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ANTIMONY-ARSENIC ORE CD-1 — A CERTIFIED REFERENCE MATERIAL

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MINERALS RESEARCH PROGRAM
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FOREWORD

The work described in this report contributes to the Canadian Certified Reference Materials Project (CCRMP). The CCRMP in turn contributes to the Mineral Technology Development Activity (Utilization Sub-Activity) of CANMET's Minerals Research Program by producing mineralogical and metallurgical reference materials (RM's) for use in industrial, commercial and government laboratories in Canada.

The CCRMP was initiated in the early seventies in response to a demand from such laboratories for RM's that were not then available. Many of these laboratories now willingly contribute analytical information which is ultimately used in the CCRMP to certify RM's.

Now that a relatively large number of reference ores and related materials have been made available, they are being used in a "feed-back" fashion to critically assess analytical methods that are essential for quality-control and research in Canadian enterprises.

R.L. Cunningham
Chief

AVANT-PROPOS

Le travail qui est décrit dans le présent rapport apporte une contribution au Programme canadien des matériaux de référence certifiés (CCRMP). De son côté, le CCRMP collabore aux travaux de l'Activité de la mise au point des techniques minérales (Sous-activité de l'utilisation) du Programme de recherche sur les minéraux de CANMET en normalisant des matériaux minéralogiques et métallurgiques pour les différents laboratoires industriels, commerciaux et gouvernementaux au Canada.

Le CCRMP a été créé au début des années '70 pour répondre à la demande formulée par les différents laboratoires qui voulaient de tels matériaux de référence qui n'étaient pas disponibles auparavant. Ainsi, plusieurs laboratoires effectuent maintenant des travaux analytiques et par la suite léguent volontairement les informations nécessaires au CCRMP pour certifier des matériaux de référence.

Maintenant qu'une quantité relativement abondante de minerais de référence et apparentés sont disponibles, on les utilise rétro-activement afin d'évaluer les méthodes analytiques employées par les compagnies canadiennes pour contrôler la qualité et faire de la recherche.

R.L. Cunningham
Chef

CANMET REPORT 77-63

ANTIMONY ORE CD-1:- A CERTIFIED REFERENCE MATERIAL

by

G.H. Faye*, W.S. Bowman** and R. Sutarno**

SYNOPSIS

As a facet of the Canadian Certified Reference Materials Project, an antimony ore, CD-1, has been prepared as a compositional reference material. Approximately 270 kg of raw ore was dry-ground to minus 74 μm, blended, tested for homogeneity by X-ray fluorescence and chemical methods, and bottled in 200-g units.

In a "free-choice" program for the certification of CD-1, 20 laboratories provided analytical results for antimony and arsenic on each of two bottles of the ore. A statistical treatment of the data yielded recommended values for the two constituents which are: antimony - 3.57% and arsenic - 0.66%.

Although CD-1 should be protected from unnecessary exposure to air, its overall bulk composition is not expected to change significantly through oxidation of sulphides during its expected lifetime of 5-10 years.

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Note: Major contributions to the certification of CD-1 were also made by other members of the staff of the Mineral Sciences Laboratories and by laboratories in many other organizations.

INTRODUCTION

This report describes the characterization and preparation of samples of antimony ore, CD-1 for use as a certified compositional reference material. The work is a facet of the Canadian Certified Reference Materials Project (CCRMP), to certify mainly materials that are representative of Canadian ore deposits, and have potential value in conventional analytical or earth sciences laboratories. Certified reference ores and related materials issued previously in the CCRMP are described in a catalogue that is available from the Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa, Canada[1].

CD-1 was chosen as a reference material because it contains significant concentrations of both antimony and arsenic, and thus should be especially useful in assessing methods in which there is potential interference between these elements.

An interlaboratory scheme was used to obtain analytical results for antimony and/or arsenic from 20 laboratories which used methods of their choice. For antimony, a large majority of laboratories used atomic absorption spectroscopy, whereas for arsenic, volumetric methods involving a separation by distillation were preferred.

NATURE AND PREPARATION OF CD-1

CD-1 was donated to the CCRMP in late 1974 and is from the Lake George Mine of Consolidated Durham Mines and Resources Limited at Prince William in New Brunswick. In approximate order of decreasing abundance, the following minerals are present in CD-1: quartz, mica, clay minerals, stibnite, pyrite, arsenopyrite, pyrrhotite, and traces of chalcopyrite and chalcostibnite. A detailed study of the Lake George antimony deposit has also revealed the presence of a suite of minor lead and copper sulphantimonides including: fuloppite, plagionite, tetrahedrite and bournonite[2]. The approximate chemical composition and a particle size analysis of CD-1 are given in Tables 1 and 2 respectively.

