Interlaboratory Quality Control Study No. 5
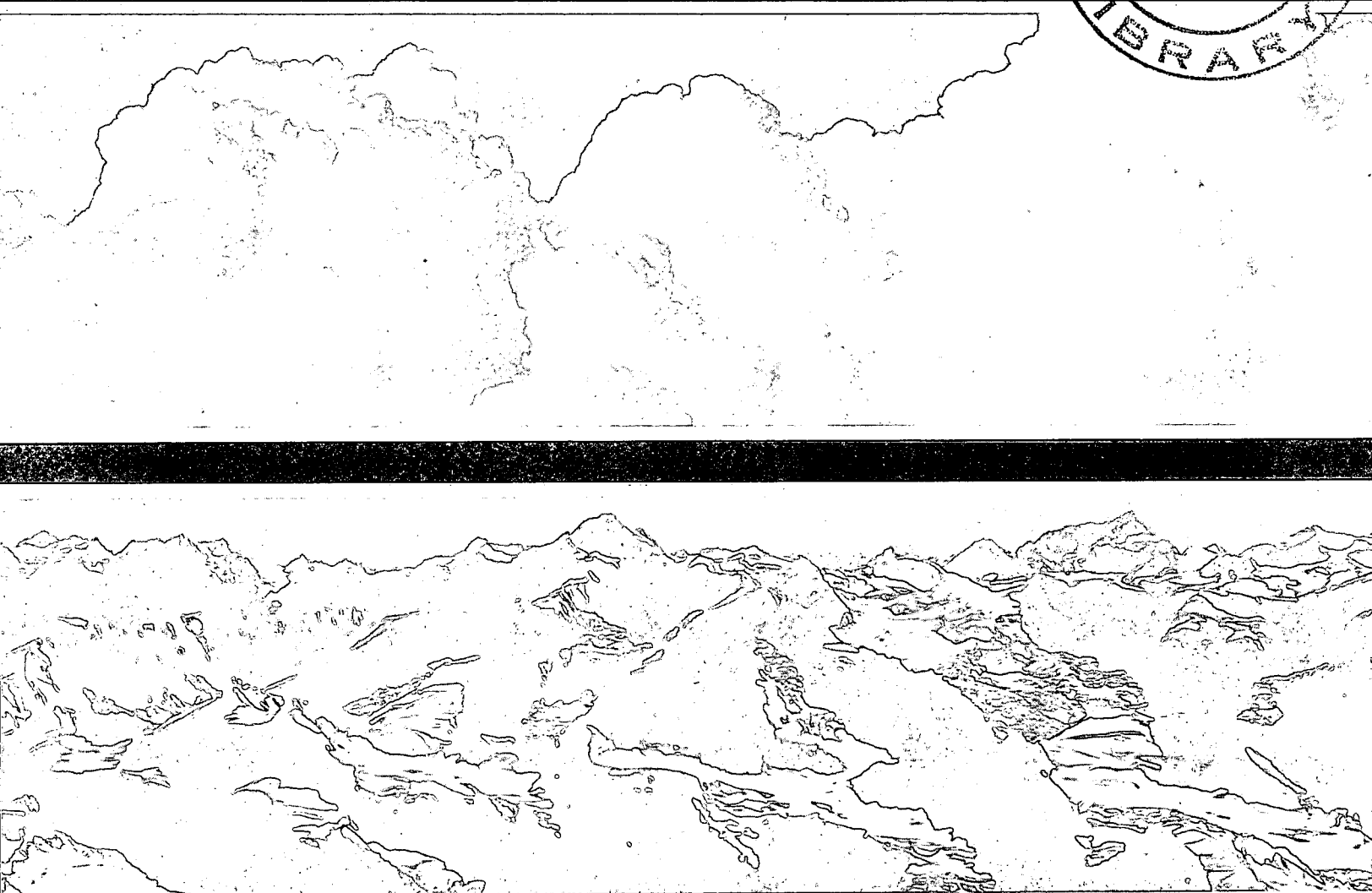
Chromium, Iron, Molybdenum and Vanadium

