WRC WATER RESEARCH CENTRE

COLLABORATIVE ANALYSIS OF SEWAGE SLUDGE
(EP 1343C)

Final Contract Report to the Department of the Environment

R D Davis and C H Carlton-Smith

February 1981

41-M

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WRC ENVIRONMENTAL PROTECTION
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SUMMARY

Concentrations of potentially toxic elements in sewage sludges, and soils receiving sludge, are monitored by Water Authorities to prevent addition of excess amounts of metals to agricultural land. Much of the error in estimating the concentrations of metals in these materials is probably incurred in sampling but it is important to know the extent of analytical error and to identify methods which give the most accurate results. The WRC has therefore undertaken an inter-laboratory study for the DOE to compare the results of determinations of metals made by different laboratories on prepared samples of sewage sludges and soil. The study has involved more than one hundred laboratories, of which ninety have submitted results. The results have shown that the accuracy of determinations of Cd, Cu, Ni, Pb and Zn in sludges was usually acceptable (MPD $< \pm 15\%$) but determinations of Cd and Ni at the lower concentrations of interest proved difficult. Determinations of Cr in both sludges and soils and determinations of all metals in soils were subject to comparatively high errors (MPD $> \pm 15\%$). Digestion procedures which used sulphuric acid produced anomalous results for Pb and Cr. Dry ashing was associated with comparatively high errors of precision. There was little difference between the other wet digestion methods tested except that digestion with a mixture of nitric and perchloric acid recovered more metals (except Cu) from the soil sample than the other procedures. The results suggested that adequate determinations of metals (except Cr) in sludge can be made by procedures involving wet digestion (without sulphuric acid) followed by atomic absorption spectrophotometry. More work is needed to improve methods for the determination of Cr and low levels of Cd and Ni on sludges, and of all elements in soils. This is of importance if concentrations of metals in soils are used to monitor applications of sludge to agricultural land. A comparison of methods for determining extractable Cu, Ni and Zn in soil showed that an EDTA method was substantially more accurate than an acetic acid method. Limited results were obtained for the part of the exercise concerned with Mo, Hg, As, Se, F and B. These elements are subject to guidelines where sludge is used on land and further work is clearly needed on methods for their determination in both sludges and soils.

CONTENTS

1. INTRODUCTION

Sewage sludge results from the separation and concentration of much of the polluting waste material from sewage. Concentrations of metals, and sometimes other potentially toxic elements, in sludge are monitored by Water Authorities on a routine basis to avoid contamination problems in sludge treatment and disposal and to comply with guidelines[1] for the utilisation of sludge on land, which is now the principal disposal route for UK sludge. In this connection, concentrations of metals in soils are also of relevance.

Much of the error in estimating concentrations of metals in sludges and soil is probably incurred in sampling but it is important to know the extent of analytical error and to identify methods which give the most accurate results in terms of precision and bias. The WRC has therefore undertaken an inter-laboratory study for the Department of the Environment to compare the results of metal determinations made by different laboratories on prepared samples of sewage sludges and soil. Instructions and samples (3 sludges, 1 soil, 1 aqueous solution) were distributed to just over one hundred laboratories, of which ninety have submitted results. The purpose of the exercise was to review the adequacy (in terms of precision and bias) of current methods of analysis as a preliminary stage in the development of recommended methods.

2. MATERIALS AND METHODS

2.1. SAMPLES

2.1.1. Sample selection

Samples selected for the inter-laboratory analysis were known to be representative of the sludges and soils which laboratories are required to analyse on a routine basis in connection with the utilisation of sludge on agricultural land. Previous inter-laboratory exercises have sometimes been criticised because the samples tested were unrepresentative, containing, for instance, unusually high concentrations of metals. The samples chosen were as follows:

A. Crude sludge treated with lime and copperas, from East Hyde sewage treatment works near Luton.

B. Anaerobically digested sludge, from Rye Meads sewage treatment works.

C. Crude sludge treated with polyelectrolyte, from Sandy sewage treatment works.

D. Soil (sandy loam) from Great Billing, near Northampton.

E. Aqueous solution (5% concentrated nitric acid) containing cadmium, chromium, copper, nickel, lead and zinc.

The three sludges used are currently disposed of by utilisation on agricultural land. Samples A and B had concentrations of metals near to the median values associated with sludges in England and Wales, whilst sample C was of "domestic sludge" and contained lower concentrations of metals to provide a good test of analytical methods. Sample A was treated with lime and copperas during its production and the results for this sample would show up any particular problems associated with the high concentrations of calcium and iron found in this kind of sludge. Sample D was of "background" (uncontaminated) soil. This had the disadvantage that the concentrations of metals it contained were low but it would be difficult to isolate any analytical problems particularly associated with soil from results obtained with sludge-treated soil. Also, 'background' soils are usually sampled and analysed for metals before sludging operations begin. The aqueous sample (E) contained concentrations of cadmium, chromium, copper, nickel, lead and zinc within the ranges likely to occur in digests of sludge. Results for sample E would be free of errors associated with digestion procedures and matrix effects which would permit estimation of the extent of errors from these sources in the other samples. Results for sample E would also act as a check against laboratories' standard solutions.

2.1.2. Sample preparation

An essential part of the exercise was to ensure that the bulked samples were as homogeneous as possible before sub-samples were taken and distributed. Otherwise, it would be necessary to separate analytical errors from errors associated with inadequate homogenisation of the original samples. Apart from being grossly non-uniform, sludge, particularly crude sludge, is difficult to homogenise because of its fibrous content. Preliminary grinding of the samples was done by the Department of Industry, Warren Spring Laboratory. Subsequently, the samples were sieved to pass 2 mm at the WRC, mixed, and tested for homogeneity by taking sub-samples for analysis by atomic absorption spectrophotometry (AAS) for 2 elements (Cu, Zn) and neutron activation analysis (NAA) for 22 elements (Na, K, Sc, Cr, Mn, Fe, Co, Ga, As, Rb, Sn, Sb, Cs, Ba, La, Ce, Sm, Eu, Gd, Hf, Ta, and Th).

Coefficients of variation associated with Cu and Zn analyses done at this stage were in the range 3.1% (Zn in sample A) to 7.1% (Zn in sample C). Detailed results are shown in Appendix A. More grinding was done and the samples sieved to pass 0.5 mm and mixed. At this stage 20 sub-samples of each bulked sample were taken and analysed for Cd, Cr, Cu, Ni, Pb and Zn by AAS following wet digestion, and for a further 22 elements in 8 sub-samples by NAA. Results from the AAS analysis (Appendix A) showed that coefficients of variation were now <4% for Cd and Zn, and <5% for Cu and Ni. Comparatively high values were obtained for Cr in soil D (8.70%) and for Pb in all samples (4.80-8.98%). Analytical errors associated with analyses of this type at the WRC are of the order of 2-5% for Cd, Cr, Cu, Ni and Zn and about 7% for Pb. Despite the higher values for Cr and Pb, it now seemed that sample heterogeneity accounted for <2% of the errors for each sample and this finding was supported by the NAA results. Sub-samples were taken for distribution to participating laboratories.

2.2. COLLABORATING LABORATORIES

Results were received from the following laboratories:

Anglian Water Authority	16
North West Water Authority	16
Northumbrian Water Authority	3
Severn-Trent Water Authority	3
Southern Water Authority	2
South West Water Authority	2
Thames Water Authority	26
Welsh Water Authority	1
Wessex Water Authority	1
Yorkshire Water Authority	4
Scottish Regional Councils	11
Ministry of Agriculture, Fisheries and Food	3
Department of Industry	1
Water Research Centre	1
Total	90

To preserve anonymity, each laboratory is represented in the results by a code number

2.3. DESIGN OF THE EXPERIMENT

2.3.1. Mandatory part

Detailed instructions were distributed to participating laboratories together with sheets on which to insert results. A set of the instructions sent to collaborating laboratories is included as Appendix B of this report. The instructions asked for the minimum amount of work by laboratories, in terms of sample numbers, which was compatible with the statistical requirements of the exercise. It was felt that a larger work-load might dissuade many laboratories from taking part, and that this would be regrettable. Laboratories were asked to determine 'total' concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the three samples of sludge, the soil sample, and the aqueous solution by means of duplicate determinations made on five occasions over a period of three to six weeks. Laboratories were also asked to determine 'extractable' concentrations of Cu, Ni and Zn in the soil sample on the same basis of duplicate determinations on five occasions. No methods were specified for 'total' metals but laboratories were asked to use two methods of the Standing Committee of Analysts (SCA) for the determination of extractable metals in the soil sample. Appendix D describes the methods used by laboratories for determining 'total' metals. The SCA methods for extractable metals are in Appendix K and laboratories' own methods are in Appendix L.

2.3.2. Voluntary part

Apart from the metals in the mandatory part of the exercise, it is recommended that five other elements (Mo, Hg, As, Se and B) should be monitored where sludge is used on land and another element (F) is also of interest in this connection. Laboratories were asked to determine 'total' concentrations of these elements in the three sludges and the soil by their currently used methods. For this part of the exercise, laboratories were asked to do five replicate determinations on a single occasion in the 3-6 week period.

3. RESULTS

3.1. GENERAL

Statistics relating to individual laboratory means are shown in the appendices, and averages for all laboratories are presented below in a series of summary tables, one for each element. There are also summary tables of

statistics relating to the main methods used by laboratories to determine "total" concentrations of metals. The distribution of populations of laboratory means for each element is described in the appendices by graphs and tables of statistics based on grouped data. Included below are cumulative distribution diagrams of laboratory accuracy for each element, averaged over all samples.

Statistical methods used in the analysis of results are described in Appendix C. Errors are considered under two headings, random errors (precision) and systematic errors (bias). The terms precision and bias are discussed in detail in WRC Technical Report TR 66[2]. The summary tables of results in the appendices show three variables: CV_t%, D% and MPD%. CV_t% is a measure of the total random error or precision associated with each individual result from a laboratory. It is composed of errors arising within and between batches of analyses, significant between-batch error ($P = <0.05$) being indicated by an asterisk. D% is a measure of bias and shows the deviation of a laboratory's mean result from the estimated "true" or "correct" value. In this report, the "true" value is an estimate based on the average of the means of all the results received, but excluding outliers on the basis described in Appendix C. MPD% is a measure of accuracy combining both precision and bias; it is the maximum probable deviation that a laboratory mean might reach with 95% confidence.

The summary tables below of results for all laboratories include overall average values of the mean and standard deviation together with the range and number of laboratories included for various statistics. These include laboratory mean and CV_t%, D% and MPD% described above together with extra precision statistics associated with the extent of within-batch and between-batch errors and the incidence of a significant between-batch effect. An important observation on the results of the exercise is that the figures quoted for accuracy relate to determinations performed in duplicate on five occasions. Samples for routine analysis usually receive less rigorous treatment than this. The number of mean values (i.e. laboratories) included for each element and sample varied because not all laboratories were able to complete the full programme of analysis. Usually, no more than two mean values were excluded as outliers in the calculation of the "true value" except in the special cases of Pb, and Cd in sample D (see sections 3.2.1.5. and 3.2.1.1. respectively). Overall deviation (±D%) was estimated by averaging the absolute deviation of individual laboratory means, i.e., disregarding the sign, otherwise the overall

deviation would be zero since the "true" value was a mean of all results. This is also true for overall values of maximum possible deviation (±MPD%). However, in the tables summarising the accuracy of digestion procedures the direction of deviation was taken into account to see whether individual procedures were associated with either positive or negative deviation. In these tables D% is a true measure of bias.

3.2. MANDATORY PART

3.2.1. "Total" metals in sludges and soil

Methods used by laboratories are shown in Table D1 (Appendix D). A space in any section indicates that definite information concerning that parameter was not received. It does not necessarily mean that filtration, for instance, was not used. All laboratories used conventional atomic absorption spectrophotometry (AAS) for the determination of "total" metals on the mandatory list. The method of sample preparation is described by a code letter in the summary tables below. The percentage of laboratories using each method and its code letter are shown in the following table:

TABLE 1. Methods of sample preparation used by laboratories

Method	Code	Percentage of laboratories using method
Digest with HNO_3/H_2O_2	(a)	36
HNO_3	(b)	18
HNO_3/HCl	(c)	1
$HNO_3/HClO_4$	(d)	12
HCl/H_2O_2	(e)	1
$HClO_4/H_2O_2$	(f)	1
HNO_3/H_2SO_4	(g)	7
HCl	(h)	1
$HNO_3/H_2O_2/HCl$	(i)	4
$HNO_3/H_sSO_4/H_2O_2$	(j)	5
Dry ash before extraction	(k)	14

The precision and bias of the four most popular digestion procedures (a, b, d and k) are presented below for each element, and for Cr and Pb errors associated with methods involving sulphuric acid (g and j) have also been separated as they are of particular interest for these elements. In evaluating

the digestion procedures, results for sample E (the aqueous sample) have been omitted for obvious reasons.

3.2.1.1. Cadmium

Results for Cd are shown in Appendix E (Tables E1 and E2) and summarised in Tables 2 and 3 and Figure 1. Table 2 shows that the results of 82 laboratories were included in the calculation of the laboratory mean or "true" value for sample A which was found to be 9.09 mg/kg (dry basis). Average precision (CV_t%) of laboratories was 12.2% and in 24% of cases there was a significant between-batch effect. Average deviation (D%) for Cd in sample A was ± 15.8% and overall accuracy (MPD) ± 23.7%. Errors for the other sample of raw sludge (sample C) were broadly similar. However, unlike the results for sample C, those for sample A, which had been treated with lime-copperas, were positively skewed (Appendix E, Table E2). Average errors of Cd determinations on the sample of digested sludge (sample B) were less than for the other two sludges. Overall precision (CV_t) was 7.12%, deviation (D) was ± 6.90% and accuracy (MPD) ± 12.0% (Table 2). Greatest errors were associated with sample D: precision (CV_t), 41.4%; deviation (D), ± 63.4% and accuracy (MPD), ± 104%. Least errors were associated with sample E for which accuracy (MPD) was ± 9.34% (see also histograms of laboratory means in Figure E, Appendix E).