In late 1975, CD-1 was dry-ground, by ball-milling, to pass a minus 74 μm screen. The powdered material, weighing approximately 270 kg, was tumbled in a 570-ℓ conical blender for approximately nine hours. Upon opening the blender, the bulk material was systematically sampled and analyzed for antimony and arsenic by X-ray fluorescence and chemical methods. It was found to be sufficiently homogeneous to qualify for the interlaboratory certification program and was bottled in 200-g units.

TABLE 1

Approximate chemical composition of CD-1[a]

Constituent	wt %
Sb	3.57[b]
As	0.66[b]
Si	32.9
Al	5.5
Ca	1.4
Mg	0.6
Fe	2.8
Na	0.1
K	1.8
Pb	0.02
Cu	<0.01
S	3.1
Total C	0.2
Moisture (105°C)	0.2
L.O.I. (950°C)	4.0

[a] Except for Sb and As, results are those provided by the Chemical Laboratory of CANMET.

[b] Recommended values from Table 7.

TABLE 2

Particle size analysis (wet screen)

Mesh size (Tyler)	wt %
-200 +270	5.9
-270 +325	11.4
-325 +400	3.3
-400	76.0

INTERLABORATORY PROGRAM FOR CERTIFICATION OF CD-1

The laboratories that participated in the program for CD-1 are listed below in alphabetical order. Each of these was arbitrarily assigned a code number so that analytical results could be recorded while preserving the anonymity of the laboratory. The code numbers bear no relation to the alphabetical order of the laboratory name.

Participating Laboratories

Bondar-Clegg and Company Limited, Ottawa, Ontario.

Bondar-Clegg and Company Limited, Vancouver, British Columbia.

Canada Centre for Mineral and Energy Technology,
Mineral Sciences Laboratories (six independent analysts),
Ottawa, Ontario.

Chemex Labs Limited,
North Vancouver, British Columbia.

Cominco Limited,
Trail, British Columbia.

Geological Survey of Canada,
Central Laboratories and Administrative Services,
Ottawa, Ontario.

Hudson Bay Mining and Smelting Company Ltd.,
Flin Flon, Manitoba.

Inco Limited,
Analytical Services, Process Technology,
Copper Cliff, Ontario.

Lakefield Research of Canada, Limited,
Lakefield, Ontario.

Loring Laboratories Limited,
Calgary, Alberta.

Ministère des Richesses Naturelles,
Centre de Recherches Minérales,
Ste-Foy, Québec.

Ministry of Natural Resources,
Mineral Research Branch,
Toronto, Ontario.

Sherritt Gordon Mines Limited,
Research and Development Division,
Fort Saskatchewan, Alberta.

Thunder Bay Testing Limited,
Thunder Bay, Ontario.

X-Ray Assay Laboratories Limited,
Don Mills, Ontario.

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

The analytical results for antimony and arsenic in CD-1 are presented in Tables 3(a) and 3(b) respectively. Table 4 correlates these results with the methods used and gives information on variations of particular methods, including sample decomposition. Tables 5(a) and 5(b) give the mean values and coefficients of variation for each set of results. As indicated in Table 5, the means of several sets of results are outside the two-sigma limits and were not used in subsequent computations.

Analysis of variance

Because all sets of results for CD-1 contained five replicates for each of two bottles, a two-way ANOVA with nested design was used to examine the homogeneity between bottles, to estimate the grand mean, and to compute confidence limits[3]. The appropriate model is:

$$x_{ih\ell} = \mu + y_i + v_i + z_{ih\ell}$$

where:

$x_{ih\ell}$ is the ℓ^{th} result for bottle h in set i;

μ is the true value estimated by the grand mean $\bar{x}...$;

y_i is the discrepancy between the mean of the results from set i ($\bar{x}_{i..}$) and μ;

v_{ih} is the discrepancy between the mean of the results from bottle h in set i ($\bar{x}_{ih.}$) and $\bar{x}_{i..}$; and

$z_{ih\ell}$ is the discrepancy between $x_{ih\ell}$ and $\bar{x}_{ih.}$.

The variables y_i, v_{ih} and $z_{ih\ell}$ are normally distributed with means of zero and variances of ω^2, ψ^2, and σ^2, respectively. Assuming there are k sets, the ANOVA table on page 3 can be constructed.

Between-bottle homogeneity

The homogeneity between bottles was examined by testing the null hypothesis that $\psi^2=0$. The test statistic is given by S_2^2/S_1^2, and the values obtained for CD-1 are 2.6 and 1.3 for antimony and arsenic, respectively. The critical value for the F-distribution at 95% probability is 1.6. Thus the null hypothesis is rejected for antimony but accepted for arsenic.