R. W. Wales and D. J. McGir

REPORT SERIES NO. 26

Interlaboratory Quality Control Study No. 5

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Summary

Samples containing known amounts of chromium, iron, molybdenum and vanadium were distributed to thirteen laboratories to be analyzed by the laboratories' usual methods. The majority of laboratories determined the metals by atomic absorption; in addition, iron was determined colorimetrically for comparison. Only a few participants were able to analyze all four metals, and in the case of molybdenum and vanadium the small number of results received made it difficult to come to firm conclusions about the reliability of the method. The precision for chromium was better than in a previous study. The results obtained for iron by atomic absorption with solvent extraction were good, while the colorimetric method was intermediate in precision and sensitivity between solvent extraction and direct aspiration using atomic absorption.

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INTRODUCTION

This study is the third of a series of three quality control studies on trace metal analysis, which have covered a total of 13 metals. This study covers chromium, iron, molybdenum and vanadium. As in previous studies, synthetic samples containing various concentrations of the metals were sent to participating laboratories to be analyzed by their usual test methods. A list of the participating laboratories is given in Appendix A.

Chromium was repeated in this study, having previously been determined in Study No. 3. This was done because the precision was rather poor previously at intermediate and lower levels of chromium, and we wished to determine if there had been any improvement since the previous study, and also to see if the cause of the trouble could be pinpointed.

In this study some additional questions were asked of participants in an attempt to obtain some refinement of the statistical data. Because atomic absorption results in a group of samples may be obtained partly by direct aspiration and partly by solvent extraction, participants were asked to indicate for each result which method was used.

Also, in the case of results which were reported as being below their detection limit, participants were asked to include the actual apparent reading in brackets after their reported value, i.e. < 0.005 (0.002). This was requested because the "less than" figures often present a problem in calculating means and standard deviations of samples whose true value is close to the detection limit, especially where different laboratories report different detection limits. It was agreed not to publish the figures in brackets; they were, however, used in the calculations, so a few of the statistics in the tables will be found to have been calculated from results which are not given in the tables.

Finally, participants were asked if they determined the parameters routinely or seldom. This was asked to observed if the inclusion of laboratories who are less experienced with a test would have any adverse effect on the statistics generated.

EXPERIMENTAL DESIGN

The samples used for this study were the same type as was used for the two previous studies on metals, namely synthetic samples sent in concentrated form to be diluted by a factor of 100 by the participant before analysis.

We departed from our usual procedure this time by using purchased stock solutions (Fisher Certified Reference Standards for Atomic Absorption) for the four metals instead of solutions prepared in the laboratory. It has been our experience that these solutions are generally reliable, and they were checked in the laboratory before use.

Samples of the test solutions in both concentrated and dilute form were kept in the laboratory for storage tests for a period of six months. In all cases except iron the decrease in the apparent concentration of the metal after six months was small (0-30%) in the case of the dilute solutions and even less (0-10%) in the case of the concentrates. In the case of iron the loss was also negligible in the concentrates but about 25-40% of the iron apparently disappeared in the dilute solutions. Since most of the determinations would have been done within a few weeks, the error due to storage loss would have been negligible.

Table I gives the amounts which the samples were designed to contain after dilution by the participants.

Table 1. Designed Concentration of Diluted Samples

Sample Number	Chromium (mg/l)	Iron (mg/l)	Molybdenum (mg/l)	Vanadium (mg/l)
1	.020	.007	.002	.000
2	.050	.055	.000	.015
3	.010	.080	.001	.002
4*	.075	.055	.015	.001

*Sample 4 contained 0.500 mg/l silica to check possible interference in the iron analysis.

DATA EVALUATION

Outliers were investigated by a statistical test using tables compiled by Grubbs [1] which have been repro-

duced by ASTM [2], and using a 1% significance level. This method was used in preference to the method of Dixon [3], which was used in previous studies, because of some problems which had been encountered with the latter method. Basically, the Grubbs method consists of expressing the distance from the mean to the outlier as a multiple, T_n, of the standard deviation, then determining from the tables if there is a greater than 1% chance that a result T_n standard deviations from the mean still belongs to the same population as the others and is merely an extreme example of the normal variation within the population. If the probability was less than 1%, the value was rejected as having come from another population, which means that it was obtained by a different (or erroneous) procedure. The standard deviation for this test is calculated using all results, and of course must be recalculated if one is rejected.