Table 3 summarises results of the different digestion procedures for determinations of Cd on the sludge samples. Methods (a), (b) and (d) were subject to similar precision errors (CV_t) which were less than those for method (k). Thus overall precision (CV_t) for methods (a), (b), and (d) was about 10%, but 18% for method (k). Method (a) showed a consistent positive bias and methods (b) and (d) a negative bias for the raw sludges (samples A and C) but there was little difference in bias between methods for the digested sludge (sample B). The deviation of results for method (k) was consistent for all three sludge samples although its higher precision errors generated an overall accuracy (MPD) of 27.5% compared with 16-21% for the other digestion procedures (Table 3).

Figure 1 presents a cumulative frequency diagram of the accuracy (MPD) of results for Cd averaged over all samples except soil (sample D). Fifty per cent of laboratories achieved an accuracy (MPD) on their Cd determinations of about ± 16% and 95 per cent of laboratories had an accuracy of about ± 40%.

3.2.1.2. Chromium

Figure 2 shows that for determination of Cr, half the laboratories achieved an accuracy (MPD) of ± 30% averaged over all samples, and 95 per cent

TABLE 2. Summary of results of all laboratories for "total" cadmium

SAMPLE	OVERALL VALUES	LABORATORY MEAN	PRECISION CV_t%	PRECISION CV_{W_1}%	PRECISION CV_{W_2}%	PRECISION CV_b%	Incidence of significant between-batch effect %	DEVIATION (±)D%	ACCURACY (±)MPD%
A	$\bar{x}$	9.093	12.2	7.59	5.26	14.7	24	15.8	23.7
	s	2.096	11.5	5.18	4.31	14.7		16.3	19.8
	R	3.037-15.94	0.17-59.6	0.09-28.0	0.09-14.9	0.14-59.1		0.01-6.66	3.38-85.7
	N	82	84	64	20	20		82	82
B	$\bar{x}$	25.16	7.12	3.04	2.75	8.48	36	6.90	12.0
	s	2.27	7.54	2.48	2.78	9.21		5.98	10.1
	R	19.2-30.72	1.27-40.3	<0.04-11.1	<0.04-11.1	1.77-38.8		0.02-23.70	1.74-58.93
	N	81	81	69	45	45		81	81
C	$\bar{x}$	3.589	18.2	10.8	7.16	19.9	31	12.8	26.0
	s	0.586	11.8	8.07	5.97	11.9		9.60	15.8
	R	2.06-4.966	<0.03-47.8	<0.03-39.7	<0.03-27.0	4.49-43.6		0.31-42.6	3.32-83.8
	N	78	77	57	24	24		77	77
D	$\bar{x}$	0.971	41.4	15.8	9.60	33.4	33	63.4	104
	s	0.818	31.2	14.7	8.01	23.3		54.1	109
	R	0.098-3.625	5.31-154.8	<0.1-53.6	<0.1-20.7	7.39-88.7		0.31-273.3	2.45-572.4
	N	27	27	16	9	9		27	27
E	$\bar{x}$	0.2569	6.01	3.12	1.70	6.45	47	4.61	9.34
	s	0.0159	6.68	4.24	2.05	7.36		4.11	8.29
	R	0.208-0.3032	<0.04-36.3	<0.04-25.3	<0.04-8.33	0.98-35.6		0.04-19.03	1.13-42.16
	N	73	73	60	34	34		73	73

Units for the mean are mg/kg (dry basis) for samples A-D and mg/l for sample E

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (i.e. laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{W_1} = coefficient of variation of within-batch error

CV_{W_2} = coefficient of variation of within-batch error where between-batch error was significant

CV_b = coefficient of variation of between-batch error where significant ($P = <0.05$)

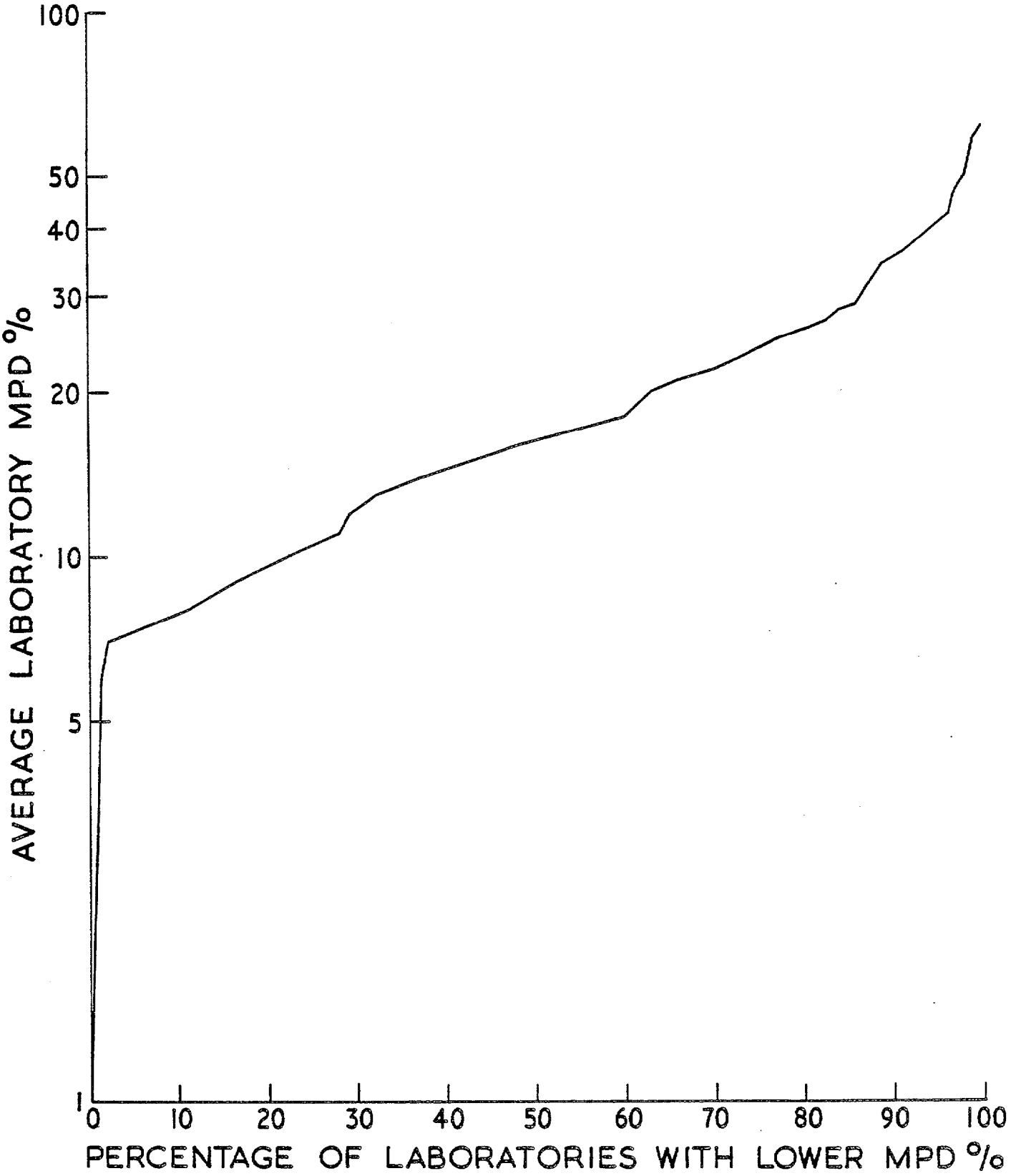
D = ± deviation from true value

MPD = ± maximum probable deviation from the true value

TABLE 3. Summary of results of different digestion procedures for "total" cadmium

Digestion procedure		No. of Labs.	Sample A			Sample B			Sample C			Overall	
			CV_t	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%
HNO_3/H_2O_2	(a)	32-33	11.4	+8.2	26.0	6.3	+0.7	11.2	16.0	+3.2	25.7	11.2	+4.1	21.0
HNO_3	(b)	14-16	8.3	-7.7	15.2	5.8	+0.4	12.1	16.8	-7.6	21.7	10.2	-4.8	16.3
$HNO_3/HClO_4$	(d)	9-10	7.5	-3.5	15.9	4.5	+1.2	8.1	14.9	-8.9	23.8	9.2	-3.9	16.2
Dry ash before extraction	(k)	8-10	13.1	+0.9	22.9	12.4	+1.2	14.9	30.6	+0.7	45.7	18.3	+0.9	27.5

Figure 1. Cumulative frequency diagram of accuracy (± MPD) of Cd determinations (excluding results for soil sample D)



of laboratories achieved ±65%. Errors associated with individual laboratory means are shown in Table F1 (Appendix F) and are summarised in Table 4. Statistics of the populations of laboratory means are shown in Table F2 and Figure F (Appendix F). Table 4 shows that average precision errors (CV_t) were lowest for sample E (6.02%) followed by the sludge samples (B, 8.88%; A, 11.8%; C, 15.9%) and the soil sample (D, 17.7%). Deviation was on average substantially lower for the aqueous sample (± 8.62%) than for the other samples (B, ± 16.6%; C, ± 24.9%; A, ± 32.0%; D, ± 34.4%) and this is reflected in the figures for average accuracy (Table 4). The distribution of laboratory mean results for sample A (Appendix F, Figure F) appears to show two peaks and the distributions of results for samples C, D and E are all significantly skewed (Appendix F, Table F2). The reasons for this become apparent from Table 5 in which it is seen that the relative bias of the different digestion procedures varied substantially. For instance, methods using H_2SO_4 (g or j) produced results which were on average 43% higher than those obtained with an HNO_3 procedure (b); this effect was evident for all samples, but particularly the soil sample. Results with procedure (a) were similar to those for (b) whilst those for (d) and (k) were intermediate between (b) and (g, j). Overall precision (CV_t) was approximately 10% for methods (b, d and k) and 15-17% for (a, g and j).

3.2.1.3. Copper

Results for Cu are shown in Appendix G and summarised in Tables 6 and 7 and Figure 3. Table 6 shows that 86 laboratories submitted results of Cu determinations in sample A. The overall precision (CV_t) of Cu results in sample A was 5.70% with most of the errors coming from between-batch effects which were significant for 42% of laboratories. Overall deviation (D) from the "true" value for Cu in sample A was 6.0% and the average accuracy (MPD) was ± 9.93%. Results for the other two sludges (B, C) followed this pattern closely. Results for Cu in soil (sample D) were associated with larger errors and the distribution of means was positive skewed (Appendix G, Table G2). This was in contrast to the distributions of means for the other samples. Precision errors (CV_t% = 16.4%) for the soil were higher than for sludges and the maximum probable deviation was much higher at nearly ± 25%. Precision was greatest and deviation least in the results associated with aqueous sample E (Table 6).

Table 7 shows that relative bias (D%) between the different digestion procedures was low. The greatest difference was seen for the soil sample (D)

TABLE 4. Summary of results of all laboratories for "total" chromium

SAMPLE	OVERALL VALUES	LABORATORY MEAN	PRECISION CV_t%	PRECISION CV_{W_1}%	PRECISION CV_{W_2}%	PRECISION CV_b%	Incidence of significant between-batch effect %	DEVIATION (±)D%	ACCURACY (±)MPD%
A	$\bar{x}$	111.5	11.8	5.02	3.69	13.1	58	32.0	39.8
	s	40.56	9.72	5.00	2.80	9.77		19.0	18.4
	R	29.1-188.1	0.84-51.7	0.01-26.6	0.01-12.4	1.94-51.3		1.06-77.52	10.13-86.9
	N	82	83	73	48	48		83	83
B	$\bar{x}$	393.8	8.88	4.03	2.81	9.33	61	16.6	22.8
	s	91.6	7.65	4.80	2.14	7.21		16.0	17.9
	R	109.3-680.0	1.23-44.8	0.56-30.2	0.56-12.5	1.21-43.0		0.13-72.68	3.58-91.01
	N	83	84	77	51	51		84	84
C	$\bar{x}$	36.24	15.9	9.85	5.50	16.5	42	24.9	34.9
	s	12.81	14.2	11.9	3.55	13.9		24.9	30.0
	R	7.92-80.8	1.90-68.7	0.96-84.1	0.96-15.4	2.8-[illegible]		0.33-150.6	2.12-202.2
	N	30	81	72	34	34		81	81
D	$\bar{x}$	32.66	17.7	7.42	6.46	19.1	62	34.4	48.2
	s	15.12	12.6	6.04	5.04	12.9		30.9	36.7
	R	5.42-88.0	2.18-66.3	0.94-32.9	0.94-20.4	3.05-66.3		0.61-169.4	1.75-226.4
	N	72	73	69	45	45		73	73
E	$\bar{x}$	2.445	6.02	2.77	2.11	8.82	50	8.62	13.5
	s	0.276	4.96	2.47	2.19	6.50		7.12	9.75
	R	1.731-3.023	0.40-20.1	0.00-9.55	0.00-8.84	0.96-18.1		0.20-30.1	1.60-38.65
	N	73	74	67	37	37		74	74