It is possible to test the null hypothesis of no difference between bottle means for each set using the *t*-test at the 5% significance level. It can be seen from Table 5 that the null hypothesis is rejected for 5 of 23 sets for antimony and 4 of 23 sets for arsenic. These results of the *t*-tests are presented graphically in Figure 1. For each set, the difference between the means of the results for the two bottles is plotted against the corresponding mean of the results for both bottles. The vertical bar represents the 95% confidence interval of the former. If a bar intersects the abscissa, the null hypothesis is accepted, i.e., there is no evidence to suggest inhomogeneity between bottles for that set of results.

It can be concluded that bottle-to-bottle differences are insignificant with respect to arsenic, and significant but very small in the case of antimony. For most applications of CD-1 as a reference material, between-bottle inhomogeneity should not pose an analytical problem.

Analysis of Variance Table

Source of variance	Sums of squares	Degrees of freedom	Mean squares	Expected mean squares
Between sets	$10 \sum_{i}^{k} (\bar{x}_{i..} - \bar{x}...)^2$	k-1	S_3^2	$\sigma^2 + 5\psi^2 + 10\omega^2$
Between bottles within sets	$5 \sum_{i}^{k} \sum_{h}^{2} (\bar{x}_{ih.} - \bar{x}_{i..})^2$	k	S_2^2	$\sigma^2 + 5\psi^2$
Between analyses within bottles	$\sum_{i}^{k} \sum_{h}^{2} \sum_{\ell}^{5} (x_{ih\ell} - \bar{x}_{ih.})^2$	8k	S_1^2	σ^2
Total	$\sum_{i}^{k} \sum_{h}^{2} \sum_{\ell}^{5} (x_{ih\ell} - \bar{x}...)^2$	10k-1		

Between-set differences

The test of the null hypothesis that $\omega^2=0$ is given by the variance ratio S_3^2/S_2^2 (23.7 for Sb and 45.3 for As). Because the critical value of the F-distribution at 95% probability is 2.1, this null hypothesis is clearly rejected in both cases. In fact, ω^2 is by far the largest component of variance and accounts for most of the spread between the confidence limits for the mean as shown below.

Estimation of consensus values and their 95% confidence limits

The consensus value is estimated by $\bar{x}...$

$$\bar{x}... = \sum_{i}^{k} \sum_{h}^{2} \sum_{\ell}^{5} x_{ih\ell}/10k$$

The variance of $\bar{x}...$ is estimated by

$$V[\bar{x}...] = S_3^2/10k$$

The 95% confidence limits for the consensus values are then given by

$$\bar{x}... \pm \left[t_{.975\ (k-1)} \cdot \sqrt{V[\bar{x}...]} \right]$$

These and other statistics computed from the ANOVA table are presented in Table 6.

Certification factor

The certification factor[4] is a measure for evaluating the quality of reference materials issued by the CCRMP. It is computed from the following expression:

$$CF = 200 \left[t_{.975(k-1)} \cdot \sqrt{V[\bar{x}...]} \right] / \bar{x}.../\overline{cv}$$

where $\overline{cv}$ is the average of the within-set coefficients of variation and is given by:

$$cv = \sum_{i}^{k} cv_i/k$$

The critical value of CF is 4. If a selected constituent has a CF greater than 4, the reference material is considered to be of unacceptable quality with respect to that constituent. Because the factors for CD-1 are both less than 4 (Table 6) the confidence of the estimate of the consensus values is as good as the average precision obtained by the contributors of the analytical results. Thus, these consensus values are accepted as recommended values. They are listed along with their 95% confidence limits in Table 7.

Discussion

The level of average within-laboratory precision ($\overline{cv}$) for both antimony and arsenic (Table 6) in CD-1 is as expected, judging from the results of a large number of previous certifications by the CCRMP for many elements over a wide range of concentrations in ores and related materials. However, even though the certification factor of 2.5 for arsenic is acceptable, the overall spread (Table 6) of 4.6% for the arsenic results is somewhat higher than normal for certified elements at a concentration of 0.66%. In other words, certification factors are usually less than 2.5 at such a level of concentration. The spread of results for antimony is essentially normal for its concentration, judging from previous certifications.

Table 4 gives an outline of most of the analytical methods used by the collaborators, including information on decompositions and separations, where available. The means for all method sets are within two standard deviations of the recommended mean (Table 7); therefore, there seems to be no statistical or chemical basis for associating a bias to any particular method or decomposition.

Stability of CD-1

Because CD-1 contains only about 7% by weight of stibnite plus arsenopyrite, the only minerals potentially prone to oxidation, it is unlikely that the bulk composition of CD-1, stored in capped bottles, could change significantly

during its expected lifetime of 5-10 years as a reference material. This statement tends to be confirmed by the fact that a selected unopened bottle containing 200 g of CD-1, stored under ambient conditions, gained only 0.09% by weight during an 8-month test period.