This procedure is based on the assumption of a normal distribution. Unfortunately, for many of the parameters in this study a small number of results were received with an abnormal distribution. In some cases where the effect of the distribution did not seem to be too great or where the presence or absence of outliers was quite obvious, the conclusions reached using the above procedure were used. In other cases, no calculations were done at all.

After rejection of outliers (which are indicated by an R in the tables), the mean, standard deviation, relative standard deviation, mean error and relative error were calculated for those samples for which the data were considered adequate. Relative standard deviation (also known as 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 added), and the relative error is the mean error expressed as a percent of the true value. Since most of the results were obtained by laboratories using the WQB (Water Quality Branch) methods [4] or equivalent methods, the statistics were calculated for the WQB methods only, and results obtained by other methods are entered below the statistical data in Tables II to VI. In the Tables and discussion that follow, the term "WQB method" is used to include the WQB methods and methods judged essentially equivalent. Results obtained by the WQB method were obtained by the procedure for "extractable" metal as defined in [4] unless otherwise stated. However in these synthetic samples the true values for extractable, total or dissolved metal should all be the same.

The "r" or "s" in the right-hand column of Tables II to VI indicates whether the laboratory reported that it determined the parameter in question routinely or seldom. The inclusion of results from laboratories who reported that they ran the tests seldom, does not appear to have had

an adverse effect on such statistics as mean error and standard deviation except in the case of chromium.

DISCUSSION OF RESULTS

Chromium

Comparing the results in Table II with the corresponding results from Study No. 3, it was observed that most of the laboratories who participated in both studies obtained somewhat better results this time. (Note that there is no correlation between the laboratory code numbers for this study and the code numbers for Study No. 3). This may indicate that the laboratories have reviewed and improved their procedures in view of the previous results.

It appears that direct aspiration yielded approximately the precision of which it is capable in both studies, but that in Study No. 3 the results obtained by extraction were not as precise as would have been expected. The precision for extraction seems better this time, although the statistics are unfortunately incomplete due to the small number of responses and the irregular distribution. Three of the four laboratories who used extraction in the present study obtained very good results. The poor overall results for chromium in Study No. 3 were apparently due to two factors: the problems some laboratories encountered with extraction, and the large number of laboratories that used direct aspiration only.

Among the laboratories who used methods other than the WQB method, Laboratory 501 obtained excellent results with a colorimetric method, and Laboratory 511 obtained moderately low results for "total" chromium. Laboratory 502 obtained results for hexavalent chromium which were reasonable in view of the higher detection limit for this method. The true values for both hexavalent and total chromium are the same as given for chromium in Table I.

Iron

The results from two laboratories for iron by atomic absorption were excluded from the calculations. Laboratory 510 apparently analyzed the concentrates in error, and Laboratory 513 had some substantial source of error which caused the results to be very high. In the case of Laboratory 513, when the T_n statistic was calculated it was found that in two samples it was slightly above the critical value and in two it was slightly below. It is evident, however, that the possibility of obtaining four values this far from the mean by chance is less than the possibility of obtaining one value this far from the mean, so it is reasonable to regard all four results as being statistical outliers.

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Table II. Chromium Analytical Results in mg/l

Sample No. Lab No.	A.A. by direct aspiration				A.A. by extraction				routine or seldom
	3	1	2	4	3	1	2	4	
503	—	—	—	—	0.010	0.020	0.054	0.077	r
504	<0.010	0.019	0.047	0.077	—	—	—	—	r
506	—	—	—	—	0.010	0.020	0.055	0.080	r
507	<0.020	<0.020	<0.020	0.100	0.001	<0.001	0.010	0.100	s
509	0.008	0.015	0.046	0.077	—	—	—	—	r
512	<0.02	0.02	0.05	0.08	0.010	0.020	0.050	0.080	r
515	0.00	0.05	0.08	0.05	—	—	—	—	s
true value	0.010	0.020	0.050	0.075	0.010	0.020	0.050	0.075	
mean	0.0054	0.0208	0.0466	0.0768				0.0843	
std. deviation	0.0050	0.0182	0.0248	0.0178				0.0106	
rel. std. dev.	92%	87%	53%	23%				13%	
mean error	-0.0046	0.0008	-0.0034	0.0018				0.0093	
relative error	-46%	4.0%	-6.8%	2.4%				12%	
	Other methods				Method				
501	0.010	0.020	0.050	0.075	colorimetric *				s
502	<0.01	<0.01	0.04	0.06	hexavalent †				s
511	0.010	0.010	0.040	0.050	total §				r