Units for the mean are mg/kg (dry basis) for samples A-D and mg/l for sample E

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (i.e. laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{W_1} = coefficient of variation of within-batch error

CV_{W_2} = coefficient of variation of within-batch error where between-batch error was significant

CV_b = coefficient of variation of between-batch error where significant (P = <0.05)

D = ± deviation from true value

MPD = ± maximum probable deviation from the true value

TABLE 5. Summary of results of different digestion procedures for "total" chromium

Digestion procedure		No. of Labs.	Sample A			B			C			D			Overall		
			CV_t	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t	D%	±MPD%
HNO_3/H_2O_2	(a)	27-33	14.3	-11.7	40.8	9.7	-6.9	23.6	17.4	-10.4	35.0	19.8	-20.2	42.2	15.1	-12.0	35.2
HNO_3	(b)	13-15	10.7	-18.8	45.1	7.5	-5.3	23.4	10.4	-21.5	27.0	14.2	-16.2	40.6	10.6	-15.2	33.6
$HNO_3/HClO_4$	(d)	7-9	8.2	+6.9	28.2	7.7	+8.2	17.6	11.7	+6.0	25.0	12.8	-2.5	35.0	10.2	+4.4	26.7
Dry ash before extraction	(k)	5-9	5.5	+10.2	26.3	5.6	+5.6	19.3	15.6	+15.0	45.6	15.5	-1.4	24.6	9.8	+1.6	29.1
HNO_3/H_2SO_4 or $HNO_3/H_2SO_4/H_2O_2$	(g or j)	9-12	14.0	+16.1	38.4	13.3	+8.8	31.6	18.3	+25.0	49.2	23.9	+68.7	100	16.9	+27.4	52.2

Figure 2. Cumulative frequency diagram of accuracy (± MPD) of Cr determinations

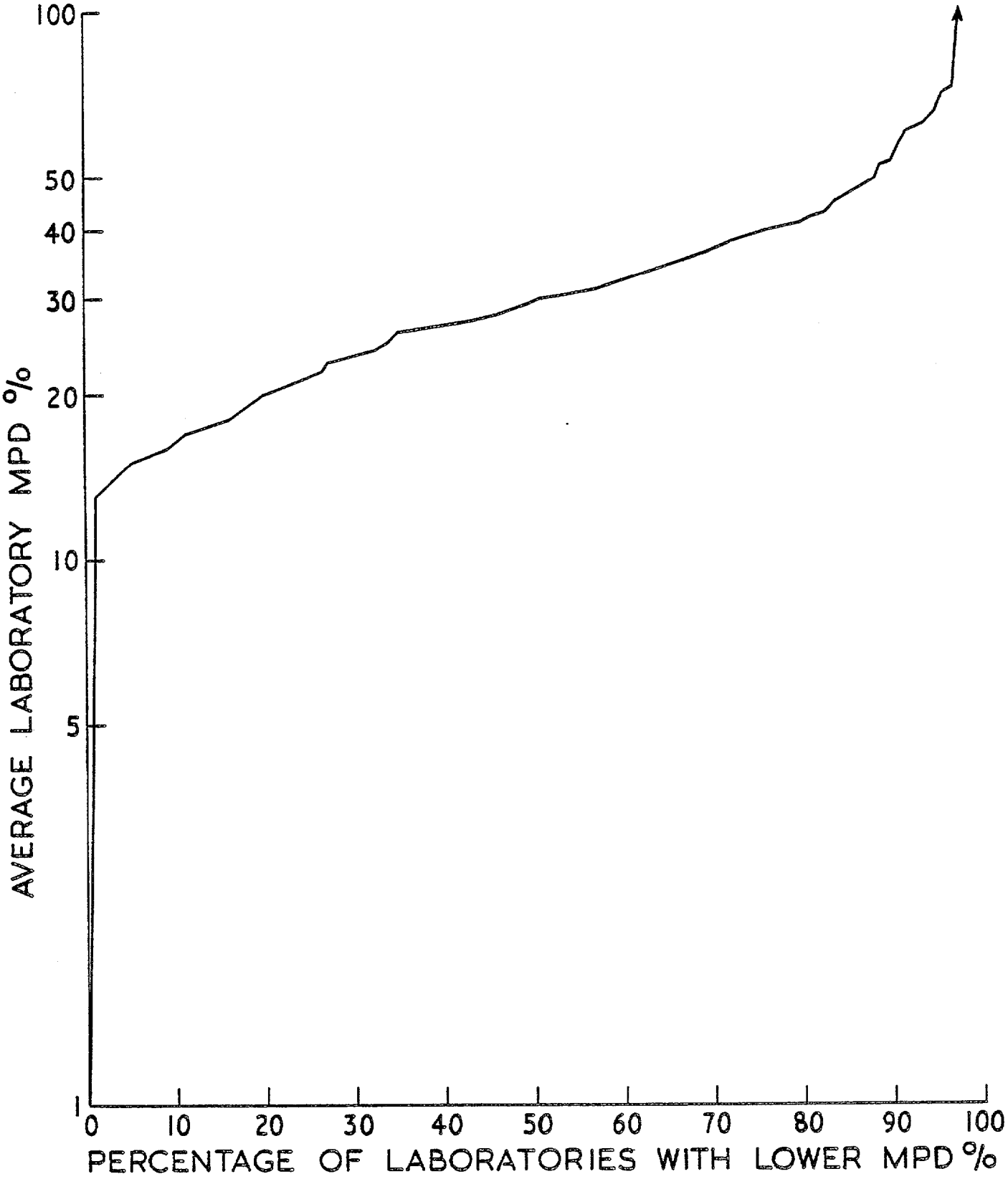


TABLE 6. Summary of results of all laboratories for "total" copper

Sample	Overall values	Laboratory mean	PRECISION CV_t%	CV_{w_1}%	CV_{w_2}%	CV_b%	Incidence of significant between-batch effect %	DEVIATION D%	ACCURACY MPD%
A	$\bar{x}$	245	5.66	3.18	2.48	5.51	42	6.02	9.93
	s	18.8	3.88	2.13	1.74	4.06		4.78	5.92
	R	198-296	0.86-18.0	0.27-10.8	0.61-7.82	1.22-22.7		0.04-20.9	1.15-28.0
	N	86	86	72	36	36		86	86
B	$\bar{x}$	799	4.53	2.54	1.96	4.86	48	5.61	8.86
	s	58.3	3.12	1.98	1.28	3.54		4.63	5.63
	R	622-948	0.68-20.4	0.27-12.3	0.27-5.73	0.56-19.8		0.11-22.2	2.50-27.9
	N	85	85	74	41	41		85	85
C	$\bar{x}$	716	5.12	3.24	2.84	5.89	37	5.72	9.30
	s	54.7	5.08	3.38	4.00	6.25		5.02	7.11
	R	572-886	0.61-40.9	0.22-22.2	0-22.4	0.56-34.3		0.19-23.6	0.89-42.2
	N	84	84	66	31	31		84	84
D	$\bar{x}$	16.4	14.43	7.92	6.17	16.40	41	12.48	24.75
	s	2.92	14.15	8.51	6.39	15.94		11.84	23.6
	R	9.29-26.0	2.66-82.9	0-42.5	0-30.2	2.31-77.2		0.24-58.3	1.1-136
	N	74	74	63	30	30		74	74
E	$\bar{x}$	2.50	4.30	1.43	1.45	5.07	65	3.56	6.68
	s	0.12	5.11	1.86	2.16	5.69		3.36	6.16
	R	2.07-2.79	0.52-25.6	0-11.3	0-11.3	0.57-25.6		0.04-16.3	0.08-30.33
	N	74	72	66	47	47		74	73

Units for the mean are mg/kg (dry basis) for samples A-D and mg/l for sample E

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (i.e. laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{w_1} = coefficient of variation of within-batch error

CV_{w_2} = coefficient of variation of within-batch error where between-batch error was significant

CV_b = coefficient of variation of between-batch error where significant ($p = <0.05$)

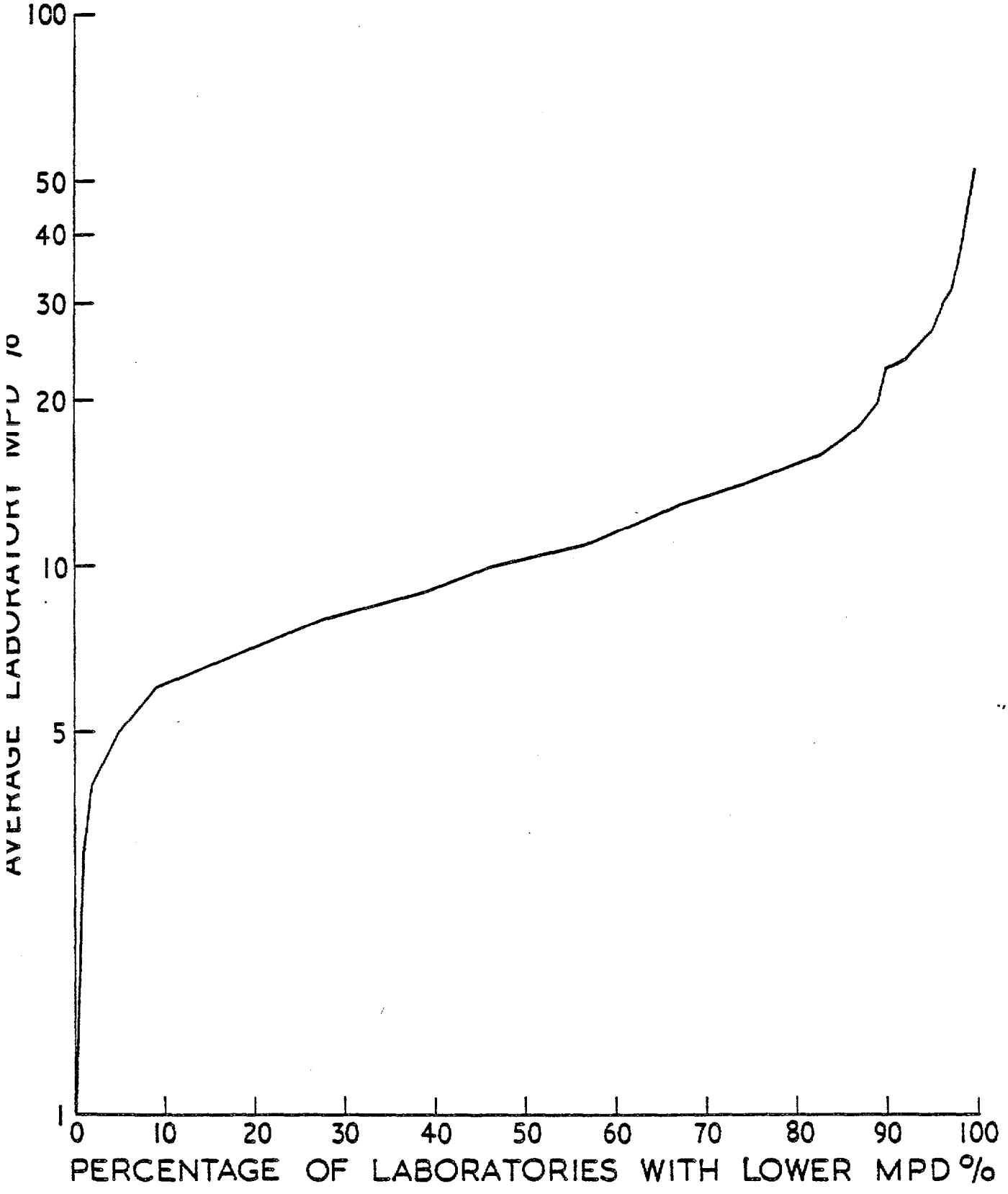
D = ± deviation from true value

MPD = ± maximum probable deviation from the true value

TABLE 7. Summary of results of different digestion procedures for "total" copper

Digestion procedure		No. of Labs.	Sample A			Sample B			Sample C			Sample D			Overall		
			CV_t	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t	D%	±MPD%
HNO_3/H_2O_2	(a)	26-32	5.9	-0.8	9.8	4.9	-0.8	8.8	5.9	+1.2	10.1	14.4	+5.8	23.5	7.5	+1.1	12.6
HNO_3	(b)	14-16	5.4	+3.4	9.5	3.6	+2.0	7.5	3.7	-1.9	8.5	10.4	+2.9	18.9	5.7	+1.6	11.1
$HNO_3/HClO_4$	(d)	9-10	5.0	+3.5	9.3	3.1	+4.2	8.6	3.6	-2.5	6.6	7.7	-5.0	14.7	4.9	-0.2	9.8
Dry ash before extraction	(k)	6-11	5.7	-2.2	10.1	6.3	-4.0	9.8	4.4	+5.8	9.1	29.7	-6.8	42.3	9.9	-1.5	15.6

Figure 3. Cumulative frequency diagram of accuracy (± MPD) of Cu determinations



where dry ashing (k) or digestion with $HNO_3/HClO_4$ (d) produced results about 10% lower than those obtained following digestion with HNO_3/H_2O_2 (a) or HNO_3 (b). Accuracy (MPD) was similar for the three wet digestion procedures and these were 3.0 - 5.8% more accurate than the dry ashing procedure.

Figure 3 shows that the median accuracy (MPD) achieved by all laboratories for Cu determinations in all samples was about ± 10% whilst 95 per cent of laboratories achieved ± 27% accuracy.