Despite the expected "stability" of CD-1 it is recommended that bottles of this material should be opened for as short a time as possible for the taking of sub-samples, and that they be kept in a desiccator when not in use.

REFERENCES

1. Faye, G.H., "Certified and provisional reference materials available from the Canada Centre for Mineral and Energy Technology as of 1976"; CANMET Report 76-3; 25 pp; 1976.

2. Abbott, D. and Watson, D., "Ore mineralogy of the Lake George antimony deposit of Consolidated Durham Mines and Resources Ltd., Fredericton, New Brunswick"; New Brunswick Research and Productivity Council; Report No. M/75/16; May 1, 1974.

3. Brownlee, K.A., "Statistical theory and methodology in sciences"; John Wiley and Sons, Inc., New York; 1961.

4. Sutarno, R. and Faye, G.H., "A measure for assessing certified reference ores and related materials"; Talanta; v. 22, pp 676-681; 1975.

Table 3(a)

Antimony results for CD-1

ANTIMONY (WEIGHT PERCENT)

											SAMPLE WT, G
LAB- 1 (A.A.)	3.640	3.570	3.640	3.590	3.640	3.590	3.570	3.640	3.640	3.640	0.5
LAB- 2 (A.A.)	3.600	3.630	3.560	3.510	3.490	3.560	3.600	3.530	3.560	3.550	0.1-0.5
LAB- 3 (A.A.)	3.740	3.740	3.760	3.720	3.700	3.680	3.670	3.680	3.660	3.630	0.5
LAB- 4 (POLAR.)	3.580	3.620	3.610	3.600	3.580	3.600	3.660	3.590	3.660	3.740	0.25
LAB- 5 (XRF)	3.520	3.520	3.510	3.470	3.520	3.570	3.520	3.570	3.610	3.510	0.5
LAB- 6 (A.A.)	3.590	3.620	3.580	3.540	3.570	3.670	3.620	3.630	3.570	3.610	0.2-0.4
LAB- 8 (A.A.)	3.560	3.560	3.540	3.560	3.540	3.560	3.580	3.560	3.560	3.560	0.5
LAB- 9 (A.A.)	3.410	3.400	3.420	3.410	3.420	3.430	3.410	3.430	3.410	3.450	1.0
LAB-10 (A.A.)	3.600	3.450	3.520	3.480	3.560	3.520	3.600	3.590	3.470	3.530	0.1
LAB-11 (VOL.)	3.390	3.420	3.420	3.450	3.420	3.420	3.420	3.390	3.450	3.420	1.0
LAB-11 (VOL.)	3.540	3.510	3.520	3.480	3.510	3.540	3.510	3.490	3.490	3.510	2.0
LAB-12 (A.A.)	3.300	3.350	3.300	3.300	3.350	3.320	3.360	3.350	3.320	3.350	0.25
LAB-12 (VOL.)	3.310	3.400	3.340	3.310	3.250	3.260	3.260	3.340	3.340	3.310	1.0
LAB-13 (A.A.)	3.590	3.590	3.600	3.630	3.550	3.620	3.630	3.660	3.670	3.620	1.0
LAB-14 (VOL.)	3.400	3.470	3.530	3.430	3.450	3.480	3.510	3.480	3.440	3.410	1.0
LAB-15 (A.A.)	3.590	3.620	3.650	3.600	3.580	3.550	3.520	3.530	3.530	3.580	0.5
LAB-16 (A.A.)	3.720	3.760	3.720	3.720	3.690	3.720	3.680	3.640	3.720	3.680	0.1
LAB-17 (A.A.)	3.570	3.590	3.590	3.590	3.590	3.590	3.590	3.580	3.570	3.580	1.0
LAB-18 (A.A.-1)	3.580	3.640	3.640	3.600	3.600	3.600	3.640	3.600	3.600	3.600	0.5
LAB-18 (A.A.-2)	3.580	3.600	3.600	3.600	3.600	3.600	3.600	3.620	3.620	3.620	0.5
LAB-18 (COLOR.)	3.630	3.630	3.590	3.610	3.610	3.650	3.610	3.640	3.610	3.590	0.5
LAB-19 (A.A.)	3.520	3.526	3.506	3.518	3.485	3.512	3.513	3.476	3.479	3.488	0.5
LAB-20 (XRF)	3.590	3.520	3.650	3.640	3.580	3.670	3.550	3.620	3.620	3.620	0.2

Table 3(b)

Arsenic results for CD-1

ARSENIC (WEIGHT PERCENT)

