precision, mg/L and

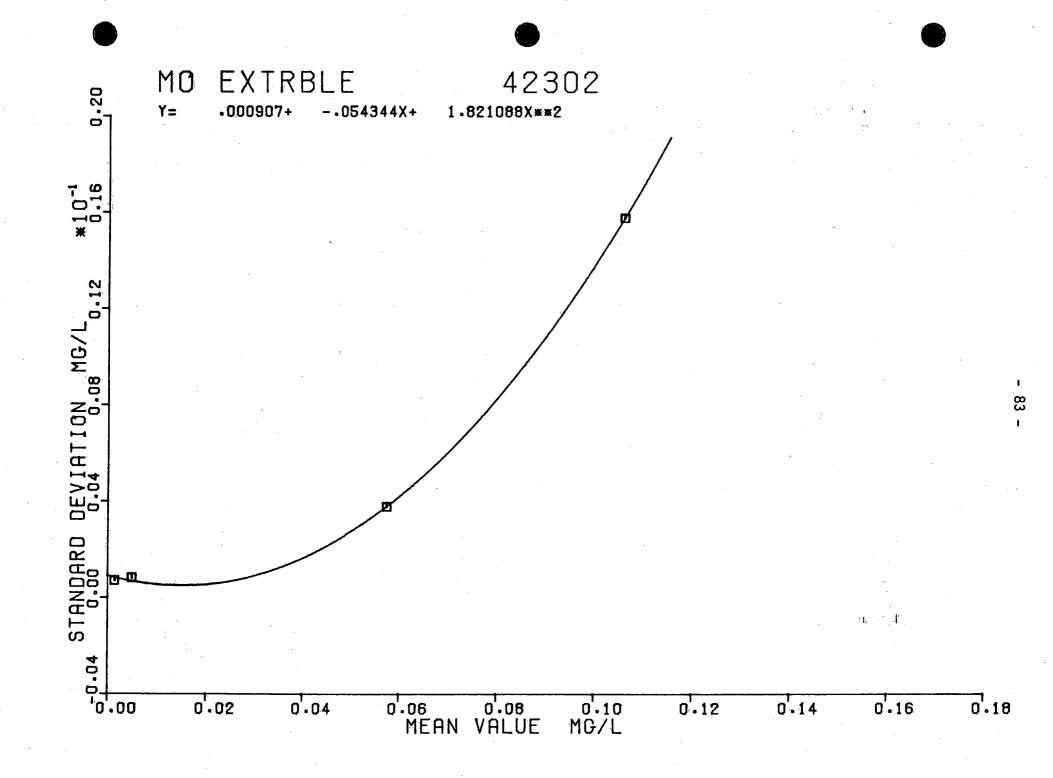
X = concentration of Molybdenum , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, Mg/L	Coefficient of Variation, percent
2	.0015	47
2	.005	16
2	.06	7
2	.1	15

10.3 The percent recoveries are 104%, 111 %, and 105 % at concentration levels of .005 , .05 , and .1 mg Mo /L respectively.

10.4 Detection Limit = 0.002 mg Mo/L



NICKEL - 28301

- 10. Precision and Accuracy
 - 10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .17 , 2.3 and 4.6 mg Ni/L to be respectively .03 , .27 and .47 mg/L, and may be expressed as follows:

 $S_{T} = 0.022 + 0.1 X$

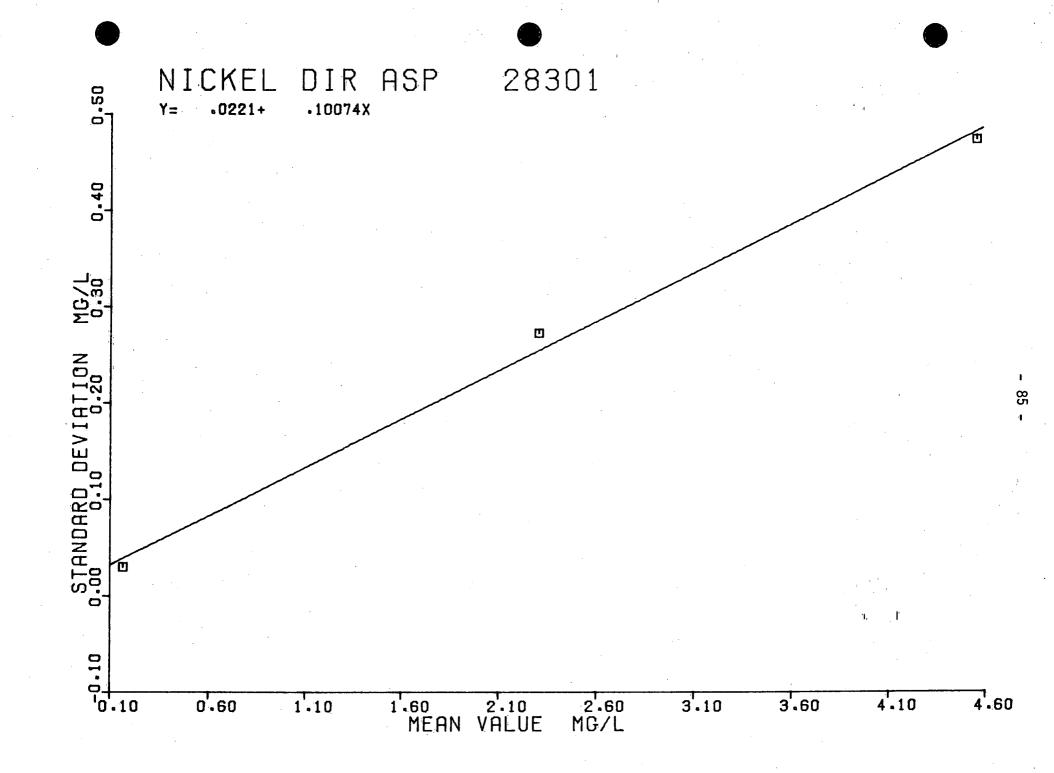
where $S_T = overall precision, mg/L and$

- X = concentration of Nickel , mg/L
- 10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
5	.17	18
5	2.3	12
5	4.6	10

10.3 The percent recoveries are 110%,103 %, and 101 % at concentration levels of .15, 2.3, and 4.5 mg /L respectively.

10.4 Detection Limit = 0.06 mg Ni/L



10.1 The precision of this method was determined on spiked and unspiked Lake Ontario waters at levels of .0019, .0044,.0492, and .09 mg Ni/L to be respectively .0007, .0013, .004, and .01 mg/L, and may be expressed as follows:

 $S_{T} = 0.000898 + 0.01527 \times + 0.984 \times^{2}$

where S_{T} = overall precision, mg/L and

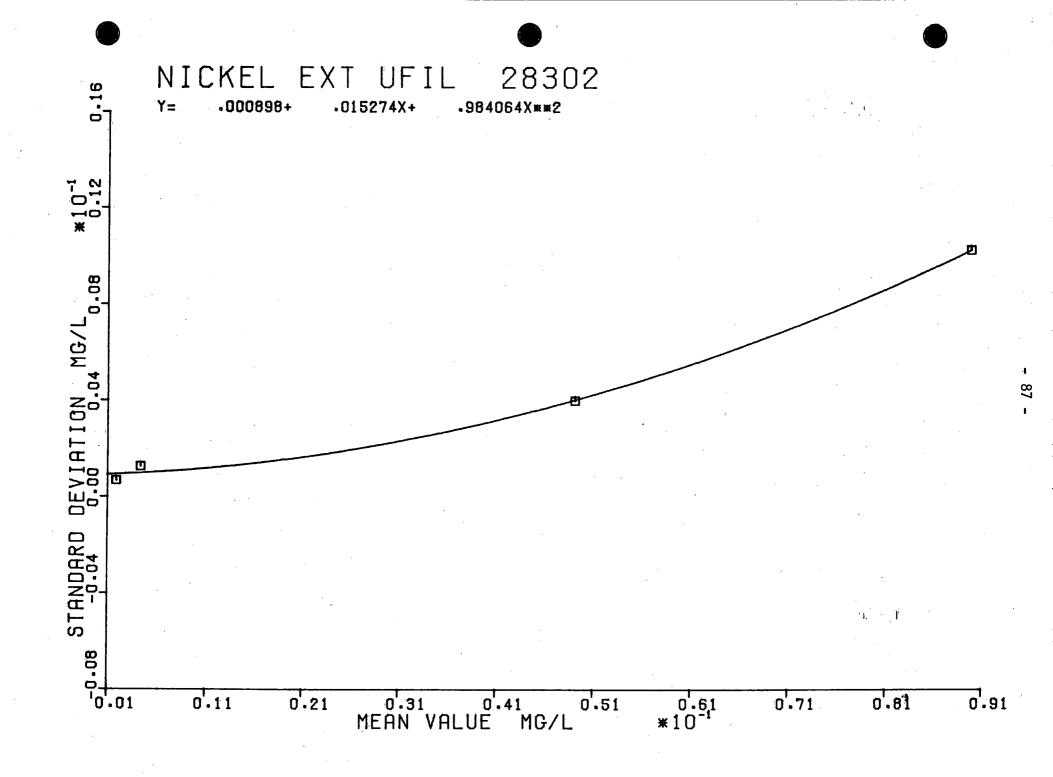
X = concentration of Nickel, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, Mg/L	Coefficient of Variation, percent
5	.0019	35
5	.0044	29
5	.0492	8
5	.09	11

10.3 The percent recoveries are 85%, 95%, and 89 % at concentration levels of .005, .05, and .1 mg Ni/L respectively.

10.4 Detection Limit = 0.002 mg Ni/L



10.1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of.105, .3, 1.3, and2.2 mg N/L to be respectively.017,.012,.019,

and .09 mg/L and may be expressed as follows:

 $S_{T} = 0.022 - 0.0449X + 0.0338X^{2}$

where S_T = overall precision, mg/L and

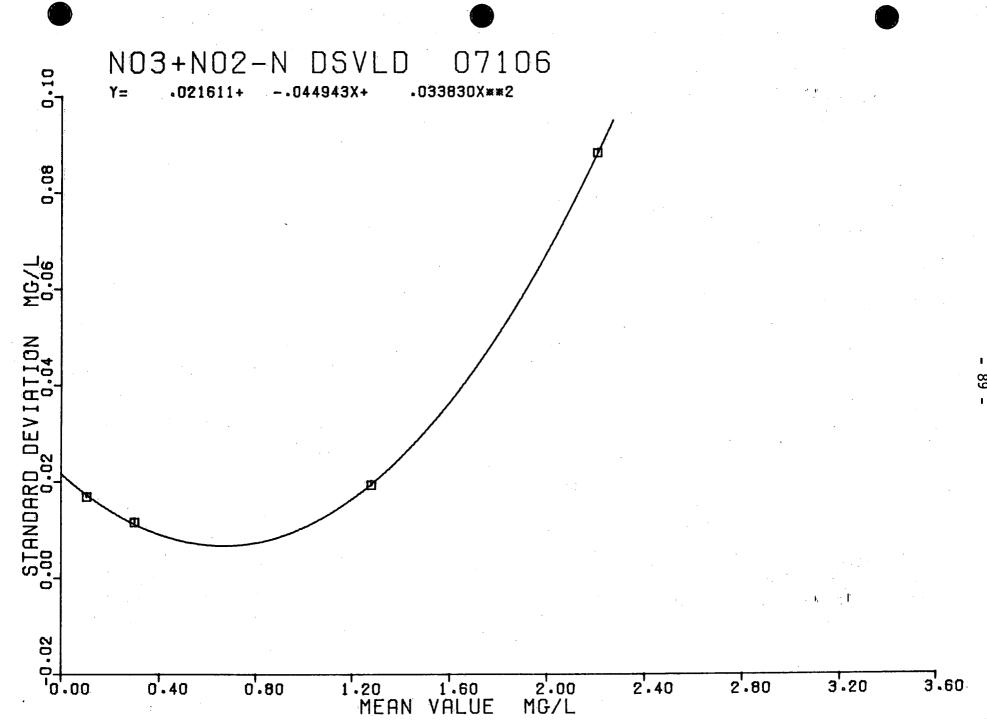
 $X = \text{concentration of NO}_3 \& \text{NO}_2 - \text{N}, \text{mg/L}$

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
3	.105	16.1
3	. 3	3.9
3	1.3	1.5
3	2.2	4.0

10.3 The precent recoveries are104%, 99 %, and 97 % at concentration levels of.101, 1.3, and 2.3mg N/L respectively.

10.4 Detection Limit = 0.03 mg N/L



10.1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of .093, .297, 1.33, and 2.1 mg N/L to be respectively.0115.015,.058,

and .173 mg/L and may be expressed as follows:

 $S_{\tau} = 0.0186 - 0.0434X + 0.0556X^2$

where S_T = overall precision, mg/L and

X = concentration of N , mg/L

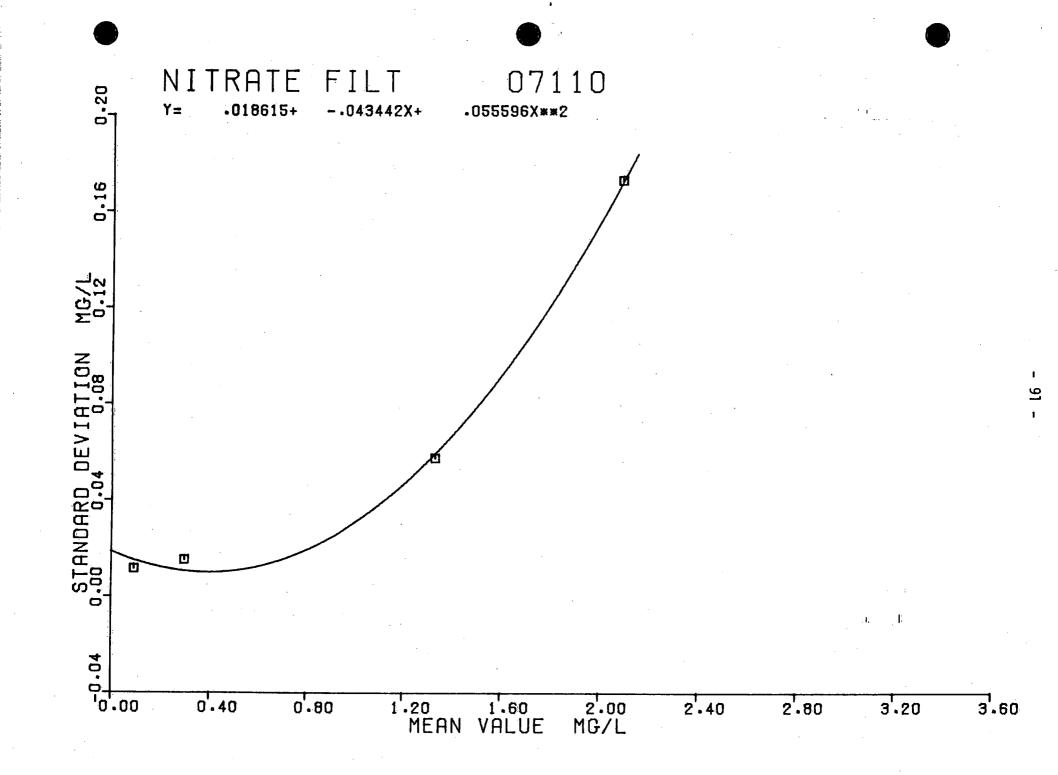
10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
2	.093	12.4
2	.297	5.1
2	1.33	4.3
2	2.1	8.2

10.3 The precent recoveries are 93%,103 %, and 92 % at concentration levels of .1 , 1.3, and2.3 mg N/L respectively.

10.4 Detection Limit = 0.02 mg N/L

- 90 -



10.1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of .009, .003, .066, and .14 mgN/L to be respectively .004, .003, .0096

and.013 mg/L and may be expressed as follows:

 $S_{T} = 0.00351 + 0.07178X$

where $S_T = overall precision, mg/L and$

X = concentration of ammonia-N, mg/L

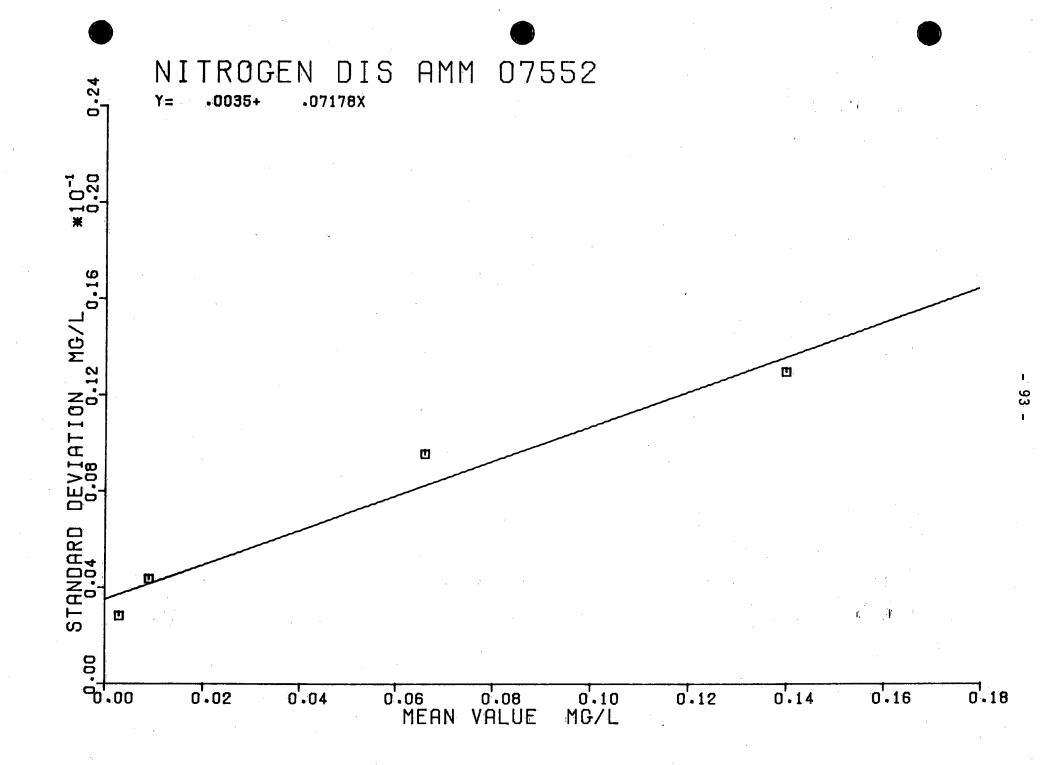
10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
3	.009	48
3	.003	94
3	.066	14.5
3	.14	9.2

10.3 The precent recoveries are 90%, 85 %, and 92 % at concentration levels of .01,.078, and .153mg N/L respectively.

10.4 Detection Limit = 0.01 mg N/L

- 92 -



TOTAL NITROGEN - 07601

10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of .15, .37, 1.64, and 3.03mg N /L to be respectively .05, .03, .17,

and .18 mg/L and may be expressed as follows:

 $S_{T} = 0.0359 + 0.0554X$

where S_T = overall precision, mg/L and

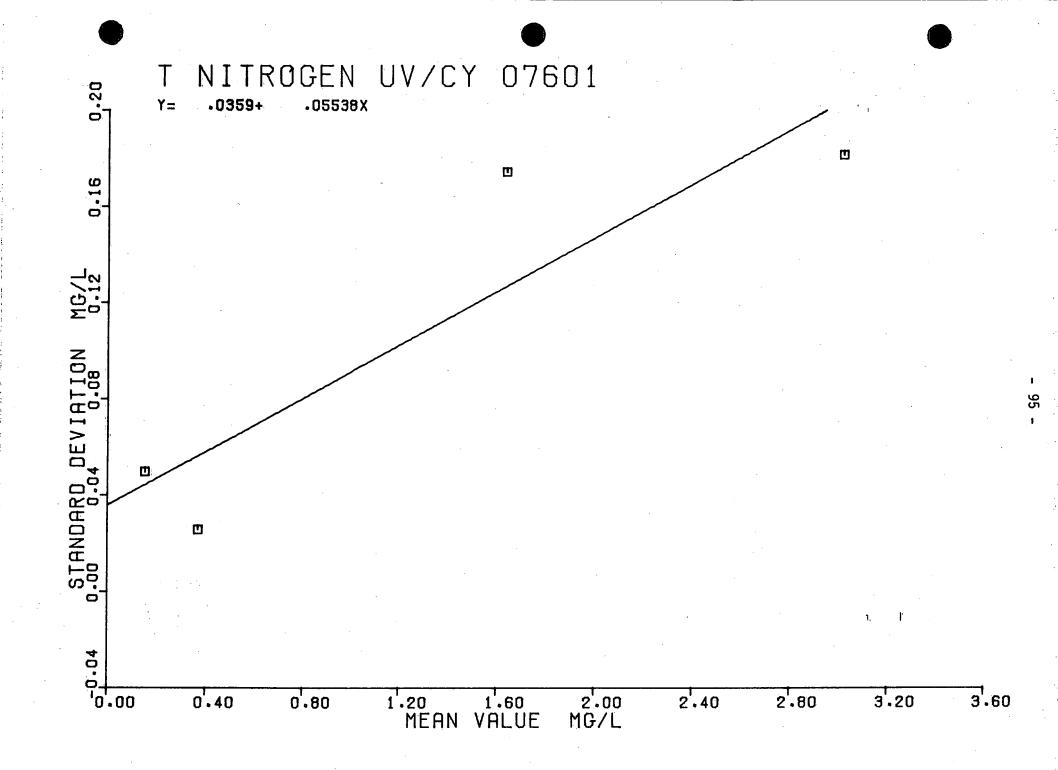
X = concentration of N , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
3	.15	32.4
3	. 37	7.0
3	1.64	10.6
3	3.03	6.0

10.3 The precent recoveries are 90%, 89 %, and 91 % at concentration levels of .17,1.85, and3.328mg N/L respectively.

10.4 Detection Limit = 0.1 mg N/L



10.1 The precision of this method was determined on synthetic waters at levels of 4.0, 6.9, and 9.1 pH units to be respectively .037, .03 and .048 pH units and may be expressed as follows:

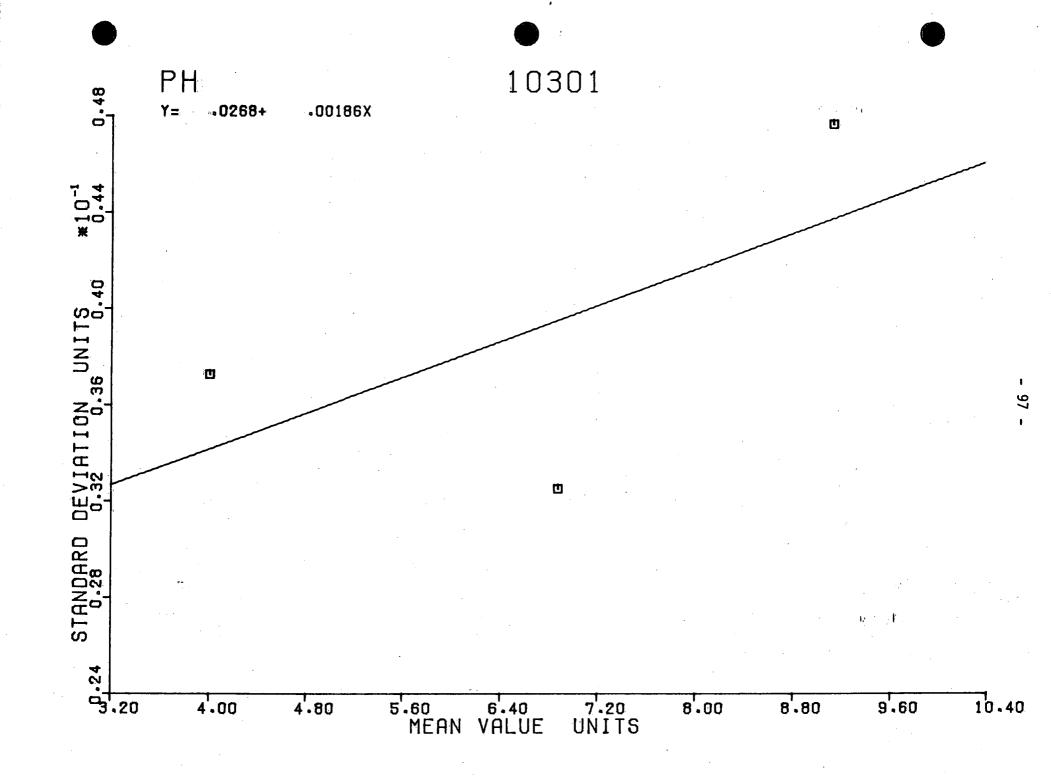
> S_T = 0.027 + 0.001856 X where S_T = overall precision, pH units and X = pH value, pH units

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, pH Units	Coefficient of Variation, percent
6	4.004	0.9
6	6.880	0.5
6	9.154	0.5

10.3 The percent receoveries are 100%, 100%, and 100% at concentration levels of 4.01, 6.87, and 9.18 pH units respectively.

10.4 Detection Limit = 0.08 pH units.



PHENOLS - 06531

- 10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on synthetic waters at levels of .005, .043, and .085 mg/L to be respectively .0006, .0026, and .0026 mg/L and may be expressed as follows:

 $S_{T} = 0.00083 + 0.0251 X$

where $S_T = overall precision, mg/L and$

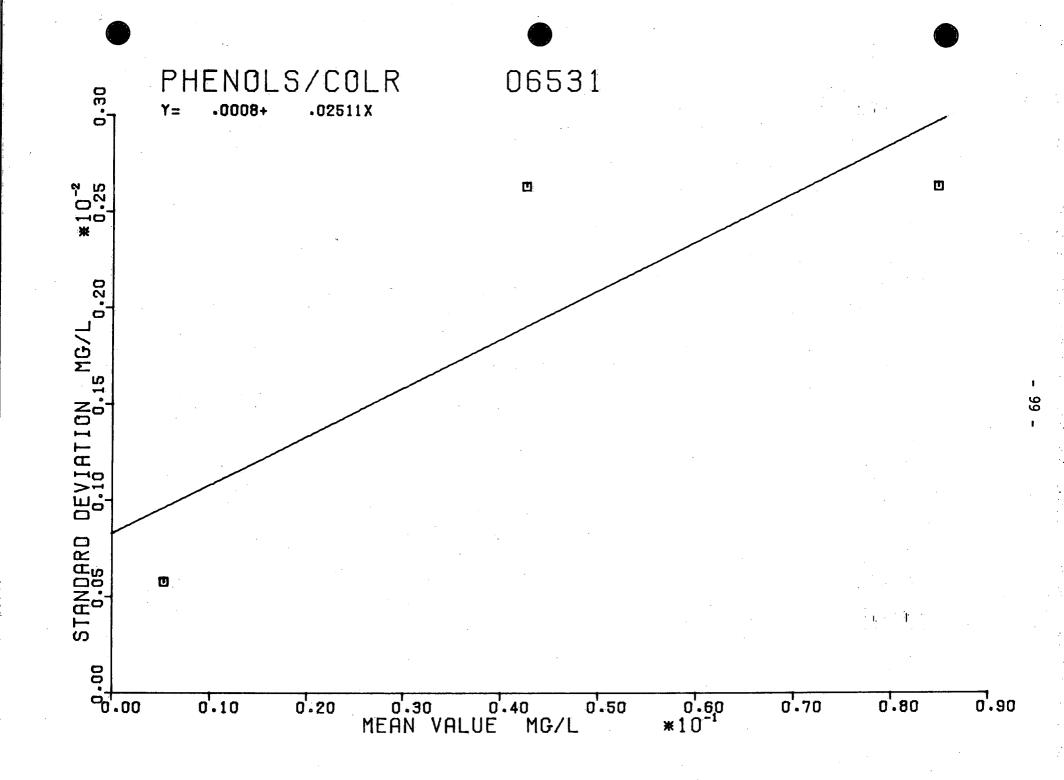
X = concentration of phenol, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
2	.0053	10.8
2	.0428	6.2
2	.0853	3.1

10.3 The percent recoveries are 118%, 95% and 95% at concentration levels of .005, .045 and .09 mg phenol/L respectively.