3.2.1.4. Nickel

Figure 4 shows that the median accuracy (MPD) of laboratories for determination of nickel on all samples was ± 15%, and 95 per cent of laboratories achieved ± 35% accuracy. Detailed results associated with laboratory means are presented in Appendix H and summarised in Table 8. Errors associated with the four most popular digestion procedures for Ni are summarised in Table 9. Average precision (CV_t) was 4.11% for Ni determinations in aqueous sample E and 5.86% and 6.25% in sludge samples A and B respectively. Precision for samples C and D was about 14% (Table 8). A similar pattern was shown by the average deviation errors so that average overall accuracy (±MPD) ranged from 7.21% (E) to about 25% (C and D) with an intermediate group (A and B) at about 12%. Examination of the distribution of grouped laboratory means (Appendix H, Table H2 and Figure H) showed that data for samples A, C and D were positively skewed. In the case of samples C and D this may be attributable to the positive bias of results obtained using digestion procedures (d) and (k) compared with procedures (a) and (b) which recovered less Ni from these samples (Table 9). Errors of the methods were broadly similar for the other samples (A and B). Overall accuracy was greatest for procedure (d), digestion with $HNO_3/HClO_4$, which generated an MPD of ± 12.9%. This method also recovered more Ni from the samples, particularly from the soil, than alternative wet digestion procedures (Table 9).

3.2.1.5. Lead

Details of errors associated with individual laboratory means are presented in Table I1 (Appendix I). It is apparent that results obtained for samples A, B and C after digestion procedures using H_2SO_4 (g or j) are substantially lower than those obtained by alternative methods. These results were omitted from the summary table for lead (Table 10) and in Table 11, which summarises errors associated with different digestion procedures, they were not used in estimating the "true" value for samples A, B and C. Similarly they were omitted from the

TABLE 8. Summary of results of all laboratories for "total" nickel

AMPLE	OVERALL VALUES	LABORATORY MEAN	PRECISION CV_t%	PRECISION CV_{W_1}%	PRECISION CV_{W_2}%	PRECISION CV_b%	Incidence of significant between-batch effect %	DEVIATION (±)D%	ACCURACY (±)MPD%
A	$\bar{x}$	146.0	6.25	3.42	2.31	5.84	48	8.51	12.7
	s	17.39	4.09	2.69	1.46	3.28		7.72	8.53
	R	100.3-203.4	1.47-25.2	0.46-13.7	<0.01-6.29	1.79-15.3		0.27-39.3	2.53-41.2
	N	86	85	76	41	41		85	85
B	$\bar{x}$	172.6	5.86	3.15	2.54	6.10	51	7.29	11.5
	s	16.22	3.92	2.25	2.01	4.14		5.87	7.54
	R	128.0-214	1.01-26.1	0.20-9.99	0.20-9.99	1.21-24.1		0.02-25.86	2.03-36.58
	N	85	85	75	43	43		85	85
C	$\bar{x}$	26.33	13.5	7.89	6.05	16.3	30	14.1	24.4
	s	4.788	10.9	6.03	4.33	13.9		11.4	20.9
	R	17.5-40.0	2.01-43.4	1.26-26.1	2.91-20.2	1.99-70.5		0.04-51.92	1.2-141.5
	N	82	82	71	25	25		82	82
D	$\bar{x}$	19.49	13.9	8.74	5.08	11.7	43	18.6	28.3
	s	4.66	12.9	11.6	3.98	7.61		14.9	20.0
	R	11.9-37.9	2.75-84.2	0.78-79.4	<0.06-15.8	3.15-33.5		0.21-48.5	5.82-102.3
	N	72	72	60	31	31		72	72
E	$\bar{x}$	2.495	4.11	1.59	1.29	4.62	61	4.06	7.21
	s	0.145	3.02	1.30	0.99	3.13		4.13	5.19
	R	2.091-2.946	<0.04-14.41	<0.04-7.21	<0.04-3.99	0.41-14.38		0.20-18.08	0.28-23.41
	N								

Units for the mean are mg/kg (dry basis) for samples A-D and mg/l for sample E

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (i.e. laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{W_1} = coefficient of variation of within-batch error

CV_{W_2} = coefficient of variation of within-batch error where between-bitch error was significant

CV_b = coefficient of variation ofbetween-batch error where significant (P = <0.05)

D = ± deviation from true value

MPD = ± maximum probable deviation from the true value

TABLE 9. Summary of results of different digestion procedures for "total" nickel

Digestion procedure		No. of Labs.	Sample A			Sample B			Sample C			Sample D			Overall		
			CV_t	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t	D%	±MPD%
HNO_3/H_2O_2	(a)	27-33	5.8	+0.4	12.1	5.2	-1.0	10.2	14.8	-4.9	21.3	12.3	-5.8	26.6	9.3	-2.7	15.5
HNO_3	(b)	14-16	8.1	-0.2	17.1	4.5	+0.6	11.9	11.7	-7.8	22.6	11.0	-10.8	29.6	8.9	-4.4	20.0
$HNO_3/HClO_4$	(d)	9-10	4.5	+0.4	10.1	4.5	+3.2	10.9	7.1	+5.3	12.2	7.2	+12.0	18.0	5.9	+5.4	12.9
Dry ash before extraction	(k)	8-11	7.0	-0.4	11.3	8.0	-0.8	12.0	18.3	+5.0	23.5	18.5	+18.2	36.2	12.4	+5.0	19.9

Figure 4. Cumulative frequency diagram of accuracy (± MPD) of Ni determinations

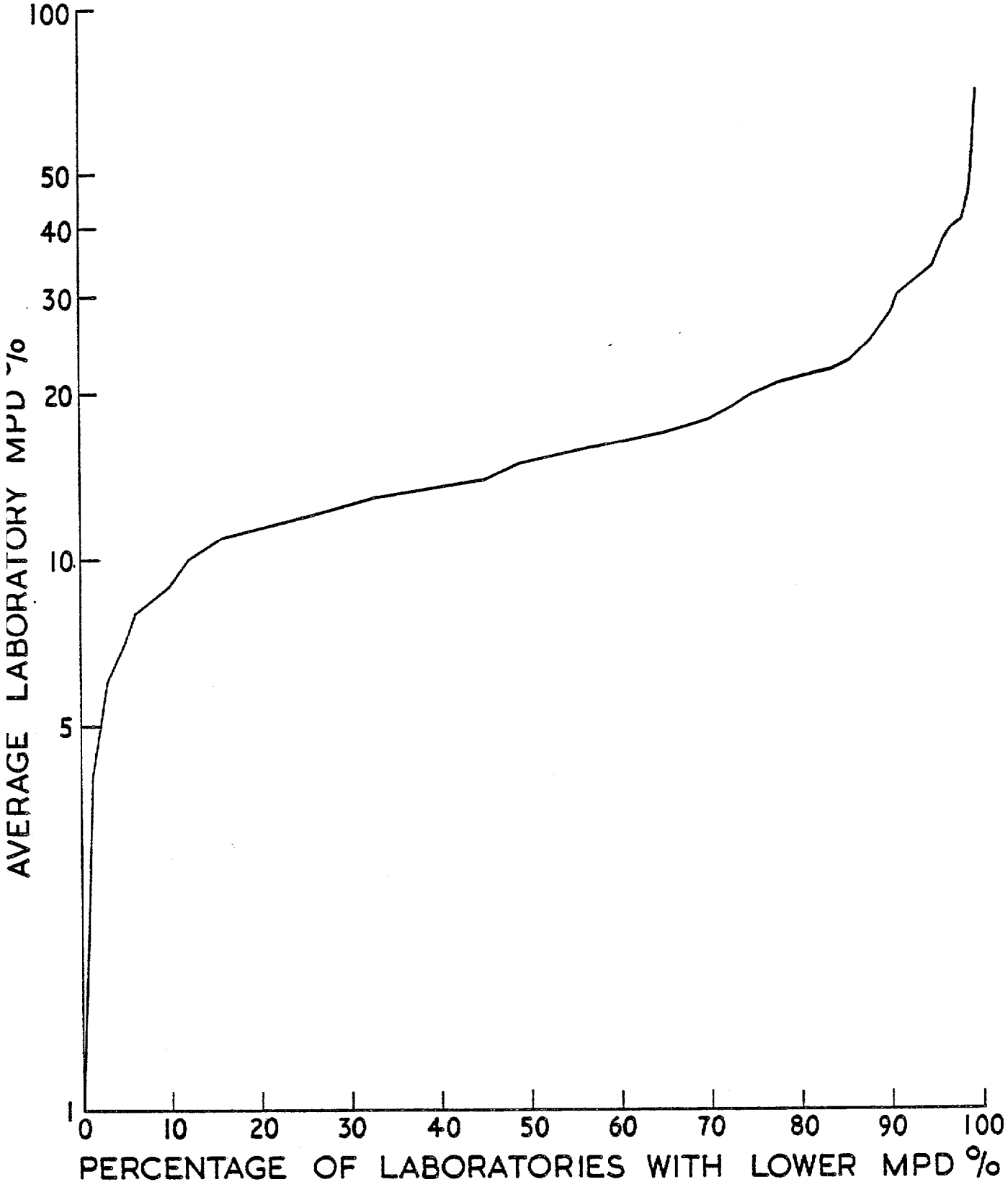


TABLE 10. Summary of results of all laboratories for "total" lead

SAMPLE	OVERALL VALUES	LABORATORY MEAN	PRECISION CV_t%	CV_{W_1}%	CV_{W_2}%	CV_b%	Incidence of significant between-batch effect %	DEVIATION D%	ACCURAC MPD%
A*	$\bar{x}$	340.8	6.73	3.57	3.20	8.24	39	8.66	13.2
	s	42.1	6.32	3.08	2.93	7.05		8.77	11.0
	R	209.3-480.0	0.92-43.2	0.66-18.4	0.66-16.3	1.62-40.0		0.06-38.0	1.44-59.
	N	74	74	60	29	29		74	74
B*	$\bar{x}$	226.8	5.90	3.67	2.82	6.07	36	6.89	10.58
	s	20.9	4.21	2.98	1.78	3.79		5.83	7.10
	R	164.1-282.2	1.41-24.0	0.68-17.2	0.68-9.04	2.00-20.0		0.13-27.7	1.16-40.
	N	72	73	60	26	26		72	71
C*	$\bar{x}$	243.4	6.99	3.94	2.69	6.38	26	6.64	11.37
	s	20.0	5.56	2.99	3.15	5.19		4.77	6.52
	R	197.2-285.9	1.38-33.6	0.00-18.2	0.00-14.5	1.48-23.0		0.78-18.98	2.45-31.
	N	72	73	60	19	19		73	73
D*	$\bar{x}$	24.0	15.9	10.1	8.03	20.4	34	15.0	26.5
	s	4.60	15.4	11.1	7.14	16.7		11.9	19.3
	R	10.6-36.0	2.14-69.3	0.00-45.2	0.00-27.4	3.56-44.8		0.54-56.1	4.74-100
	N	71	71	58	24	24		70	70
E	$\bar{x}$	2.50	3.93	2.06	1.40	3.86	49	3.53	6.36
	s	0.13	2.55	1.73	1.04	2.20		3.85	4.66
	R	2.01-2.90	0.00-11.6	0.12-9.14	0.12-5.55	0.75-9.87		0.04-19.65	0.04-24.
	N	72	72	63	35	35		72	72

* omitting results obtained by digestion procedures using H_2SO_4 (g or j)

Units for the mean are mg/kg (dry basis) for samples A-D and mg/l for sample E.

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (ie laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{W_1} = coefficient of variation of within-batch error

CV_{W_2} = coefficient of variation of within-batch error where between-batch error was significant

CV_b = coefficient of variation of between-batch error where significant ($P = <0.05$)

D = ± deviation from true value

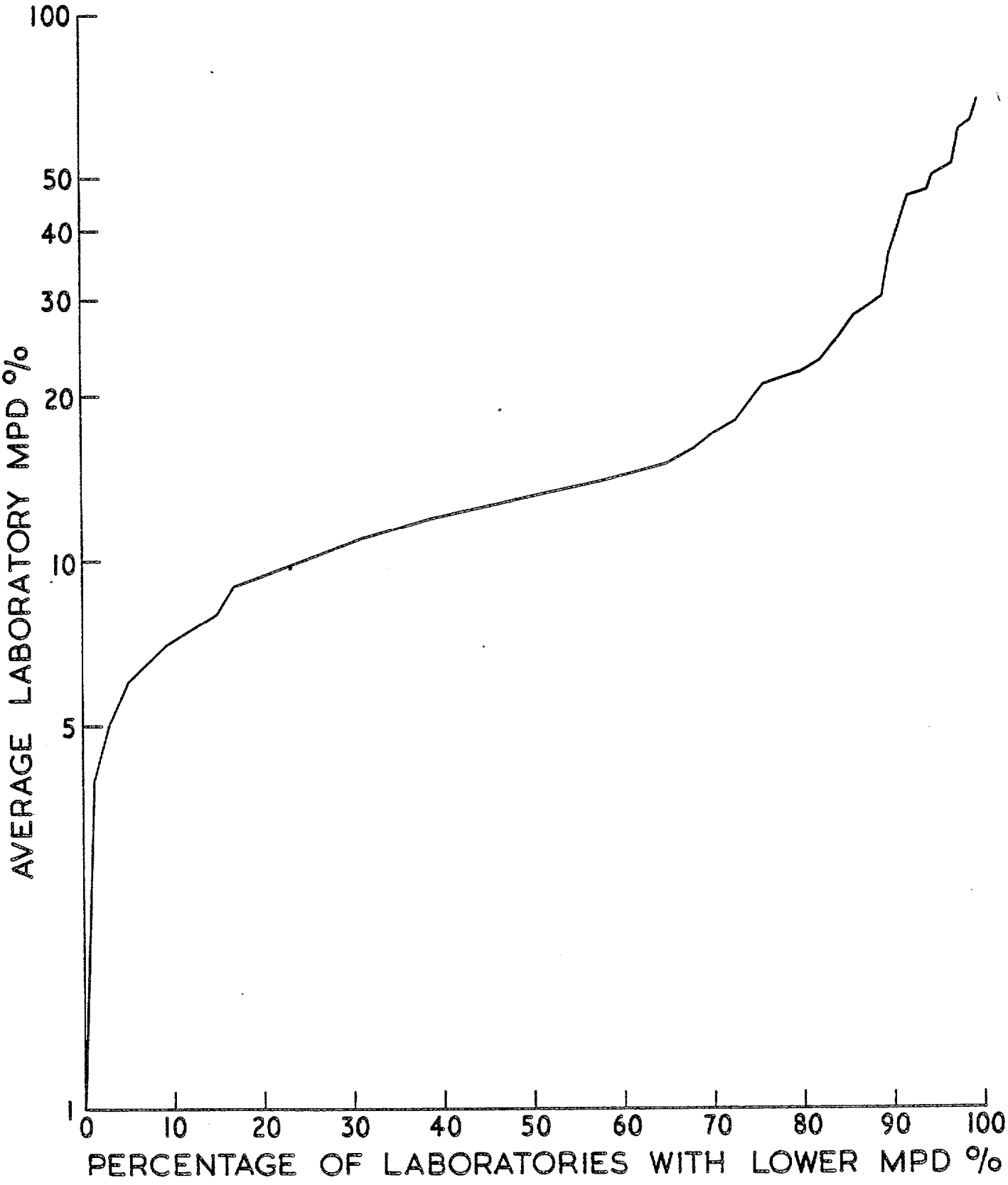
MPD = ± maximum probable deviation from the true value