											SAMPLE WT, G
LAB- 1	(VOL.)	.650	.670	.670	.670	.670	.670	.670	.670	.670	.670	1.0
LAB- 2	(COLOR.)	.633	.633	.631	.619	.618	.636	.642	.634	.613	.636	0.5-1.5
LAB- 3	(A.A.)	.640	.640	.660	.640	.660	.660	.640	.660	.660	.660	0.5
LAB- 3	(VOL.)	.610	.690	.670	.710	.710	.650	.710	.740	.710	.710	2.0
LAB- 4	(POLAR.)	.610	.600	.609	.619	.633	.608	.598	.598	.596	.572	0.25
LAB- 4	(AMP.)	.628	.639	.628	.645	.645	.639	.636	.635	.644	.644	0.25
LAB- 5	(XRF)	.597	.613	.614	.598	.614	.624	.608	.604	.598	.600	5 *
LAB- 6	(COLOR.)	.676	.690	.693	.667	.669	.664	.666	.697	.689	.665	0.5-2.0
LAB- 7	(COLOR.)	.687	.690	.682	.685	.685	.682	.680	.682	.680	.682	0.2
LAB- 8	(VOL.)	.630	.630	.630	.650	.620	.620	.630	.640	.630	.650	1.0
LAB- 9	(VOL.)	.652	.674	.654	.646	.671	.654	.653	.656	.665	.675	2.0
LAB-10	(A.A.)	.620	.590	.610	.560	.590	.560	.620	.610	.570	.590	0.1
LAB-11	(VOL.)	.690	.690	.700	.680	.690	.700	.690	.680	.700	.680	1.0
LAB-11	(VOL.)	.710	.710	.700	.700	.700	.700	.700	.690	.700	.700	1.0
LAB-12	(VOL.)	.663	.656	.663	.655	.672	.670	.684	.672	.679	.679	0.5
LAB-13	(VOL.)	.705	.696	.694	.688	.696	.703	.699	.697	.702	.699	2.5
LAB-14	(VOL.)	.561	.578	.566	.572	.564	.572	.568	.560	.577	.567	1.0
LAB-15	(VOL.)	.697	.736	.736	.736	.697	.697	.736	.736	.697	.736	0.5
LAB-15	(COLOR.)	.673	.655	.655	.663	.650	.660	.655	.650	.678	.655	1.0
LAB-16	(COLOR.)	.710	.660	.630	.660	.650	.680	.700	.650	.690	.700	0.1
LAB-17	(VOL.)	.694	.686	.692	.690	.686	.692	.688	.694	.690	.690	0.5
LAB-19	(VOL.)	.693	.701	.683	.687	.667	.705	.695	.700	.699	.702	2.0
LAB-20	(XRF)	.650	.660	.660	.650	.670	.650	.650	.650	.650	.650	8 *

*sample pelletized

Table 4

Outline of analytical methods (excluding x.r.f.)

	Decomposition & sample treatment	No. of laboratories	No. of results	Mean, wt %
Antimony				
Atomic absorption	Na_2O_2 fusion or sinter, cake dissolved in dilute HCl (some including tartaric acid).	4	40 (excluding 20 outliers)	3.60
	HNO_3 + HCl, some with additions of salts such as $(NH_4)_2S_2O_8$, KCl, tartaric acid, or prior treatment with Br_2 in CCl_4.	6	60	3.59
	HNO_3 + HF.	1	10	3.42
	$K_2S_2O_7$ fusion, cake dissolved in 6N HCl.	1	10	3.71
	* HNO_3 + H_2SO_4 + HF, fumed to SO_3, diluted with tartaric acid, insol. fused with Na_2CO_3 and added to above.	1	10	3.60
	HCl + $KClO_4$, diluted with tartaric acid.	1	10	3.50
Titrimetric	Na_2O_2 fusion, cake dissolved in HCl, As removed with H_2S, acidity adjusted, sample titrated iodometrically.	2	30	3.46
Polarographic	Fumed with $KHSO_4$ + H_2SO_4 + hydrazine, diluted with concentrated NaCl soln.	1	10	3.62
Absorptiometric	* as above	1	10	3.62
Atomic absorption	$HClO_4$, dilution with water.	1	10	0.65
	HNO_3 + HCl.	1	10	0.59
Titrimetric	HNO_3 + $KClO_3$, diluted with HCl, As(III) distilled and titrated with I_2.	5	60 (excluding 10 outliers)	0.68
	HNO_3 + HCl + H_2SO_4, fumed to SO_3, reduce with H_2PO_3, diluted with HCl, As(III) distilled and titrated with I_2.	1	10	0.69
	Unknown decomp. As(III) distilled and titrated with I_2.	1	10	0.69
	HNO_3 + H_2SO_4, As° ppt'd with $SnCl_2$ + H_2PO_3, As° dissolved and titrated iodometrically with arsenite.	1	10	0.63
	$KHSO_4$ + H_2SO_4, diluted with HCl, As(III) distilled and titrated amperometrically with $KBrO_3$.	1	10	0.64
	$K_2S_2O_7$ + H_2SO_4, diluted with HCl, As(III) distilled and titrated with $KBrO_3$.	1	10	0.72
	Na_2O_2 + Na_2CO_3 fusion, cake dissolved in H_2SO_4, As(III) distilled and titrated with I_2.	1	10	0.70
Polarographic	$KHSO_4$ + H_2SO_4, As° ppt'd with hypophosphite in HCl, filtered, dissolved in HNO_3, reduced to As(III) in HCl.	1	10	0.60
Absorptiometric	Various oxidizing acid mixtures, distillation of As(III) (or extn) absorptiometric detn as molybdenum blue complex.	4	40	0.66
	KOH fusion, cake dissolved in HCl, As distilled as arsine, absorptiometric detn as diethyldithiocarbamate complex.	1	10	0.67