*"Take 100 ml of water to fumes of sulfuric acid. Oxidize the sample with potassium permanganate while boiling. Reduce excess permanganate with dropwise addition of hydrochloric acid. Develop color using diphenylcarbazide. Record absorbance on spectrophotometer."

†The method for hexavalent chromium from Standard Methods (5).

§Shaken sample is acidified and oxidized, evaporated to dryness, redissolved in acid and determined by atomic absorption.

Table III. Iron by Atomic Absorption Analytical Results in mg/l

Sample No. Lab No.	A.A. by direct aspiration				A.A. by extraction				routine or seldom
	1	2	4	3	1	2	4	3	
503	—	—	—	—	0.007	0.065	0.065	0.093	s
504	<0.04	0.05	0.05	0.07	—	—	—	—	r
506*	—	—	—	—	0.008	0.050	0.050	0.075	r
507	0.035	0.095	0.075	0.13	—	—	—	—	r
509	<0.02	0.05	0.04	0.06	—	—	—	—	r
510	0.71R	5.24R	5.25R	7.51R	—	—	—	—	r
512	<0.04	0.06	0.06	0.08	0.007	0.060	0.060	0.080	r
513	0.10R	0.20R	0.15R	0.25R	—	—	—	—	r
514	—	—	—	—	0.004	0.050	0.052	0.080	r
515	0.03	0.06	0.05	0.10	—	—	—	—	r
true value	0.007	0.055	0.055	0.080	0.007	0.055	0.055	0.080	
mean	0.0175	0.063	0.0550	0.088	0.0065	0.0563	0.0568	0.0821	
std. deviation	0.0173	0.0186	0.0132	0.0278	0.0017	0.0055	0.0058	0.0082	
rel. std. dev.	99%	29%	24%	32%	26%	10%	10%	10%	
mean error	0.0105	0.0080	0	0.008	-0.0005	0.0013	0.0018	0.0020	
relative error	150%	15%	0	10%	-7.1%	2.4%	3.3%	2.5%	
	Other methods				Method				
506	0.008	0.055	0.055	0.080	digested †				r
511	0.014	0.050	0.050	0.070	total §				s

* Extracted with Cupferron: other labs used APDC.

† HNO₃/HCl hot plate digestion (manual) then extraction with Cupferron/n-butyl acetate.

§ Shaken sample is acidified and oxidized, evaporated to dryness, redissolved in acid and determined by atomic absorption.

Laboratory 507 also obtained consistently high results by the TPTZ method; however, the error was not nearly as large, and only one result was rejected statistically.

Table IV. Iron by TPTZ Method Analytical Results in mg/1

| Lab No. | Sample No. | | | | routine or seldom |
	1	2	4	3	
502	0.05	0.06	0.06	0.10	r
503	0.009	0.060	0.064	0.081	r
504	0.02	0.06	0.06	0.08	r
507	0.03	0.095^R	0.09	0.14	r
511	0.01	0.05	0.05	0.08	r
515	0.01	0.06	0.05	0.07	r
true value	0.007	0.055	0.055	0.080	
mean	0.0215	0.0580	0.0623	0.0918	
std. deviation	0.0162	0.0045	0.0147	0.0255	
rel. std. dev.	75%	7.7%	24%	28%	
mean error	0.0145	0.0030	0.0073	0.0118	
relative error	207%	5.5%	13%	15%	

Other colorimetric methods					
501*	0.005	0.050	0.050	0.070	r

*"Take 100 ml of water to dryness to eliminate nitric acid. Extract iron present, after reduction with hydroxylamine hydrochloride, with amyl alcohol using bathophenanthroline. Record absorbance on spectrophotometer."