10.4 Detection Limit = 0.002 mg Phenol/L



DISSOLVED ORTHO P - 15254

- 10. Precision and Accuracy

10.1 The precision of this method was determined on spiked and unspiked Lake Ontario waters at levels of .0023, .0033, .031 and .053 mg P/L to be respectively .0007, .0004, .001 and .0017 mg/L and may be expressed as follows: $S_T = 0.000335 + 0.0255 X$ where $S_T = overall precision, mg/L and$

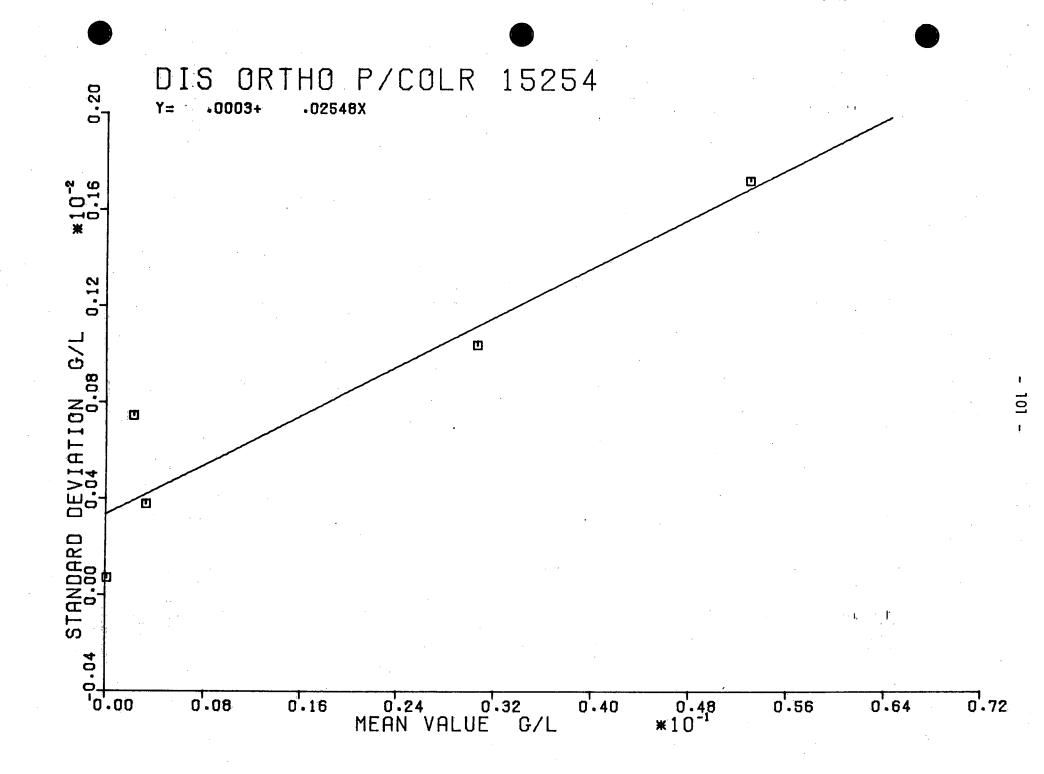
X = concentration of P, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
4	.00023	32.9
4	.0033	11.6
4	.0307	3.4
. 4	.0532	3.2

10.3 The percent recoveries are 97%, 106%, and 106% at concentration levels of .0034, .029, and .05 mg P/L respectively.

10.4 Detection Limit = 0.002 mg P/L



DISSOLVED INORGANIC P - 15353

- 10. Precision and Accuracy

10.1 The precision of this method was determined on spiked and unspiked Lake Ontario waters at levels of .009, .01, .035, and .056 mg P/L to be respectively .0036, .005, .005, and .005 mg/L and may be expressed as follows:

 $S_{T} = 0.004 + 0.023 X$

where S_T = overall precision, mg/L and

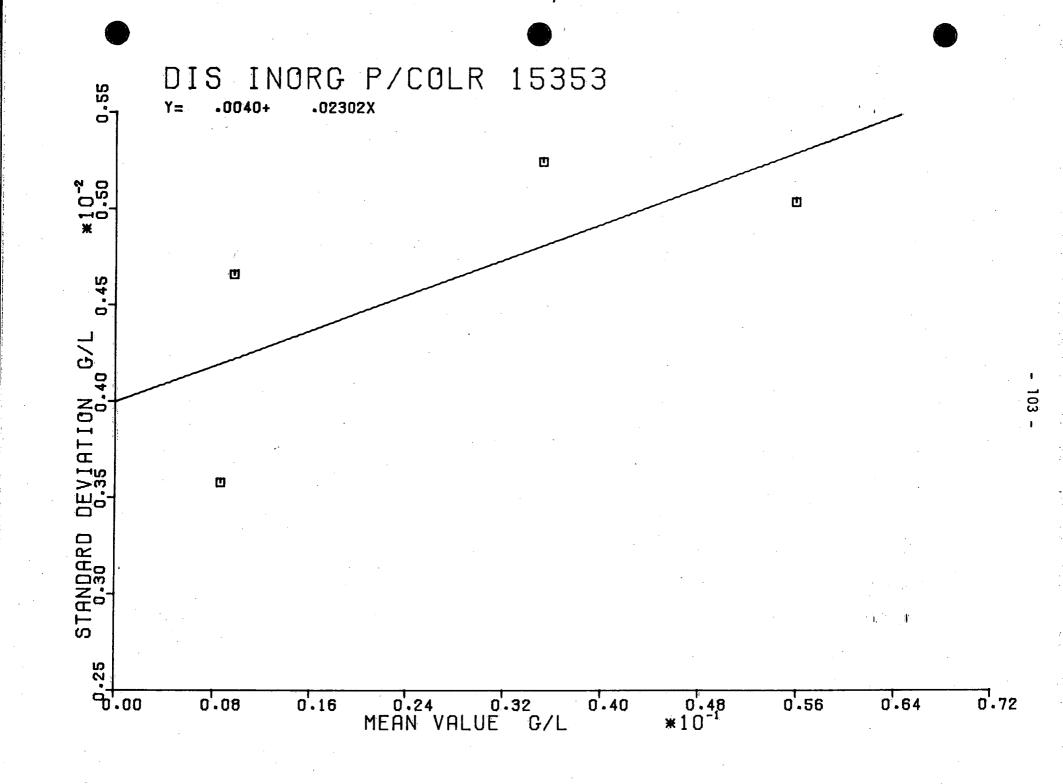
X = concentration of DIP, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
3	.0086	41.6
3	.0097	48.0
3	.0353	14.9
3	.0562	9.0

10.3 The percent recoveries are 100%, 100% and 99% at concentration levels of .0097, .035 and .0565 mg P/L respectively.

10.4 Detection Limit = 0.01 mg P/L



TOTAL PHOSPHATE 15403

10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of.0044, .0025, .2643 and .512mgP /L to be respectively.0009, .0005,

.014 and .028 mg/L and may be expressed as follows:

 $S_{T} = 0.000508 + 0.0505 X + 0.006 X^{2}$

where $S_T = overall precision, mg/L and$

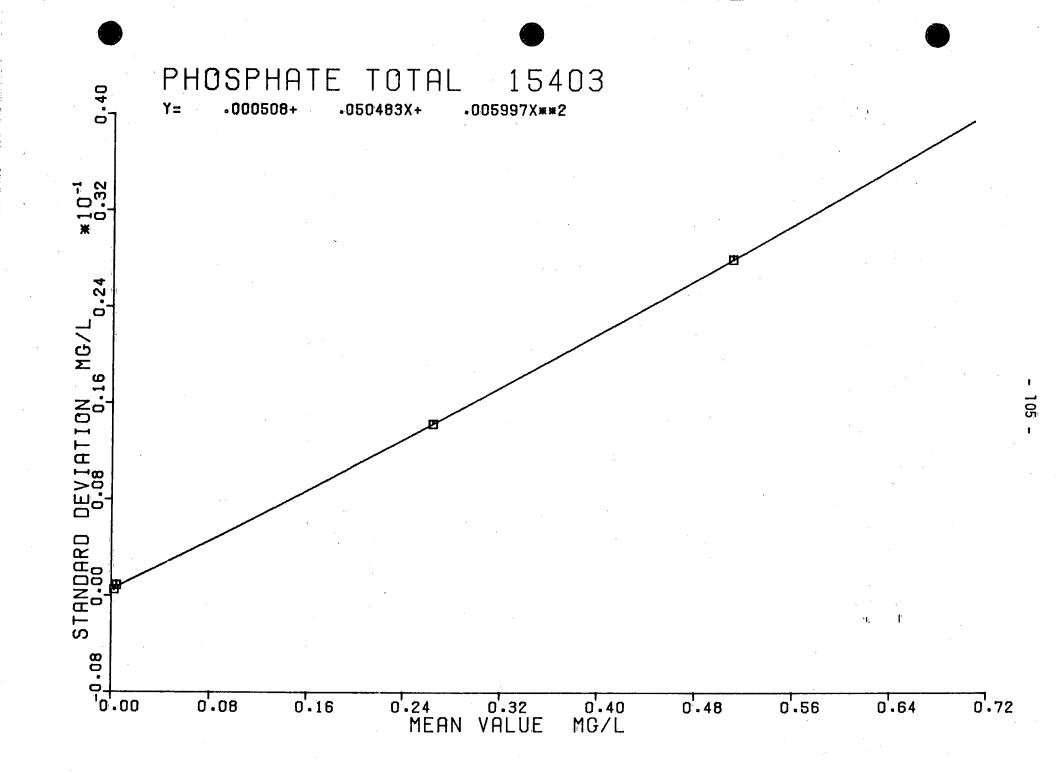
X = concentration of P, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
6	.0044	20
6	.0025	19
6	.2643	5.4
6	.5122	5.5
The precent reco	veries are 87 %	, 104 %, and 101 % at

10.3 The precent recoveries are 87 %, 104 %, and 101 % at concentration levels of .005, .25, and .5 mg P /L respectively.