Table 5(a)

Laboratory means, coefficients of variation, and summary of t-test on between-bottle antimony results for CD-1

		BOTTLE 1			BOTTLE 2			NULL HYPOTH.	OVERALL			
		N	MEAN	ST.DEV.	N	MEAN	ST.DEV.		N	MEAN	ST.DEV.	C.V.(%)
LAB- 1	(A.A.)	5	3.6160	.0336	5	3.6160	.0336	A	10	3.6160	.0317	.88
LAB- 2	(A.A.)	5	3.5580	.0589	5	3.5600	.0255	A	10	3.5590	.0428	1.20
LAB- 3	(A.A.)	5	3.7320	.0228	5	3.6640	.0207	REJECT	10	3.6980	.0413	1.12
LAB- 4	(POLAR.)	5	3.5980	.0179	5	3.6500	.0600	A	10	3.6240	.0499	1.38
LAB- 5	(XRF)	5	3.5080	.0217	5	3.5560	.0410	REJECT	10	3.5320	.0399	1.13
LAB- 6	(A.A.)	5	3.5800	.0292	5	3.6200	.0361	A	10	3.6000	.0374	1.04
LAB- 8	(A.A.)	5	3.5520	.0110	5	3.5640	.0089	A	10	3.5580	.0114	.32
LAB- 9	(A.A.)	5	3.4120	.0084	5	3.4260	.0167	A	10	3.4190	.0145	.42
LAB-10	(A.A.)	5	3.5220	.0602	5	3.5420	.0536	A	10	3.5320	.0547	1.55
LAB-11	(VOL.)	5	3.4200	.0212	5	3.4200	.0212	A	10	3.4200	.0200	.58
LAB-11	(VOL.)	5	3.5120	.0217	5	3.5080	.0205	A	10	3.5100	.0200	.57
LAB-12	(A.A.)	5	3.3200	.0274	5	3.3400	.0187	A	10	3.3300*	.0245	.74
LAB-12	(VOL.)	5	3.3220	.0545	5	3.3020	.0402	A	10	3.3120*	.0464	1.40
LAB-13	(A.A.)	5	3.5920	.0286	5	3.6400	.0235	REJECT	10	3.6160	.0353	.98
LAB-14	(VOL.)	5	3.4560	.0488	5	3.4640	.0391	A	10	3.4600	.0419	1.21
LAB-15	(A.A.)	5	3.6080	.0277	5	3.5420	.0239	REJECT	10	3.5750	.0425	1.19
LAB-16	(A.A.)	5	3.7220	.0249	5	3.6880	.0335	A	10	3.7050	.0331	.89
LAB-17	(A.A.)	5	3.5860	.0089	5	3.5820	.0084	A	10	3.5840	.0084	.24
LAB-18	(A.A.-1)	5	3.6120	.0268	5	3.6080	.0179	A	10	3.6100	.0216	.60
LAB-18	(A.A.-2)	5	3.5960	.0089	5	3.6120	.0110	REJECT	10	3.6040	.0126	.35
LAB-18	(COLOR.)	5	3.6140	.0167	5	3.6200	.0245	A	10	3.6170	.0200	.55
LAB-19	(A.A.)	5	3.5110	.0162	5	3.4936	.0178	A	10	3.5023	.0185	.53
LAB-20	(XRF)	5	3.5960	.0522	5	3.6160	.0428	A	10	3.6060	.0462	1.28
								TOTAL	230	3.5474	.1053	2.97

* outside two-sigma limits of 3.3367 to 3.7580, not used in computations.