TABLE 11. Summary of results of different digestion procedures for "total" lead

Digestion procedure		No. of Labs.	Sample A			B			C			D			Overall		
			CV_t	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t	D%	±MPD%
HNO_3/H_2O_2	(a)	27-32	6.8	+0.7	13.9	6.0	-0.8	11.8	6.6	-0.7	11.4	12.8	-3.6	22.6	7.9	-1.0	14.7
HNO_3	(b)	14-16	6.6	-1.1	15.1	6.1	+0.5	11.8	8.8	+0.5	13.3	14.4	-2.1	25.1	8.9	-0.5	16.1
$HNO_3/HClO_4$	(d)	9-10	9.5	-4.0	15.3	6.5	-0.7	10.5	6.0	+1.0	10.2	7.8	+6.2	14.6	7.4	+0.8	12.6
Dry ash before extraction	(k)	7-11	6.9	-0.9	10.5	6.4	0.0	8.9	8.3	-0.7	9.9	32.4	+14.6	45.7	12.4	+2.6	9.2
HNO_3/H_2SO_4 or $HNO_3/H_2SO_4/H_2O_2$	(g or j)*	7-11	36.2	-62.7	70.2	37.3	-51.5	62.9	33.4	-41.7	53.0	35.5	-3.6	62.4	35.7	-43.0	62.1

* Lab. means obtained by using either of these methods were not included in estimating the true value for samples A, B and C

Figure 5. Cumulative frequency diagram of accuracy (± MPD) of Pb determinations



statistics of populations of grouped laboratory means (Appendix I, Table I2) but are included in the corresponding graphs (Appendix I, Figure I). They are also included in the cumulative frequency diagram of laboratory accuracy for Pb (Fig. 5) and may explain the sharply rising tail to this graph. Figure 5 shows that the median value for laboratory accuracy (MPD) for Pb was ± 13% and 95 per cent of laboratories achieved ± 50% accuracy. Table 10 shows that average precision errors (CV_t) for Pb determinations on the three sludges were about 6% compared with values of CV_t of 3.9% for the aqueous sample E and 15.9% for the soil sample D. Average deviation (± D%) followed the same trend of being similar for all three sludges, lower for the aqueous sample E and higher for the soil sample D.

Table 11 shows that digestion procedures using H_2SO_4 (g and j) produced results which were on average 42-46% lower than those obtained by the alternative procedures. This effect was most marked for the three sludge samples, particularly A (lime-copperas treated) but did not apply to the soil sample (Table 11 and Appendix I, Figure I). Precision errors were also very high (36%) for the H_2SO_4 methods (Table 11). The other methods showed little difference in bias with respect to the sludge samples but for the soil sample D dry ashing (k) gave results 8% higher than those obtained with $HNO_3/HClO_4$ (d) and about 17% higher than those for HNO_3/H_2O_2 (a) and HNO_3 (b). Digestion with $HNO_3/HClO_4$ (d) therefore gave the highest Pb results of the wet digestion techniques used on the soil. For this sample, average precision was considerably less (i.e. CV_t was higher, Table 11) for the dry ashing procedure (k) than for the wet digestion procedures with the exception of the H_2SO_4 methods (g and j) which were also comparatively imprecise.

3.2.1.6. Zinc

Errors associated with individual laboratory results for Zn are shown in Table J1 (Appendix J) and are summarised in Table 12 and Figure 6. Table 13 summarises errors associated with different digestion procedures. Average accuracy (MPD%) for the aqueous sample (E) was ± 6.21%, for sludge A ± 9.45%. and about ± 11% for sludges B and C; but accuracy for the soil sample D ± 17.41% (Table 12). Figure 6 shows that the median value achieved by laboratories for Zn determinations on the five samples was just under ± 10% (mean ± 11.5%) and 95% of laboratories achieved ± 23% accuracy. Table 13 shows that for determinations of Zn in sludge there was little difference in either bias or precision attributable to digestion procedure. However, for

TABLE 12. Summary of results of all laboratories for "total" zinc

SAMPLE	OVERALL VALUES	LABORATORY MEAN	PRECISION CV_t%	PRECISION CV_{W_1}%	PRECISION CV_{W_2}%	PRECISION CV_b%	Incidence of significant between-batch effect %	DEVIATION D%(±)	ACCURACY MPD%(±)
A	$\bar{x}$	2,633	5.53	3.07	2.29	5.91		5.70	9.45
	s	210	4.01	2.34	1.55	3.28		5.55	6.72
	R	1,961-3,276	0.7-28.8	0.46-14.1	0.46-6.73	1.14-14.43		0.08-25.52	1.90-32.17
	N	86	86	76	35	35	41	86	86
B	$\bar{x}$	1,361	6.27	3.09	2.37	6.57		6.68	11.07
	s	130	5.22	2.79	1.77	5.83		6.80	9.19
	R	1,002-1,747	1.11-33.6	0.20-18.0	0.2-8.38	1.36-33.3		0.07-28.36	1.40-59.07
	N	83	83	76	45	45	54	83	83
C	$\bar{x}$	602.6	7.12	3.44	2.71	8.68		6.76	11.76
	s	54.4	5.28	2.45	2.13	6.48		5.94	7.79
	R	477.5-762	1.17-34.5	0.57-12.1	0.57-8.91	1.02-15.7		0.17-26.45	2.01-36.81
	N	84	84	92	35	35	42	84	84
D	$\bar{x}$	79.98	9.66	5.62	3.98	9.57		10.86	17.41
	s	12.02	8.89	5.59	3.47	8.48		10.32	13.22
	R	36.1-110.7	1.49-37.8	0.74-22.7	0.74-12.3	1.29-30.8		0.39-54.86	2.09-70.96
	N	74	74	61	34	34	46	74	74
E	$\bar{x}$	9.956	3.44	1.80	1.14	3.31		3.87	6.21
	s	0.610	3.42	2.54	0.97	2.38		4.71	5.50
	R	7.64-12.00	0.2-21.6	0.14-17.4	0.14-5.06	0.83-10.9		0.04-23.26	0.46-25.67
	N	74	75	65	36	36	48	74	73

Units for the mean are mg/kg (dry basis) for samples A-D and mg/l for sample E

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (i.e. laboratories) included

CV_t = total coefficient of variation associated with individual res

CV_{W_1} = coefficient of variation of within-batch error

CV_{W_1} = coefficient of variation of within-batch error where between-batch error was significant

CV_b = coefficient of variation of between-batch error where signif (P = <0.05)

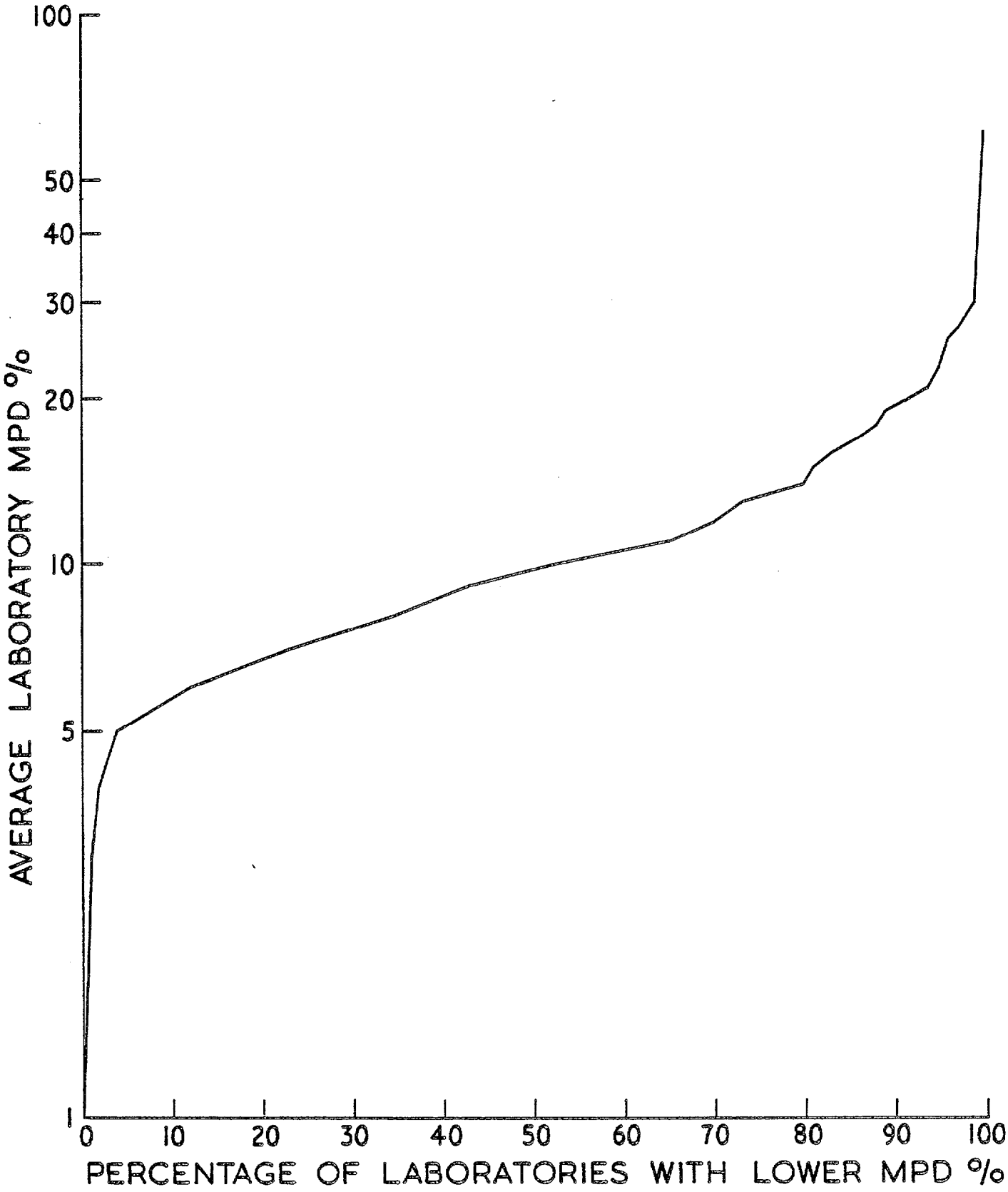
D = ± deviation from true value

MPD = ± maximum probable deviation from the true value

TABLE 13. Summary of results of different digestion procedures for "total" zinc

Digestion procedure		No. of Labs	Sample A			B			C			D			Overall		
			CV_t	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t	D%	±MPD%
HNO_3/H_2O_2	(a)	26-33	5.4	-1.2	9.1	5.9	-0.8	9.7	6.8	-1.0	11.9	8.2	-4.7	15.3	6.5	-1.8	11.3
HNO_3	(b)	14-16	4.8	+4.0	9.7	4.0	+2.3	7.6	4.3	+3.5	9.3	7.3	-2.8	15.3	5.1	+1.7	10.4
$HNO_3/HClO_4$	(d)	9-10	4.5	+2.8	6.8	4.5	+4.5	8.7	6.5	+4.2	10.7	5.6	+11.0	15.5	5.3	+5.7	10.6
Dry ash before extraction	(k)	7-11	6.6	+0.1	8.6	5.4	+2.8	8.8	6.6	-1.4	9.0	14.2	+9.0	19.5	8.0	+2.2	11.1

Figure 6. Cumulative frequency diagram of accuracy (± MPD) of Zn determinations



the soil sample D results obtained using methods (d) or (k) were 12-16% higher than those for methods (a) and (b) and precision errors associated with method (d) ($HNO_3/HClO_4$) were lower than for any of the other digestion procedures.