10.4 Detection Limit = 0.002 mg P/L



POTASSIUM - 19103

10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on synthetic,

spiked and unspiked Lake Superior waters at levels of .32, .43, 13.96, and 27.6mg K/L to be respectively .088, .092, .75,

and 1.35 mg/L and may be expressed as follows:

 $S_{T} = 0.071 + 0.0508X - 0.000162X^{2}$

where S_T = overall precision, mg/L and

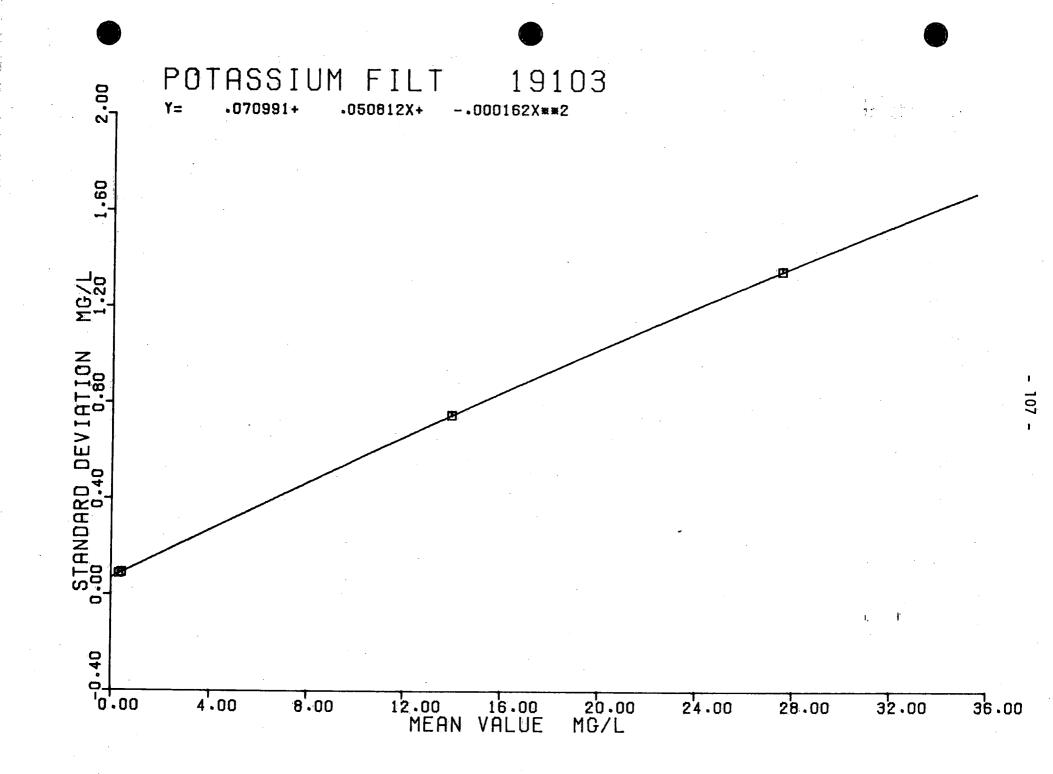
X = concentration of K, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

N	umber of Labs	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
	5	.316	27.8
	5	. 426	21.6
	5	13.96	5.4
	5	27.59	4.9

10.3 The precent recoveries are 96%, 98 %, and 98 % at concentration levels of .33, 14.3, and 28. lmg K/L respectively.

10.4 Detection Limit = 0.2 mg K/L



SILICA 14102

10. <u>Precision and Accuracy</u>

10.1

The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of .10, SiO₂ 2.5 ,11.3, and19.8mg /L to be respectively.005,.082,.67 , and .96 mg/L and may be expressed as follows:

 $S_{T} = 0.000112 + 0.0509X$

where S_T = overall precision, mg/L and

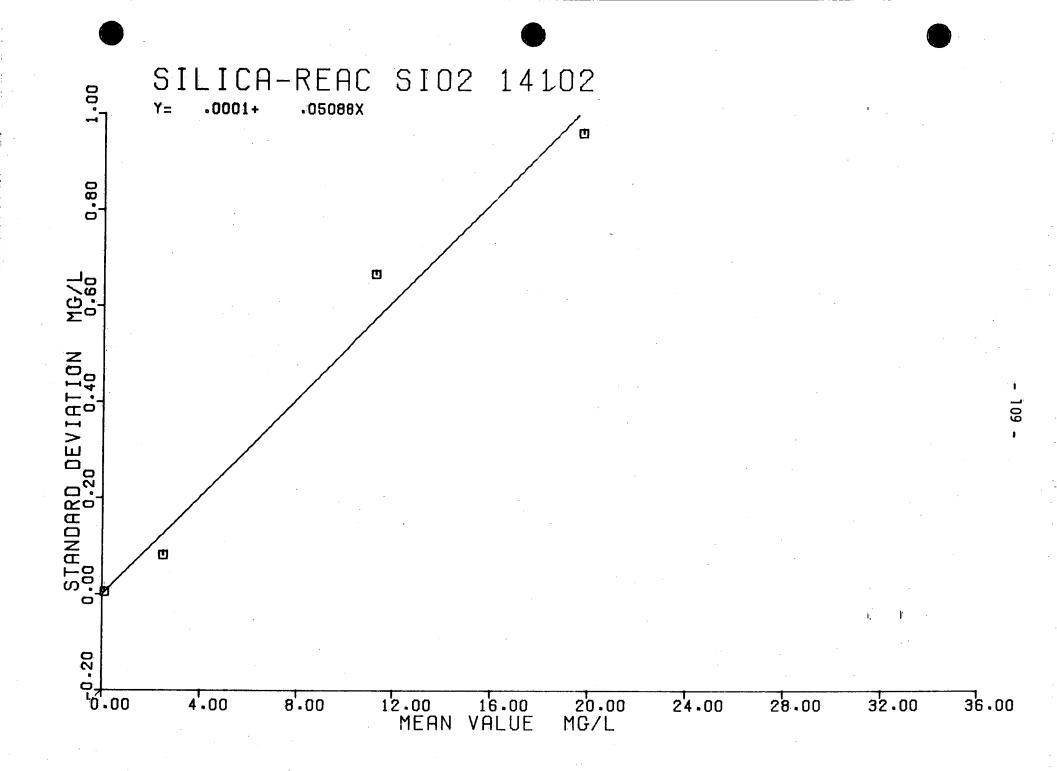
 $X = \text{concentration of } SiO_2$, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
4	. 10	5.0
4	2.5	3.3
4	11.3	5.9
4	19.8	4.9

10.3 The precent recoveries are 97%,102 %, and101 % at concentration levels of.107,11.04, and19.6mg // respectively.

10.4 Detection Limit = 0.01 mg Si02/L



SODIUM 11103

10. Precision and Accuracy

10.1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of .63, 1.25,46.93 and 91.4mgNa/L to be respectively.054,.082,1.81,

and 2.93 mg/L and may be expressed as follows:

 $S_T = 0.0264 + 0.0444X - 0.000138X^2$

where $S_T = overall precision, mg/L and$

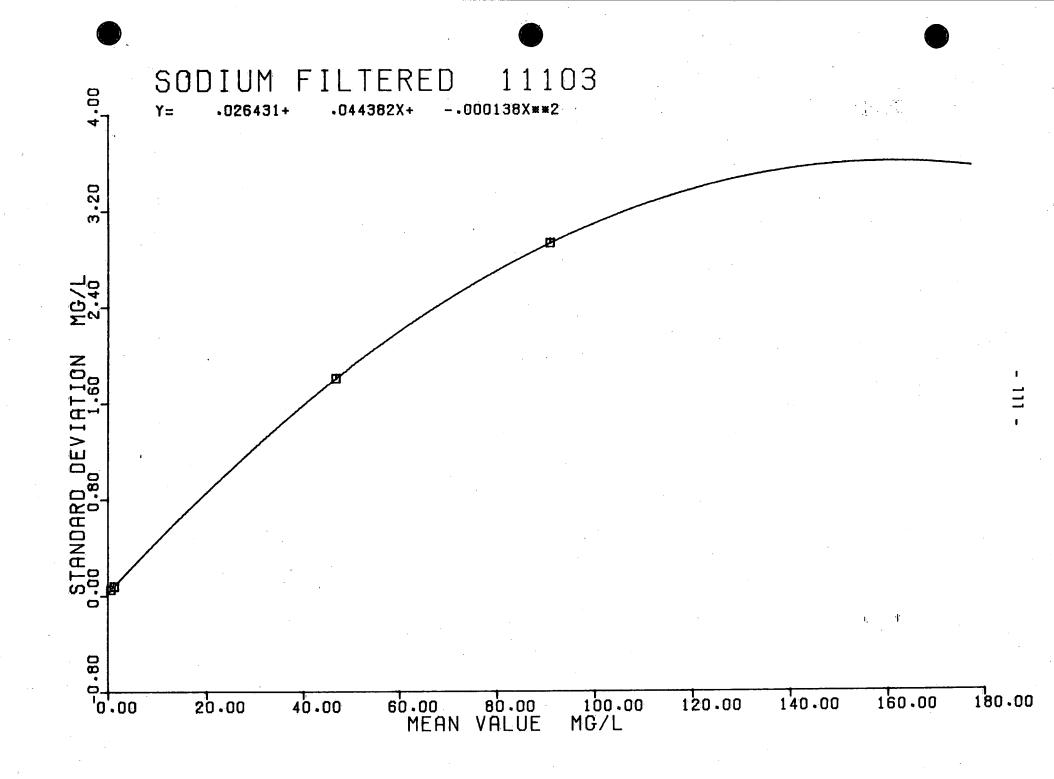
X = concentration of Na , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of Variation, percent
5	.625	8.6
5	1.25	6.5
5	46.93	3.8
5	91.38	3.2
The survey of		.