Table 5(b)

Laboratory means, coefficients of variation and summary of t-test on between-bottle arsenic results for CD-1

		BOTTLE 1			BOTTLE 2			NULL HYPOTH.	OVERALL			
		N	MEAN	ST.DEV.	N	MEAN	ST.DEV.		N	MEAN	ST.DEV.	C.V.(%)
LAB- 1	(VOL.)	5	.6660	.0089	5	.6700	0.0000	A	10	.6680	.0063	.95
LAB- 2	(COLOR.)	5	.6268	.0076	5	.6322	.0111	A	10	.6295	.0094	1.50
LAB- 3	(A.A.)	5	.6480	.0110	5	.6560	.0089	A	10	.6520	.0103	1.58
LAB- 3	(VOL.)	5	.6780	.0415	5	.7040	.0329	A	10	.6910	.0378	5.48
LAB- 4	(POLAR.)	5	.6142	.0125	5	.5944	.0134	REJECT	10	.6043	.0160	2.66
LAB- 4	(AMP.)	5	.6370	.0086	5	.6396	.0043	A	10	.6383	.0065	1.02
LAB- 5	(XRF)	5	.6072	.0089	5	.6068	.0104	A	10	.6070	.0091	1.50
LAB- 6	(COLOR.)	5	.6790	.0119	5	.6762	.0156	A	10	.6776	.0132	1.95
LAB- 7	(COLOR.)	5	.6858	.0029	5	.6812	.0011	REJECT	10	.6835	.0032	.47
LAB- 8	(VOL.)	5	.6320	.0110	5	.6340	.0114	A	10	.6330	.0106	1.67
LAB- 9	(VOL.)	5	.6594	.0124	5	.6606	.0093	A	10	.6600	.0103	1.57
LAB-10	(A.A.)	5	.5940	.0230	5	.5900	.0255	A	10	.5920	.0230	3.88
LAB-11	(VOL.)	5	.6900	.0071	5	.6900	.0100	A	10	.6900	.0082	1.18
LAB-11	(VOL.)	5	.7040	.0055	5	.6980	.0045	A	10	.7010	.0057	.81
LAB-12	(VOL.)	5	.6618	.0068	5	.6768	.0057	REJECT	10	.6693	.0099	1.48
LAB-13	(VOL.)	5	.6958	.0061	5	.7000	.0024	A	10	.6979	.0049	.70
LAB-14	(VOL.)	5	.5682	.0068	5	.5688	.0063	A	10	.5685 *	.0062	1.09
LAB-15	(VOL.)	5	.7204	.0214	5	.7204	.0214	A	10	.7204	.0201	2.80
LAB-15	(COLOR.)	5	.6592	.0090	5	.6596	.0109	A	10	.6594	.0094	1.43
LAB-16	(COLOR.)	5	.6620	.0295	5	.6840	.0207	A	10	.6730	.0267	3.97
LAB-17	(VOL.)	5	.6896	.0036	5	.6908	.0023	A	10	.6902	.0029	.42
LAB-19	(VOL.)	5	.6862	.0127	5	.7002	.0037	REJECT	10	.6932	.0115	1.66
LAB-20	(XRF)	5	.6580	.0084	5	.6500	.0000	A	10	.6540	.0070	1.07
								TOTAL	230	.6588	.0403	6.11

* outside two-sigma limits of 0.5783 to 0.7393, not used in computations.

Table 6

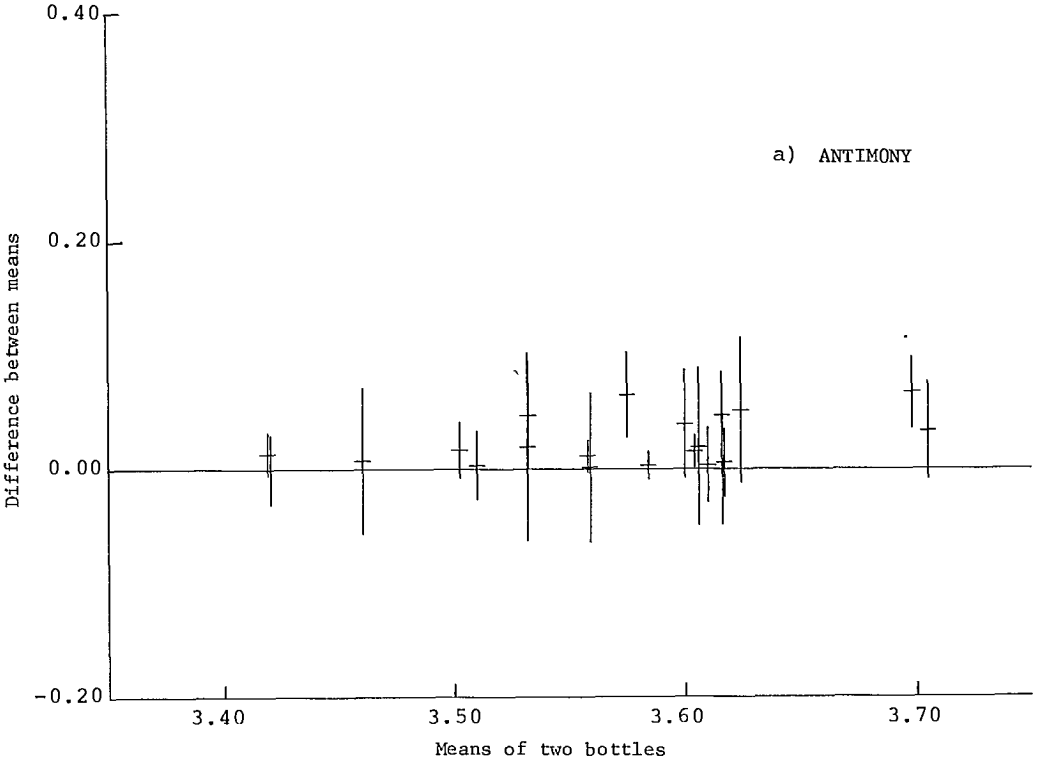
Estimation of statistical parameters for CD-1 (after rejection of outliers)