3.2.2. Extractable metals in soil

Laboratories were asked to determine extractable metals in soil sample D using methods suggested by the SCA (Appendix K). Laboratories which tried these methods usually deviated from the instructions in that they used proprietary solutions of standards and diammonium EDTA. Some laboratories also used their own methods (Appendix L) to determine extractable metals. Frequently these were the methods recommended in ADAS Advisory Paper No. 10[3] or MAFF Bulletin 27[4]. The methods in these two publications are effectively identical. The EDTA method differs from the SCA method in that the extractant is buffered at pH 4 instead of pH 7. For the HAc method an extraction period of 0.5 his recommended; the SCA recommend 16 h.

Results obtained by laboratories using the SCA methods are presented in Appendix M, Tables M1 and M2, and Table M3 presents results for laboratories' own methods. Summary tables below compare results for the SCA methods with results for 'own' methods i.e. ADAS 10[3], MAFF Bulletin 27[4].

3.2.2.1. Copper

Results for extractable Cu are summarised in Tables 14 (SCA methods) and 15 (own methods). The mean concentration of Cu found using the SCA, EDTA method was 5.65 mg/kg and for the own EDTA method 5.47 mg/kg was found. Accuracy (MPD) for the two methods was ± 13.9% and ± 16.3% respectively. The HAc methods extracted less Cu, producing mean values of 1.34 mg/kg (SCA, Table 14) and 1.05 mg/kg (own, Table 15). The HAc methods were less accurate than the EDTA methods; average accuracy for the SCA, HAc method was ± 31.8% (Table 14) and for the HAc, own method it was ± 61.4% although this latter figure was based on the results of only seven laboratories.

3.2.2.2. Nickel

Results for extractable Ni are summarised in Tables 16 (SCA methods) and 17 (own methods). There was close agreement between the results and accuracy of the SCA and own EDTA methods. However, the own HAc method extracted less Ni and was less accurate than the SCA, HAc method. Table M2 (Appendix M) shows that the population of results obtained using the SCA, EDTA method was normally distributed but results from the SCA, HAc method were positively skewed; this was the case for Cu and Zn as well as Ni.

TABLE 14. Summary of results of all laboratories for extractable copper (SCA methods)

SCA method	Overall values	Mean conc found	PRECISION CV_t%	CV_{w_1}%	CV_{w_2}%	CV_b%	Incidence of significant between-batch effect %	DEVIATION D%	ACCURACY MPD%
EDTA	$\bar{x}$	5.65	9.20	5.39	2.87	10.94	43	7.13	13.9
	s	0.52	9.01	8.91	1.80	8.23		5.74	9.33
	R	4.54-8.06	0.69-49.2	0.87-58.4	0.87-7.37	2.94-37.5		0.44-20.9	2.92-44.4
	N	48	49	43	21	21		48	48
HAc	$\bar{x}$	1.341	24.51	17.35	10.30	30.06	14	21.02	31.78
	s	0.383	16.73	11.08	3.24	22.17		18.91	20.74
	R	0.70-2.23	8.22-67.3	5.8-42.4	5.8-13.2	8.45-57.2		1.94-56.5	10.22-96.0
	N	29	30	21	4	4		29	23

Units for the mean are mg/kg (dry basis)

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (i.e. laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{w_1} = coefficient of variation of within-batch error

CV_{w_2} = coefficient of variation of within-batch error where between-batch error was significant

CV_b = coefficient of variation of between-batch error where significant ($P = <0.05$)

D = ± deviation from the true value

MPD = ± maximum probable deviation from the true value

TABLE 15. Summary of results of all laboratories for extractable copper (own methods)

'OWN' METHOD	OVERALL VALUES	MEAN CONCENTRATION FOUND	PRECISION CV_t%	PRECISION CV_{W_1}%	PRECISION CV_{W_2}%	PRECISION CV_b%	Incidence of significant between-batch effect %	DEVIATION ±D%	ACCURACY ±MPD%
EDTA	$\bar{x}$	5.473	7.01	3.92	2.17	7.58	43	10.4	16.3
	s	0.811	2.93	3.00	1.43	2.39		10.1	10.2
	R	3.369-6.68	2.26-12.6	0.87-11.1	0.87-4.65	4.08-11.2		1.94-38.4	3.75-28.4
	N	14	14	12	6	6		14	14
HAc	$\bar{x}$	1.045	35.7	24.6	-	-	0	36.8	61.4
	s	0.479	31.1	18.8	-	-		22.8	23.2
	R	0.312-1.733	4.73-91.9	6.08-50.9	-	-		10.7-70.1	25.5-98.6
	N	7	7	4	0	0		7	7

Units for the mean are mg/kg (dry basis)

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (ie laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{W_1} = coefficient of variation of within-batch error

CV_{W_2} = coefficient of variation of within-batch error where between-batch error was significant

CV_b = coefficient of variation of between-batch error where significant ($P = <0.05$)

D = ± deviation from the true value

MPD = ± maximum probable deviation from the true value

TABLE 16. Summary of results of all laboratories for extractable nickel (SCA methods)

SCA METHOD	OVERALL VALUES	MEAN CONCENTRATION FOUND	PRECISION CV_t%	PRECISION CV_{W_1}	PRECISION CV_{W_2}%	PRECISION CV_b%	Incidence of significant between-batch effect %	DEVIATION D%	ACCURACY MPD%
EDTA	$\bar{x}$	2.095	9.58	5.25	3.72	10.0	50	10.9	17.8
	s	0.277	5.71	4.37	2.33	5.42		7.44	8.07
	R	1.542-2.76	1.92-28.4	0.9-23.4	<0.04-8.34	3.51-28.0		0.14-31.74	1.67-36.80
	N	46	46	41	23	23		46	46
HAc	$\bar{x}$	2.296	25.5	12.1	9.83	33.4	43	20.1	41.6
	s	0.629	17	8.13	7.21	14.6		18.3	32.7
	R	0.88-3.967	1.44-61.5	<0.05-30.1	<0.05-24.8	10.4-56.3		0.13-72.78	4.53-172.26
	N	42	42	35	18	18		42	42

Units for the mean are mg/kg (dry basis)

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (ie laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{W_1} = coefficient of variation of within-batch error

CV_{W_2} = coefficient of variation of within batch error where between-batch errors was significant

CV_b = coefficient of variation of between-batch error where signicant (P = <0.05)

D = ± deviation from the true value

MPD = ± maximum probable deviation from the true value

TABLE 17. Summary of results of all laboratories for extractable nickel (own methods)

OWN METHOD	OVERALL VALUES	MEAN CONCENTRATION FOUND	PRECISION CV_t%	PRECISION CV_{W_1}%	PRECISION CV_{W_2}%	PRECISION CV_b%	Incidence of significant between-batch effect %	DEVIATION D%	ACCURACY MPD%
EDTA	$\bar{x}$	2.031	10.5	5.95	8.35	17.6	29	7.56	17.2
	s	0.219	6.84	3.0	1.58	0.14		7.06	11.2
	R	1.755-2.389	2.55-19.9	1.90-7.23	7.23-9.47	17.5-17.7		0.35-17.6	6.11-38.5
	N	7	7	7	2	2		7	7
HAc	$\bar{x}$	1.630	30.4	16.7	14.2	39.2	45	28.7	56.3
	s	0.595	23.7	10.1	11.0	27.2		20.6	32.3
	R	1.020-2.667	7.54-88.4	4.33-32.0	4.33-32.0	13.9-82.4		1.84-61.6	30.1-135.1
	N	11	11	8	5	5		11	11

Units for the mean are mg/kg (dry basis)

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (ie laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{W_1} = coefficient of variation of within-batch error

CV_{W_2} = coefficient of variation of within batch error where between-batch error was significant

CV_b = coefficient of variation of between-batch error where significant ($P = <0.05$)

D = ± deviation from the true value

MPD = ± maximum probable deviation from the true value

TABLE 18. Summary of results of all laboratories for extractable zinc (SCA methods)

SCA METHOD	OVERALL VALUES	MEAN CONCENTRATION FOUND	PRECISION CV_t%	PRECISION CV_{W_1}%	PRECISION CV_{W_2}%	PRECISION CV_b%	PRECISION Incidence of significant between-batch effect %	DEVIATION D%	ACCURACY MPD%
EDTA	$\bar{x}$	7.290	11.4	4.93	3.93	14.6	36	±8.41	±16.7
	s	0.844	-	-	-	-		-	-
	R	5.612-9.875	1.54-42.3	<0.04-15.0	<0.04-8.17	2.10-48.9		0.22-35.5	2.00-46.
	N	45	45	37	16	16		45	45
HAc	$\bar{x}$	8.920	12.3	7.26	4.63	11.8	28	±15.6	±24.3
	s	1.983	-	-	-	-		-	-
	R	4.464-16.24	0.94-44.8	0.0-28.8	0.0-23.9	0.879-37.9		0.28-82.06	1.78-98.
	N	47	47	35	13	13		48	48

Units for the mean are mg/kg (dry basis)

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (i.e. laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{W_1} = coefficient of variation of within-batch error

CV_{W_2} = coefficient of variation of within-batch error where between-batch error was significant

CV_b = coefficient of variation of between-batch error where significant (P = <0.05)

D = ± deviation from the true value

MPD = ± maximum probable deviation from the true value

3.2.2.3. Zinc

Results for Zn are summarised in Tables 18 and 19. Both the SCA and own EDTA methods extracted a similar amount of Zn, finding 7.29 and 7.58 mg Zn/kg respectively in the soil sample. Precision and accuracy were greater for the own EDTA method although only five laboratories completed this analysis. Errors were larger for HAc methods, particularly the HAc own method which extracted less Zn from the sample than the SCA, HAc method.

3.3. VOLUNTARY PART

3.3.1. "Total" elements in sludges and soil

Methods used by laboratories for the determination of Mo, Hg, As, Se, F and B are set out in Appendix N and the results are presented in Appendix O and in summarised form in Tables 20-22 below. For these elements laboratories were asked to carry out five replicate determinations on a single occasion, and there was no aqueous sample. Mean values and their coefficients of variation are reported for all elements. "True" values were calculated for Mo and Hg only; the bias of laboratory means for these elements is reported in Appendix O (Tables O1 and O2), and the average deviation of individual laboratory means is shown in Tables 20 and 21 for Mo and Hg respectively. "True" values were not calculated for As, Se, F and B because insufficient results were submitted for these elements.

3.3.1.1. Molybdenum

Methods used for the determination of Mo are shown in Table N1 (Appendix N). A wide range of methods was used including two colorimetric procedures and XRF as well as AAS with either an air/acetylene or N_2O/acetylene flame. The limited number of results does not permit any firm conclusions to be drawn about the efficacy of the different techniques used. Fourteen sets of results were submitted and Table 20 shows that these varied widely although the sludge samples presumably contained appreciable concentrations of Mo.

3.3.1.2. Mercury

Fifteen sets of results were submitted for Hg and the methods used are outlined in Table N2 (Appendix N). All laboratories used methods based on generation of elemental Hg although preliminary digestion procedures varied widely. Some laboratories used the same preliminary procedure as for the elements on the mandatory list; it is obviously convenient to do this. Six laboratories used a method based on the procedure recommended by the SCA[5].

TABLE 19. Summary of results of all laboratories for extractable zinc (own methods)

OWN METHOD	OVERALL VALUES	MEAN CONCENTRATION FOUND	PRECISION CV_t%	PRECISION CV_{W_1}%	PRECISION CV_{W_2}%	PRECISION CV_b%	Incidence of significant between-batch effect %	DEVIATION D%	ACCURACY MPD%
EDTA	$\bar{x}$	7.579	7.46	4.81	-	-	40	7.06	12.3
	s	0.813	3.78	0.31	-	-		7.27	8.0
	R	6.725-8.916	3.18-13.3	4.59-5.03	-	-		0.65-17.6	3.75-22.4
	N	5	5	2	0	0		5	5
HAc	$\bar{x}$	6.980	13.9	7.06	3.99	10.3	44	24.8	36.6
	s	3.121	10.2	6.86	2.35	7.65		36.6	46.5
	R	3.132-17.76	1.72-35.5	0.78-22.4	0.78-6.77	1.53-20.2		2.58-154.4	6.07-203.5
	N	16	16	13	7	7		16	16

Units for the mean are mg/kg (dry basis)

$\bar{x}$ = mean value

s = standard deviation of any laboratory mean

R = range

N = number of means (ie laboratories) included

CV_t = total coefficient of variation associated with individual results

CV_{W_1} = coefficient of variation of within-batch error

CV_{W_2} = coefficient of variation of within batch error where between-batch error was significant

CV_b = coefficient of variation of between-batch error where significant ($P = <0.05$)

D = ± deviation from the true value

MPD = ± maximum probable deviation from the true value

TABLE 20. Summary of results of all laboratories for "total" molybdenum

Sample	Overall values	Laboratory mean	Coefficient of variation %	Deviation %
	$\bar{x}$	14.1	19.4	29.3
A	R	7.9-25.1	4.54-48.8	2.8-78.0
	N	13	8	12
	$\bar{x}$	34.4	9.55	47.0
B	R	<10-95.7	2.73-15.8	3.66-178
	N	13	8	12
	$\bar{x}$	9.13	30.1	61.6
C	R	<2-23.3	4.67-76.8	27.3-155
	N	13	7	11
	$\bar{x}$	2.02	28.2	-
D	R	0.52-3.44	5.81-53.8	-
	N	11	3	-

$\bar{x}$ = mean value
R = range for laboratory means
N = number of means (ie laboratories) included