10.3 The precent recoveries are107%,101 %, and 99 % at concentration levels of.585,46.7, and92.1mgNa/L respectively.

10.4 Detection Limit = 0.1 mg Na/L



SPECIFIC CONDUCTANCE - 02041

10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on synthetic waters at levels of 1.21, 17.8, 515 and 978 μsie/cm to be respectively .35, .81, 15.1, and 22.8 μsie/cm and may be expressed as follows:

 $S_{T} = 0.8705 + 0.0235 X$

where $S_T = overall precision, usie/cm and$

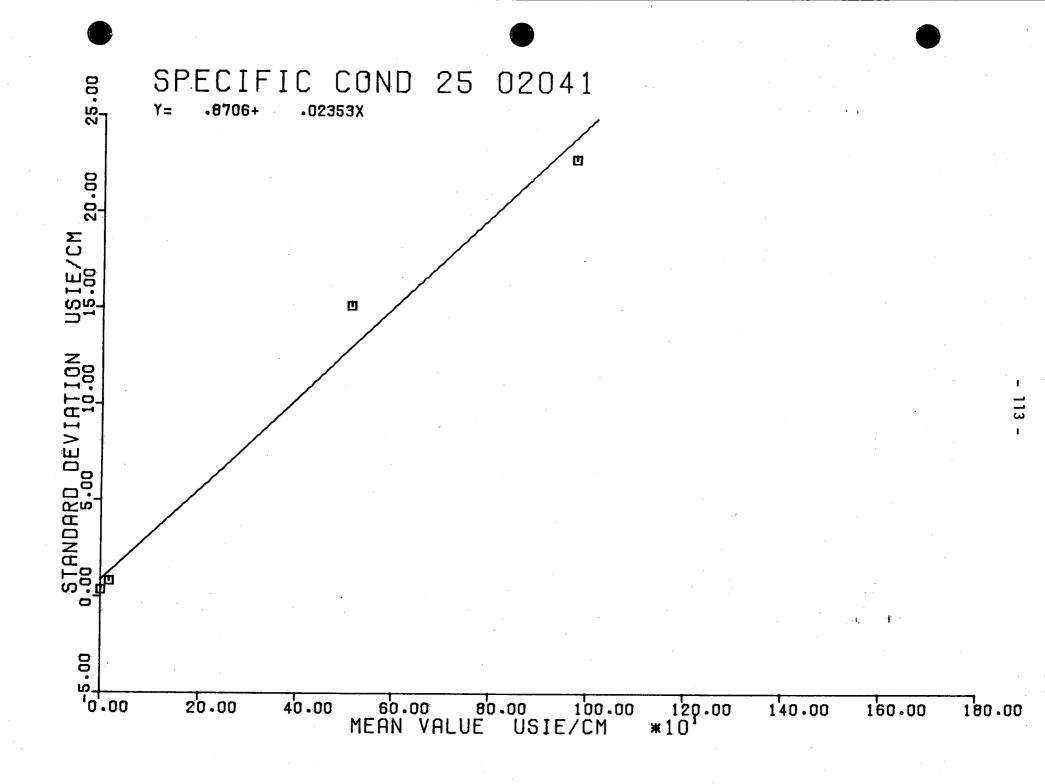
X = specific conductance value, μ sie/cm

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, µsie/cm	Coefficient of Variation, percent
6	1.214	28.7
6	17.84	4.6
	515.0	2.9
6	977.7	2.3

10.3 The percent recoveries are 108%, 99% and 98% at concentration levels of 16.5, 519.7 and 1000 $\mu sie/cm$ respectively.

10.4 Detection Limit = 2.0 µsie/cm



STRONTIUM - 38301

10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on spiked and unspiked Lake Ontario waters at levels of .18, .22 , 2.2 , and 3.9 mg Sr/L to be respectively .01, .02 , .145 , and .42 mg/L, and may be expressed as follows:

 $S_T = 0.0143 - 0.00197 X + 0.0277 X^2$

where S_{T} = overall precision, mg/L and

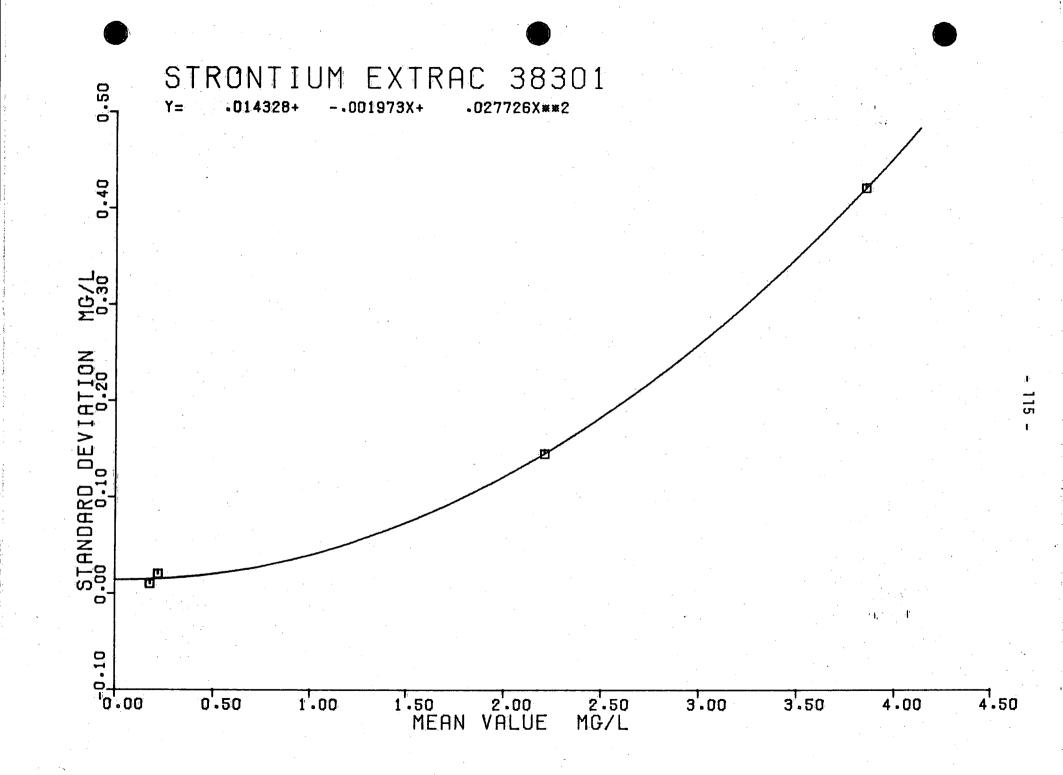
X = concentration of Strontium, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, Mg/L	Coefficient of <u>Variation, percent</u>
5	.18	6
5	.22	9
5	2.2	7
5	3.9	11

10.3 The percent recoveries are 96%, 92 %, and 84% at concentration levels of .2 , 2.4 , and 4.5 mg Sr/L respectively.

10.4 Detection Limit = 0.03 mg Sr/L



10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on synthetic, spiked and unspiked Lake Superior waters at levels of 3.9, 3.6,98, and 201 mg^{SO}4/L to be respectively.86,.87,6.6,

and 4.2 mg/L and may be expressed as follows:

 $S_{T} = 1.58 + 0.02X$

where $S_T = overall precision, mg/L and$

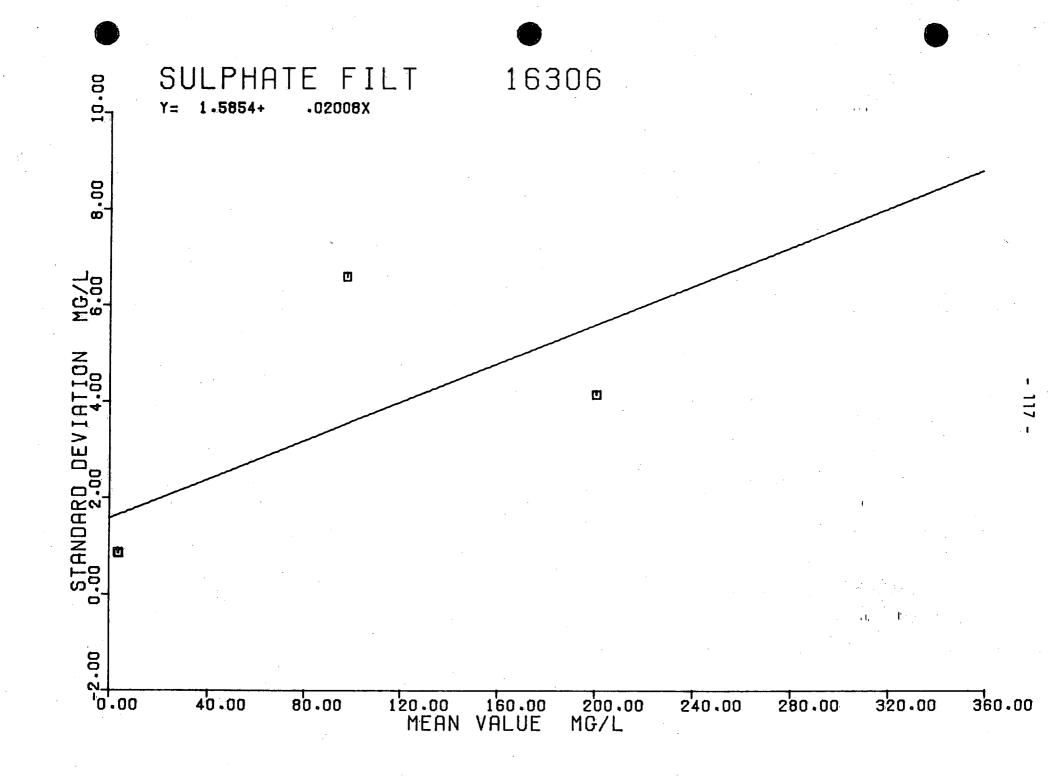
 $X = \text{concentration of } SO_4$, mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, Mg/L	Coefficient of <u>Variation, perc</u> ent
5	3.9	22
5	3.6	24
5	. 98	6.7
5	2 01	2.1