Element	No. of Labs	No. of sets	Total no. of results	Median, %	Mean, %	95% confidence limits for the mean		Spread, %	Av. within-lab cv, %	Certification factor
						Low, %	High, %			
Antimony	18	21	210	3.580	3.569	3.534	3.604	1.96	0.86	2.3
Arsenic	18	22	220	0.667	0.663	0.648	0.678	4.56	1.81	2.5

Table 7

Recommended values for CD-1

	Antimony	Arsenic
Recommended value, %	3.57	0.66
95% Confidence limits		
Low, %	3.53	0.65
High, %	3.60	0.68



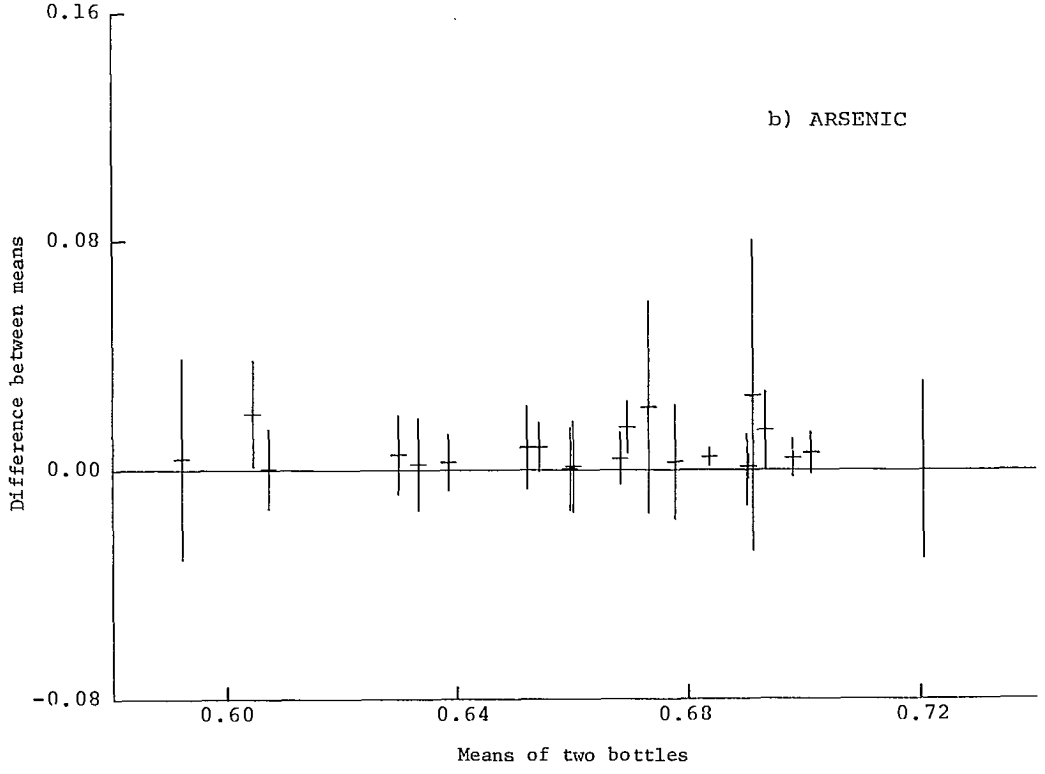


Figure 1. Degree of homogeneity of antimony and arsenic in CD-1. Vertical bars represent 95% confidence interval for the difference between the means of two bottles for each laboratory.