TABLE 21. Summary of results of all laboratories for "total" mercury

Sample	Overall values	Laboratory mean	Coefficient of variation %	Deviation %
	$\bar{x}$	1.41	16.6	31.1
A	R	0.1-3.63	0.00-36.6	0.71-157
	N	14	10	14
	$\bar{x}$	4.16	14.0	27.7
B	R	0.125-6.94	4.45-40.0	3.13-66.8
	N	15	11	15
	$\bar{x}$	1.61	15.0	26.9
C	R	<0.10-3.08	4.06-35.4	1.24-91.3
	N	11	7	11
	$\bar{x}$	0.130	44.4	103.6
D	R	0.033-0.87	25.0-94	1.54-569
	N	8	5	9

$\bar{x}$ = mean value

R = range for laboratory means

N = number of means (ie laboratories) included

TABLE 22. Summary of results of all laboratories for "total" arsenic selenium, fluorine and boron

	Sample	Overall values	Laboratory mean	Coefficient of variation %
Arsenic				
		$\bar{x}$	2.12	13.2
	A	R	<1-2.35	3.0-27.4
		N	5	4
		$\bar{x}$	4.15	9.63
	B	R	3.00-5.38	4.54-19.9
		N	5	5
		$\bar{x}$	3.42	8.86
	C	R	3.02-4.42	4.38-21.4
		N	5	5
		$\bar{x}$	14.4	9.30
	D	R	13.8-14.9	5.60-13.0
		N	2	2
Selenium				
		$\bar{x}$	0.49	10.4
	A	R	0.25-<1.0	-
		N	3	1
		$\bar{x}$	2.49	34.5
	B	R	1.20-4.70	9.27-82.4
		N	3	3
		$\bar{x}$	1.98	25.1
	C	R	0.86-4.0	10.1-53.7
		N	3	3
	D	$\bar{x}$	0.30	5.65
		N	1	1
Fluorine				
		$\bar{x}$	119.2	3.72
	A	R	86.4-139	2.70-4.74
		N	3	2
		$\bar{x}$	327	5.08
	B	R	286-356	4.25-5.90
		N	3	2
	C	$\bar{x}$	266	7.53
		R	222-337	5.32-9.74
		N	3	2
	D	$\bar{x}$	129.9	6.30
		R	33.7-226	-
		N	2	1
Boron				
	A	$\bar{x}$	42.6	19.7
		N	1	1
	B	$\bar{x}$	73.6	18.9
		N	1	1
	C	$\bar{x}$	49.2	23.1
		N	1	1

$\bar{x}$ = mean value
R = range for laboratory means
N = number of means (ie laboratories) included

All laboratories determined Hg by flameless AAS except for one which used an atomic fluorescence method. Results for Hg are presented in Table O2 (Appendix O) and in Table 21 below which shows that for every sample the range of mean values reported by laboratories spanned more than one order of magnitude. Errors were particularly large for determinations on the soil sample which contained the lowest concentration of Hg.

3.3.1.3. Arsenic

Five sets of results were received for As. Methods used are shown in Table N3 (Appendix N) and results in Table O3 (Appendix O) and Table 22 below. All laboratories determined As by AAS as the hydride but various different ways of generating the hydride were used (Appendix N, Table N3). Smaller samples were involved but the range shown by the mean results was not as wide as that for Hg.

3.3.1.4. Selenium

Only three laboratories submitted results of Se determinations and only one of these attempted the soil sample. One laboratory used a fluorimetric method and the other two used AAS following hydride generation (Appendix N, Table N3). Results varied between the three laboratories but errors were lowest for the laboratory using the fluorimetric method where precision (CV) was about 10% for the sludge samples and only 5.7% for the soil sample (Appendix O, Table O3). The results are summarised in Table 22 below.

3.3.1.5. Fluorine

Three laboratories submitted results of F determinations and all used an ion selective electrode (ISE) following solubilisation of F (Appendix N, Table N5). Average coefficient of variation associated with the mean results varied from 3.72 to 7.53% (Table 22); results of individual laboratories are summarised in Table O3 (Appendix O).

3.3.1.6. Boron

A single laboratory submitted results for B and used a colorimetric carminic acid procedure (Appendix N, Table N6). Results are shown in Table O3 (Appendix O) and Table 22 below.

4. DISCUSSION

4.1. "TOTAL" METALS IN SLUDGES AND SOIL

As large an inter-laboratory comparison as this has the advantage that the results obtained should be representative of the errors currently associated with routine methods of determining metals in sewage sludges and soils. It has had the disadvantage that it was impossible to present every individual result in this report; in excess of 30,000 individual results were involved. The report has therefore concentrated on the main objective of the exercise which was to establish the extent of errors associated with routine metal determinations on samples of sludges and soil. For this purpose the errors associated with results from individual laboratories assume more importance than the actual results themselves. Nevertheless, mean results of individual laboratories can be calculated, if wished, using the "true" values in Tables 2, 4, 6, 8, 10 and 12 together with the deviation data (D%) for individual laboratories in Tables E1, F1, G1, H1, I1 and J1 respectively.

Part of the analysis of results has been concerned to compare errors associated with particular digestion procedures. The comparison has concentrated on three wet digestion procedures (a, HNO_3/H_2O_2; b, HNO_3; d, $HNO_3/HClO_4$) and dry ashing (k). The other digestion procedures used by laboratories have been ignored either because they were inadequately represented in the results or because they were associated with apparently anomalous results for some elements e.g. Pb and procedures using H_2SO_4. The comparisons between digestion procedures are not entirely definitive. It is possible that differences between results apparently attributable to digestion procedure were confounded by further variations in other parts of the method e.g. whether or not laboratories used filtration, background correction etc. (Appendix D, Table D1). In assessing the performance of different digestion procedures it should be noted that the estimates of bias are based on a "true" value which is the mean of all results. The most widely used method (a, HNO_3/H_2O_2) will therefore tend to show the least deviation from the "true" value merely because it was used by the most laboratories. Thus, the extent of differences in deviation shown by the various methods is more important than the absolute deviation from the "true" value shown by particular methods. Bias for aqueous sample E was not usually carried over to the other samples analysed by the same laboratory, suggesting that faulty standards were not a

common source of errors. It is outside the scope of this report to deal in any detail with the reasons for the differences in results produced by the various digestion procedures. Current methods of determination of contaminants in sewage sludges and soils have recently been reviewed in a report which draws attention to some of the problems that may be encountered[6]. Thompson[7] has recently reviewed techniques in atomic absorption spectrophotometry.

Figure 7 presents a cumulative frequency diagram of laboratory accuracy (MPD%) averaged for all samples and elements on the mandatory list (except Cd in sample D, see 4.1.1. below). The median MPD for the 90 laboratories and 92 sets of results was ± 16% and 95 per cent of laboratories achieved an MPD of ± 36%. Differences in the precision and accuracy of metal determinations for the various samples are shown in Table 23. Greatest errors were associated with determinations of Pb and Cr in all samples, and with the determination of all metals in the soil sample (D). This could have important implications if soil analyses were to replace sludge analyses (used to calculate loading rates of metals per unit area) as principal criteria governing applications of sludge to agricultural land. The results for Cd in sample D exemplify the problems of determining the low but significant concentrations of certain metals which have to be measured in sludge-treated soils.

Table 24 presents a summary of the errors produced by the four most widely used digestion procedures, averaged for all elements. It is convenient for laboratories to use a digestion procedure appropriate for all six metals and this would preclude the use of procedures involving H_2SO_4 which produced apparently anomalous results for Pb and Cr (see 4.1.5. and 4.1.2. below). The other methods used (Table 1) were insufficiently represented to permit valid comparisons. Greatest precision errors (CV_t) were associated with sample D (soil) and lowest errors with sample B (digested sludge); errors for the other samples (raw sludge) were intermediate (Table 24). This may reflect the fact that the soil sample contained lower concentrations of elements than the sludge sample and that most laboratories involved in the exercise were better acquainted with the determination of metals in sludges than in soils. Precision errors associated with dry ashing (k) were slightly higher than for the other methods (Table 24). Dry ashing procedures involve an extra 'step' compared with wet digestion methods. Relative deviation between the different procedures was greatest for the soil sample (D) but showed a similar trend for the sludges (A, B, C, Table 24). Thus dry ashing (k) or digestion with $HNO_3/HClO_4$ (d) tended to recover more metal (except Cu) than digestion with HNO_3 (b) or HNO_3/H_2O_2 (a).

Figure 7. Cumulative frequency diagram of accuracy (± MPD) of all metal determinations (excluding results for Cd in soil sample D)

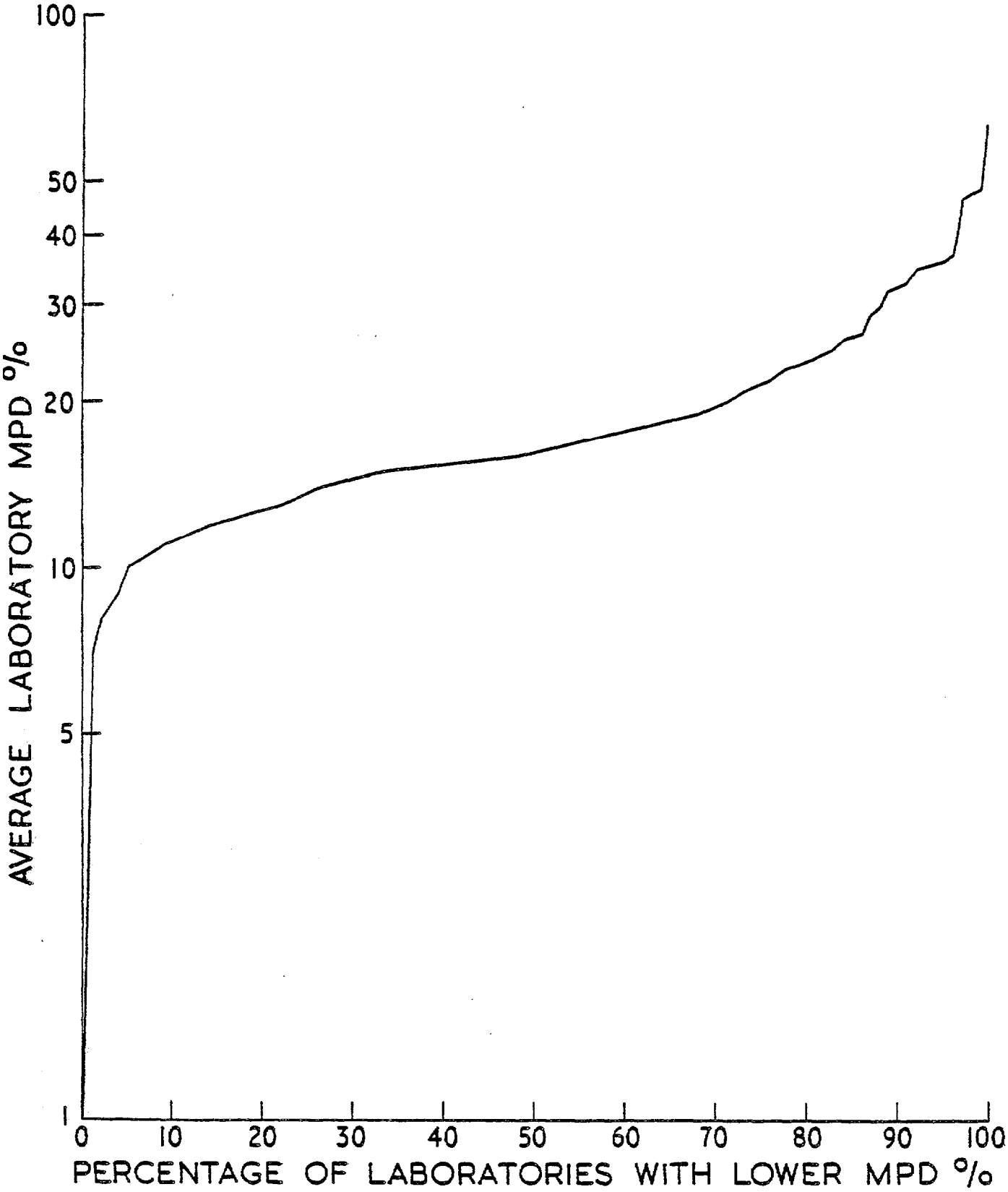


TABLE 23. Overall precision (CV_t) and accuracy (±MPD%) of determinations for 'total' concentrations of metals in the five samples

	ELEMENT																							
	Cd				Cr				Cu				Ni				Pb*				Zn			
	$\bar{x}$ †	CV_t%	±D%	±MPD%	$\bar{x}$	CV_t%	±D%	±MPD%	$\bar{x}$	CV_t%	±D%	±MPD%	$\bar{x}$	CV_t%	±D%	±MPD%	$\bar{x}$	CV_t%	±D%	±MPD%	$\bar{x}$	CV_t%	±D%	±MPD%
A. Crude sludge (lime-copperas)	9.09	12.2	15.8	23.7	112	11.8	32.0	39.8	245	5.66	6.02	9.93	146	6.25	8.51	12.7	341	6.73	8.66	13.2	2633	5.53	5.70	9.45
B. Digested sludge	25.2	7.12	6.90	12.0	394	8.88	16.6	22.8	799	4.53	5.61	8.86	173	5.86	7.29	11.5	226.8	5.90	6.89	10.6	1361	6.27	6.68	11.1
C. Crude sludge (poly-electrolyte)	3.59	18.2	12.8	26.0	36.2	15.9	24.9	34.9	716	5.12	5.72	9.30	26.3	13.5	14.1	24.4	243.4	6.99	6.64	11.4	603	7.12	6.76	11.8
D. Soil ('background')	0.97	41.4	63.4	104	32.7	17.7	34.4	48.2	16.4	14.4	12.5	24.8	19.5	13.9	18.6	28.3	24.0	15.9	15.0	26.5	80.0	9.66	10.9	17.4
E. Aqueous sample	0.257	6.01	4.61	9.34	2.45	6.02	8.62	13.5	2.50	4.30	3.56	6.68	2.50	4.11	4.06	7.21	2.50	3.93	3.53	6.36	9.96	3.44	3.87	6.21

* results obtained by digestion procedures using H_2SO_4 (g and j) omitted for samples A–C

† $\bar{x}$ = mean (or "true") value of all laboratories in mg/kg dry matter but mg/l for sample E.