10.3 The precent recoveries are 98%, 100%, and 104% at SO4 concentration levels of 3.9, 98, and 201 mg /L respectively.

10.4 Detection Limit = $2 \text{ mg SO}_4/L$



TURBIDITY - 02073

10. Precision and Accuracy

10.1 The precision of this method was determined on synthetic waters at levels of .091, .661, 106, and 216 JTU to be respectively .037, .079, 11.6, and 14.9 JTU and may be expressed as follows:

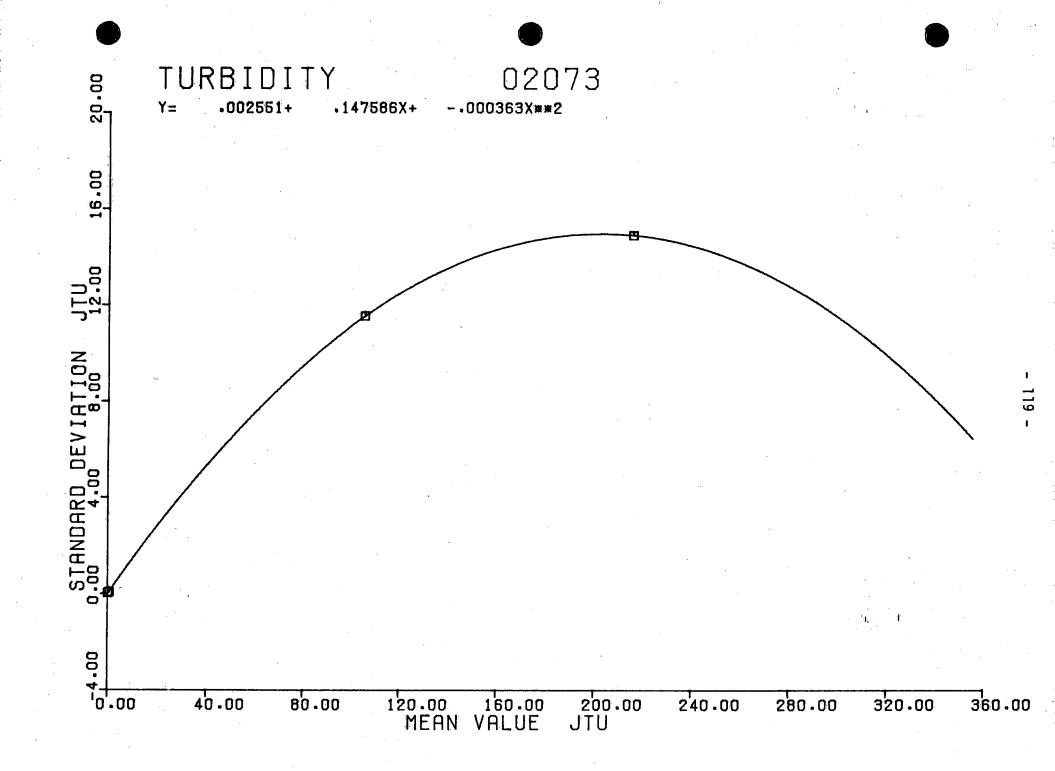
 $S_T = 0.00255 + 0.1476 \times -0.00036 \times 2^2$ where $S_T =$ overall precision, JTU and X = turbidity value, JTU

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs	Mean, JTU	Coefficient of Variation, percent
5	.091	40.2
5	.661	12.0
5	105.86	10.9
5	216.42	6.9

10.3 The percent recoveries are 111%, 96%, and 98% at concentration levels of .59, 110, and 220 JTU respectively.

10.4 Detection Limit = 0.2 JTU



VANADIUM - 23301

10. Precision and Accuracy

10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .27, 72.0 and 149 mg V/L to be respectively .05, 4.2 and 6.6 mg/L, and may be expressed as follows:

 $S_{\tau} = 0.0346 + 0.072 X - 0.000185 X^2$

where S_{T} = overall precision, mg/L and

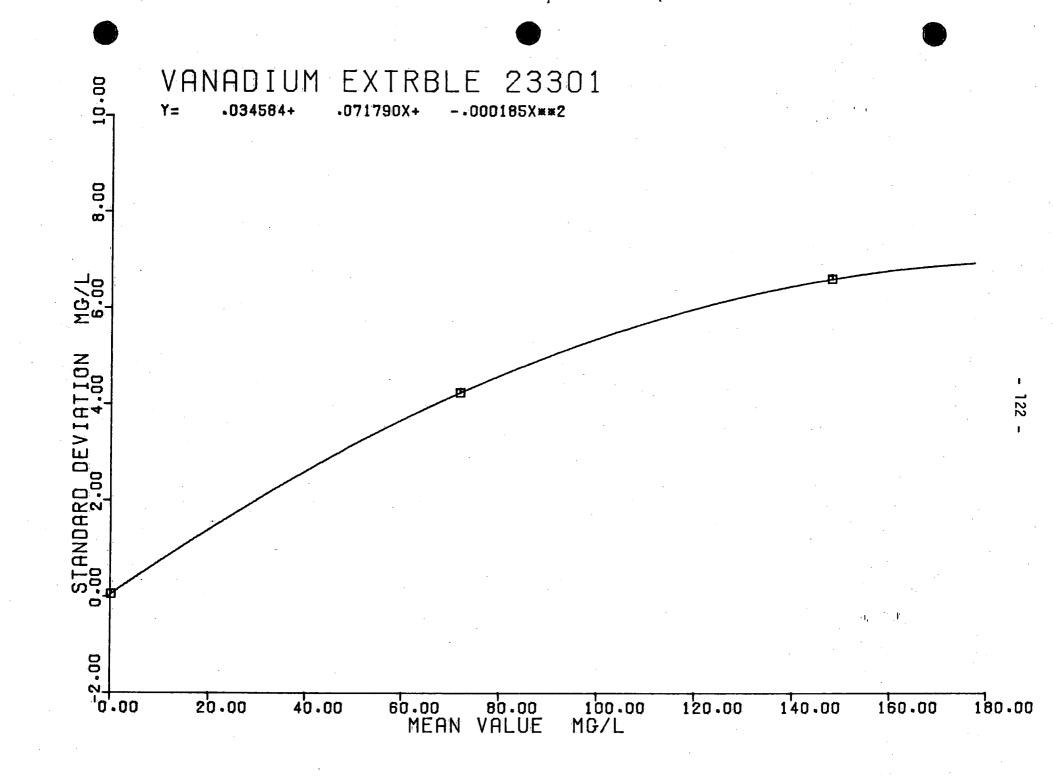
X = concentration of Vanadium , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
2	.27	20
2	72.0	6
2	149.0	4

10.3 The percent recoveries are 89%,107 %, and 110 % at concentration levels of .3 , 70 , and 135 mg V/L respectively.

10.4 Detection Limit = 0.1 mg V/L



VANADIUM - 23302

- 10. Precision and Accuracy
 - 10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .005 ,- .074 and .15 mg V/L to be respectively .001 , .033, and .005 mg/L, and may be expressed as follows:

$$S_{T} = 0.00094 - 0.0271 X + 0.37 X^{2}$$

where S_{T} = overall precision, mg/L and

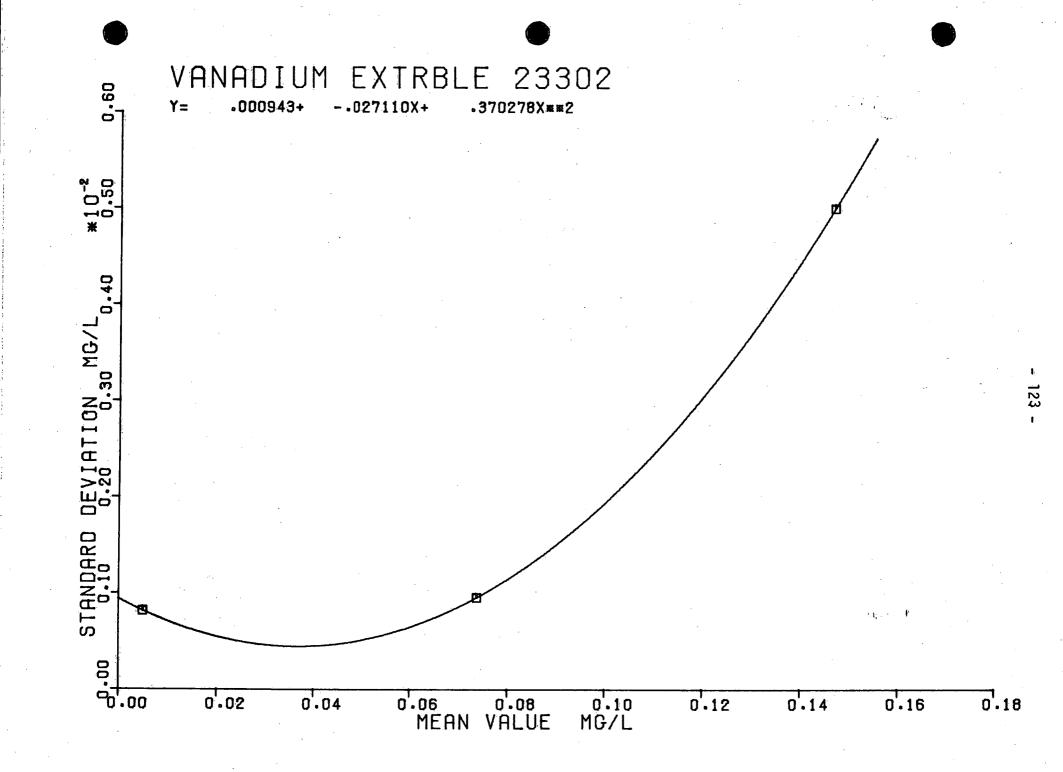
X = concentration of V , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of <u>Variation, percent</u>
2	0.005	16
2	0.074	1
2	0.15	3