Only four laboratories determined iron by atomic absorption with solvent extraction, including one laboratory that used Cupferron and three that used APDC as the chelating agent. This is not a large enough sample to make a valid evaluation of the method; however, the results that were received indicate good precision and accuracy with no outliers among the four laboratories taken as a group.

Direct aspiration demonstrated lower sensitivity and precision, as would be expected. The TPTZ (2,4,6-tripyridyl-s-triazine) colorimetric method [(4)] has an intermediate sensitivity and precision. The means for iron by the TPTZ method in Table IV were high for all samples, but this was due to high results from one or two laboratories rather than to any general bias. Although more results were received for direct aspiration and for the TPTZ method than for solvent extraction, the number of results is still small enough that one moderately high result can make a substantial difference in the mean and standard deviation. It is hoped to repeat this parameter in the future with a larger number of participants.

Sample 4 was identical in iron content to sample 2 but contained 0.5 mg/l silica to check for possible interference. There was no significant difference by any method in either individual results or averages, and there was also no difference after six months' storage, indicating no interference at this level. A rather low level of silica was used in the expectation that a detectable interference might be encountered. It would be desirable to repeat this test at a higher silica level.

The two laboratories that performed some sort of digestion of the sample before analysis by atomic absorption obtained acceptable results, as did the laboratory that used the bathophenanthroline colorimetric method.

Molybdenum

Four laboratories used the WQB method (4) for molybdenum (extraction with benzoin α-oxime in n-butyl acetate after bromine oxidation), and the results in Table V show that reasonable precision and accuracy were obtained and that molybdenum levels of 1 microgram per liter and possibly less can be determined with reasonable certainty.

Table V. Molybdenum Analytical Results in mg/1

| Lab No. | Sample No. | | | | routine or seldom |
	2	3	1	4	
WQB Method:					
503	<0.001	0.001	0.001	0.012	s
506	0.000	0.001	0.002	0.025	r
507	<0.002	0.00065	0.001	0.0125	r
512	<0.0005	0.0010	0.0020	0.0150	s
true value	0.000	0.001	0.002	0.015	
mean	—	0.0009	0.0015	0.0161	
std. deviation	—	0.0002	0.0006	0.0061	
rel. std. dev.	—	19%	38%	38%	
mean error	—	−0.0001	−0.0005	0.0011	
rel. error	—	−8.8%	−25%	7.5%	
Other Methods:					
501*	<0.005	<0.005	<0.005	0.015	s
504†	<0.04	<0.04	<0.04	<0.04	s
509†	<0.1	0.2	<0.1	<0.1	s
514§	<0.003	0.015	<0.003	0.080	r

* "Take 100 ml of water to dryness with perchloric acid. Extract the thiocyanate complex formed with amyl acohol — carbon tetrachloride. Record absorbance on spectrophotometer."

† Direct aspiration only.

§ Extracted with A.P.D.C.

Two laboratories determined molybdenum in all samples by direct aspiration, which is quite inadequate both for these samples and for nearly all natural samples. Laboratory 514 used extraction with APDC instead of benzoin α-oxime; the results were only fair, and in fact two would have been rejected as outliers if these results had been analyzed along with those from the other four laboratories that used extraction. Laboratory 501 used a colorimetric method which gave good results and better

sensitivity than their quoted detection limit would indicate (based on results which were excluded from the table).

Vanadium

There were not enough useable results for vanadium to calculate any meaningful statistical data; however, the three laboratories who extracted their samples obtained generally good results. Two laboratories used direct aspiration which is inadequate for vanadium as for molybdenum.

Table VI. Vanadium Analytical Results in mg/1

Lab No.	Sample No.				routine or seldom
	1	4	3	2	
503	<0.001	0.001	0.002	0.015	s
504*	<0.04	<0.04	<0.04	<0.04	s
506	0.000	0.001	0.002	0.012	r
509*	<0.1	<0.1	<0.1	<0.1	s
512	<0.001	0.001	0.002	0.015	s
true value	0.000	0.001	0.002	0.015	

* Direct aspiration only.

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