10.3 The percent recoveries are104%, 104%, and 103% at concentration levels of .005, .07, and .14 mg V/L respectively.

10.4 Detection Limit = 0.002 mg V/L



ZINC - 30304

10. Precision and Accuracy

10.1 The precision of this method was determined on spiked Lake Ontario water at levels of .05 ,_1.0 and 2.0 mg Zn/L to be respectively .0096, .04 and .06 mg/L, and may be expressed as follows:

 $S_{\tau} = 0.0087 + 0.0279 X$

where $S_T = overall precision, mg/L and$

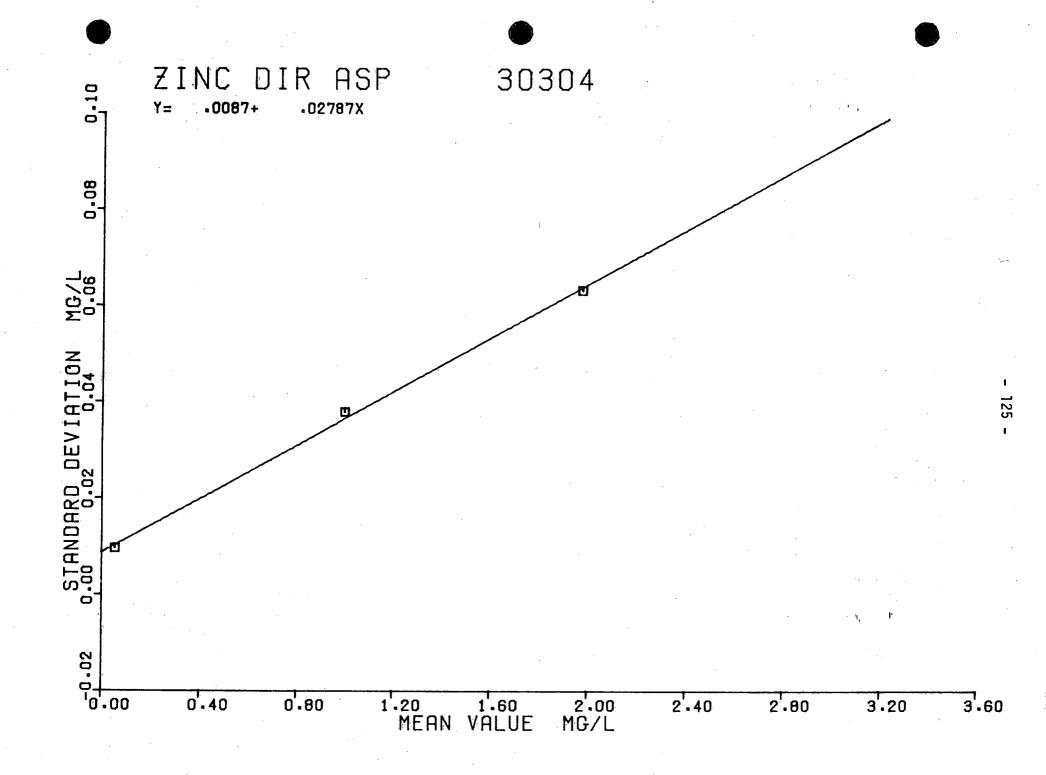
 $X = \text{concentration of} \quad Zinc , mg/L$

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, mg/L	Coefficient of Variation, percent
5	.05	18
5	1.0	4
5	2.0	3

10.3 The percent recoveries are104%, 110%, and 109% at concentration levels of .05, .91, and 1.8 mgZn/L respectively.

10.4 Detection Limit = 0.02 mg Zn/L



10. <u>Precision and Accuracy</u>

10.1 The precision of this method was determined on spiked and unspiked Lake Ontario waters at levels of .0023, .0028 , .03 , and .06 mg Zn/L to be respectively .001 , .0005 , .0023, and .003 mg/L, and may be expressed as follows:

 $S_{T} = 0.000564 + 0.075 X - 0.579 X^{2}$

where S_T = overall precision, mg/L and

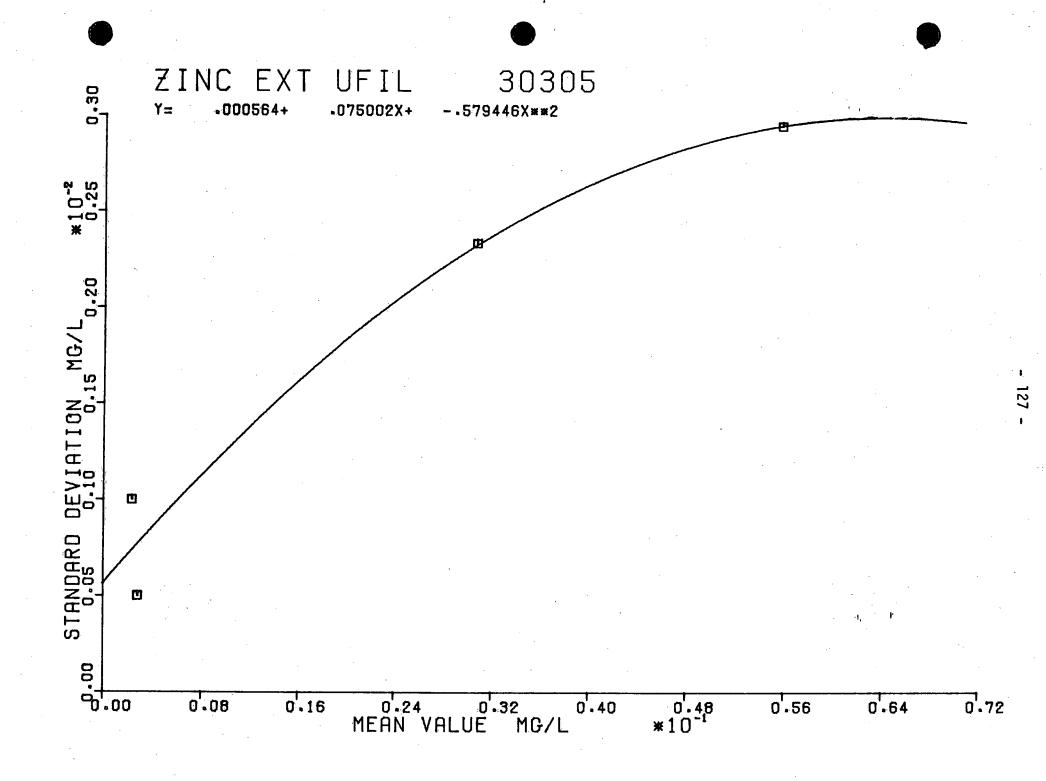
X = concentration of Zinc , mg/L

10.2 The precision may also be expressed in terms of the coefficient of variation as follows:

Number of Labs.	Mean, Mg/L	Coefficient of Variation, percent
5	.0023	42
5	.0028	18
5	.03	8
5	.06	5

10.3 The percent recoveries are 68%, 98%, and 94% at concentration levels of .004, .03, and 0.6 mg Zn/L respectively.

10.4 Detection Limit = 0.001 mg Zn/L



REFERENCES

ACS Committee on Environmental Involvement, 1980. Anal. Chem., <u>52</u>, 2242.

Analytical Methods Manual, 1979. Inland Waters Directorate, Water Quality Branch, Ottawa, Canada.

ASTM Standards on precision and accuracy for various applications, 1977. Standard D2777-77. Standard practice for determination of precision and bias of methods of committee D-19 on water.

Chau, A.S.Y. The role of standard reference materials in analytical quality assurance for environmental studies. WHO Bulletin. In press.

Chau, A.S.Y. and Cheam, V., 1978. Proposed quality control study designs for generating specification statements for W.Q.B. Methods Manual. Memorandum to Chief, Laboratory Operations Division.

Cheam, V., 1979. IRQC Studies No. 51-54. Summary report, July 1979. Summary of IRQC Studies No. 51-54 - Detection limit, precision and accuracy of the methods for trace metals. Cheam, V., 1979. IRQC Studies No. 55-56. Summary report, November 1979. Summary of IRQC Studies No. 55-56 - Detection limit, precision and accuracy of WQB methods for major cations, Arsenic, selenium and total P.

Cheam, V., 1980. IRQC Studies No. 60-61. Summary report, May 1980. Summary report on IRQC Studies No. 60-61 - Specification studies on anions, nutrients, alkalinity and mercury methods.

Cheam, V., 1980. IRQC Studies No. 62-63. Summary report, July 1980. Summary report on IRQC Studies No. 62-63 - Specification studies of WQB Methods on miscellaneous inorganic parameters.

Cheam, V., 1980. IRQC Studies No. 68-69. Summary report, September 1980. Summary report - Specification study on Lithium, Beryllium, Antimony, Boron, and silver methods.

Cheam, V., 1981. Specification Statements for major ions, nutrients, physical parameters, arsenic and mercury methods in water. Report to Head, QAMS.

Demayo, A. and Hunt, E., 1975. Naquadat Users Manual. Inland Waters Directorate, WQB, Ottawa, Canada.

15606

- 130 -

Grubbs, F.E., 1969. Procedures for detecting outlying observations in samples, Technometrics, 11(1), 1-21.

Grubbs, F.E., 1979. Personal Communcation.

्रद्ध

Howe, L., 1978. Result advisor of ASTM D-19. Personal Communication.

NAQUADAT Dictionary of Parameter Codes, 1981. Data and Instrumentation Section, Water Quality Branch, Environment Canada.

Smith, R., 1978. Water Analysis in South Africa, Interlaboratory Comparison Studies. Part II: COD, pH and Electrical Conductivity Analyses. Water SA, 4(1), 4-9.

Standard Methods for the examination of Water and Wastewater, 1975. American Public Health Association, Washington, D.C.

Uriano, G.A. and Gravatt, C.C., 1977. The role of reference materails and reference methods in chemical analysis, CRC Critical Reviews in Analytical Chemistry, 361.