TABLE 24. Summary of results of different digestion procedures for "total" concentrations of all elements

Digestion procedure		No. of Labs.	Sample A			Sample B			Sample C			Sample D*			Overall		
			CV_t	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t%	D%	±MPD%	CV_t	D%	±MPD
HNO_3/H_2O_2	(a)	33	8.3	-0.7	18.2	6.3	-1.6	12.6	11.3	-2.1	19.2	13.5	-5.7	26.0	9.6	-2.1	18.4
HNO_3	(b)	16	7.3	-3.4	18.6	5.3	+0.1	12.4	9.3	-5.8	17.1	11.5	-5.8	25.9	8.2	-3.6	17.8
$HNO_3/HClO_4$	(d)	11	6.1	+1.0	14.3	5.1	+3.4	10.7	8.3	+0.9	14.8	8.2	+4.3	19.6	7.2	+2.0	14.8
Dry ash before extraction	(k)	11	7.5	+1.3	15.0	7.4	+0.8	12.3	14.3	+4.1	23.8	22.1	+6.7	33.7	11.8	+1.8	18.7

* excluding results for cadmium

For the soil sample this difference amounted to approximately 10% (Table 24). It is possible that the more drastic procedures (d, k) resulted in better solubilisation of metals from the samples, particularly from the more recalcitrant soil matrix. Individual elements were subject to more pronounced effects than Table 24 can reveal and these are discussed below.

4.1.1. Cadmium

Average accuracy of Cd determinations on the digested sludge was ± 12% compared with ± 9.3% on aqueous sample E, suggesting that laboratories experienced little difficulty in measuring the concentrations of about 25 mg Cd/kg dry solids often found in this kind of sludge (Table 2). The raw sludge samples contained lower concentrations of Cd and average accuracy for these samples was about ± 25%. Precision errors associated with dry ashing were higher than for the other procedures. There were no marked differences in recovery of Cd by the different procedures except that digestion with HNO_3/ H_2O_2 (a) tended to produce the highest concentrations particularly for sample A (lime-copperas, raw sludge) and sample D (soil), Table 3. Distributions of laboratory means for both these samples were positively skewed (Appendix E, Table E2, Figure E). This was very marked in the case of the soil sample and is undoubtedly due to the fact that results of 48 laboratories were omitted from the calculation of overall values because they reported results either as below a limit of detection (sometimes as high as 5 mg/kg dry solids) or as simply 'not detectable'. As a result the "true" value for sample D in Table 2 (0.971 mg/kg dry soil) is misleadingly high and the deviation statistics are of very limited value. Thus results for Cd in sample D were omitted in the compilation of Tables 3 and 24 and Figures 1 and 7. Nevertheless, the results for sample D clearly illustrate that many laboratories do not find the determination of low concentrations of Cd in soil to be easy. For monitoring Cd in agricultural soils receiving sludge, laboratories have to work in the range 0.1 - 3.3 mg Cd/kg dry soil.

4.1.2. Chromium

Determinations of Cr were subject to comparatively large errors, even in aqueous sample E, confirming that Cr analysis is subject to difficulties during both sample preparation and AAS. Cr determinations on the soil sample were less accurate (MPD ± 48.2%) than those associated with the sludge samples (MPD ± 23-40%) following the trend seen for other elements (Table 4). The

comparison of errors associated with different digestion procedures was of considerable interest for Cr (Table 5). In general, substantially higher results were produced by procedures which had used H_2SO_4. Dry ashing or digestion with $HNO_3/HClO_4$ produced results about 25% lower and results for the popular methods using HNO_3/H_2O_2 (a) or just HNO_3 (b) were 40-45% lower. This pattern was marked for samples C and D but much less so for samples A and B where there appeared to be two groups, one consisting of procedures (a) and (b) producing lower results than the other (d, k, g and j). A detailed investigation would be needed to isolate the source of these differences as, apart from effects due to digestion procedure, Cr determinations by AAS are particularly prone to inter-element and oxidation-state effects[6,8,9].

4.1.3. Copper

Errors associated with Cu determinations were comparatively low to the extent that the average precision of laboratories (CV_t, Table 6) was 4-6% for the three sludges (A-C) and the aqueous sample (E), and the average maximum probable deviation of laboratories (Table 6) was less than 10% for these samples. Comparison of results for the aqueous standard with results for the sludges suggests that only 2-3% of errors were incurred during digestion or could be attributed to matrix effects. Results for sludge A (lime-copperas treated) compared closely with results for sludges B and C suggesting that the added calcium and iron in sludge A were not giving rise to interference problems. As with the other elements, results for Cu in soil D were subject to the largest errors: CV_t = 16.4% and MPD = ± 24.8% (Table 6). Factors likely to contribute to the greater errors associated with the soil sample would include the lower concentration of Cu it contained, probably in forms less readily solubilised than those in sludges. There was little real difference in the performance of the various digestion procedures except that dry ashing (k) was less precise (Table 7). It is also of interest that, in contrast to results for the other elements, wet digestion with $HNO_3/HClO_4$ (d) or dry ashing (k) extracted slightly less Cu (particularly from soil D) than wet digestion with HNO_3/H_2O_2 (a) or HNO_3 (b).

4.1.4. Nickel

Results for Ni repeated the common pattern of greatest accuracy for the aqueous sample E (MPD ± 7.2%. Table 8) and least accuracy for the soil sample D (MPD ± 28.3%). Errors for the samples of sludge and soil were inversely proportional to the concentrations of Ni they contained suggesting that for Ni

at least, the greater errors associated with the soil sample were a result of its lower concentration of Ni and not due to any 'matrix effect'. There were no discernible interference effects attributable to the lime-copperas in sample A and the accuracy of Ni determinations for this sludge and for the digested sludge (sample B) was no more than 6% less than for the aqueous sample E. Greatest accuracy was associated with wet digestion with $HNO_3/HClO_4$ (d) and this method recovered more Ni than the other wet digestion procedures. As for the other elements (except Cu) the use of $HNO_3/HClO_4$ digestion (d) or dry ashing (k) led to the finding of considerably higher concentrations of Ni in the soil sample than did the use of the HNO_3/H_2O_2 (a) or HNO_3 (b) procedures.

4.1.5. Lead

The negative bias shown by results obtained following digestion of sludge samples by methods using H_2SO_4 (g and j) was a striking feature of the results for Pb (Table 11; Appendix I, Figure I). This bias was not seen in the soil sample and was highest in the lime-copperas treated sludge. It seems likely that the effect was linked with the presence of calcium in the sample and may have resulted from co-precipitation of calcium and lead sulphates*. Precision errors (CV_t%) were also high (for all samples) for methods using sulphuric acid (Table 11). Methods involving sulphuric acid seem to be unsuitable for the determination of Pb. Even with the inclusion of these results, median laboratory accuracy for Pb in all samples was ± 13% (Figure 5) and the mean ± 17.6%. It is also of interest that substantially higher results for Pb in soil sample D were obtained by dry ashing methods (k) although errors of precision were also high for this method (Table 11). Digestion with $HNO_3/HClO_4$ (d) produced the highest results of the wet digestion procedures and precision errors (CV_t) associated with soil analysis were also comparatively low for this method (Table 11).

4.1.6. Zinc

Average errors associated with determinations of Zn were comparatively low with a median accuracy (MPD) of ± 10% (Figure 6) and a mean of ± 11.5%. Errors followed the usual pattern of being lowest for the aqueous sample (MPD ± 6.21%) and highest for the soil sample (MPD ± 17.41%) with the sludge samples between these extremes (MPD ± 9-12%, Table 12). It is of interest that the

* Personal communication from J D Welsh, Water Research Centre

highest recovery of Zn from the soil sample D was again achieved by the $HNO_3/HClO_4$ wet digestion procedure (d) and this method was also more precise than alternative procedures for this sample.

4.2. EXTRACTABLE METALS IN SOIL

The extractants recommended in the SCA procedures removed 8.2 - 11.8% of 'total' metal from soil except in the case of EDTA and Cu; the EDTA extracted 34.5% of 'total' Cu. From the results obtained with the own methods (ADAS Advisory Paper 10[3], MAFF Bulletin 27[4]) it appeared that the amount of metal extracted from soil was little affected by buffering the EDTA at pH 4 ('own' method) or pH 7 (SCA method). This is of interest if it means that results obtained by the two methods are compatible for diagnostic purposes. Conversely, the SCA, HAc method (shaking period 16 h) extracted rather more metal from soil than the own method (shaking period 0.5 h). This suggests that the 0.5 h shaking period of the HAc, own method, may not be enough to permit the soil and extractant to equilibrate fully.

For all elements, errors associated with the SCA, EDTA method were substantially less than those accruing from the SCA, HAc method. It is also of interest that the accuracy of the SCA, EDTA method was in fact greater than the accuracy of 'total' determination for these elements. Again, this applied to all elements. Average accuracy (MPD) of the SCA, EDTA method was ± 16.1%; average accuracy for determinations of 'total' Cu, Ni and Zn in the soil sample was ± 23.5%.

4.3. OTHER ELEMENTS (Mo, Hg, As, Se, F, B) IN SLUDGES AND SOIL

Comparatively few laboratories (Mo, 12; Hg, 14; rest, 5 or less) undertook determinations of these elements. If this is representative of the extent to which these elements are regularly determined in sludge and soil then it is of some interest since all are subject to maximum recommended loading rates to soil where sludge is used on agricultural land[1]. Routine monitoring of these elements may be unnecessary in many cases, depending on the occurrence of industrial dischargers in the catchment of the sewage treatment works, but it would be prudent to determine these elements occasionally in all sludges utilised on agricultural land. For Mo, the recommended maximum loading rate is such that this element may be the principal factor limiting application rates of some sludges to land. Methods varied widely amongst the twelve laboratories which attempted Mo determinations (Appendix N, Table N1) and so did the results they produced (Table 20). Results of Hg determinations were even more variable

(Table 21). Methods for the determination of Mo[10] and Hg[5] in sludges have recently been published. Few laboratories submitted results for the remaining elements. More work would seem to be needed on the testing of methods of determination of all these elements in sludges and soil. It would be convenient if, whenever possible, methods for them involved the same ashing procedures as for the more commonly determined metals. Alternatively, instrumental procedures involving no digestion might be preferred for occasional determinations of some of these elements at a central laboratory.

5. CONCLUSIONS

5.1. DETERMINATION OF 'TOTAL' Cd, Cr, Cu, Ni, Pb and Zn

If an accuracy (MPD) of ± 15% is taken as an arbitrary level of acceptable analytical error then the results of the inter-laboratory comparison have shown that:

(i) Determinations of Cu, Pb and Zn were acceptable except for the soil sample.

(ii) Determinations of Ni were acceptable except for the soil sample and one of the samples of raw sludge (C).

(iii) Determinations of Cd were acceptable only for the digested sludge (B) and aqueous sample (E).

(iv) Determinations of Cr were unacceptably inaccurate except for the aqueous sample (E).

It would appear that work is needed to improve the accuracy of determinations of all six metals in soils. In sludges, Cr determinations were particularly inaccurate and there were also problems in determining the lower concentrations of Cd and Ni found in 'domestic' sludges.

Wet digestion procedures using sulphuric acid tended to produce anomalously low results for Pb (apparently in proportion to the Ca content of the sample). Dry ashing procedures tended to generate greater precision errors than wet digestion methods, particularly for the soil sample. Results showed that the $HNO_3/HClO_4$ method tended to recover more metal (except Cu) from the soil sample than the other wet digestion procedures and was also slightly more precise. With the exception of methods involving H_2SO_4, there was little overall difference between the errors of the other wet digestion procedures treated statistically, suggesting that any of these could produce results of acceptable accuracy provided they were used properly. The HNO_3 method used by

a laboratory associated with some of the most accurate results has recently been published[11].

5.2. DETERMINATION OF EXTRACTABLE Cu, Ni AND Zn IN SOIL

Average accuracy (MPD) of results obtained with the SCA, EDTA method (± 16.1%) was approximately twice that obtained with the SCA, HAc method (± 32.6%) and was better than the accuracy associated with determinations of 'total' concentrations of these elements in soils (± 23.5%). Since much of the error in estimating metal concentrations in sludges and soils is probably incurred in sampling, it is desirable that methods should balance a need for adequate throughput of samples against analytical accuracy. In this connection some aspects of the SCA methods for extractable metals (Appendix K) could be simplified.

5.3. DETERMINATION OF 'TOTAL' Mo, Hg, As, Se, F and B.

The small number of laboratories submitting results, the range of methods used and the wide range of results obtained all serve to underline the need for further work on methods for the determination of the above elements in sludges and soils.

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REFERENCES

1. DEPARTMENT OF THE ENVIRONMENT/NATIONAL WATER COUNCIL. Report of the Working Party on the Disposal of Sewage Sludge to Land. DOE/NWC Standing Technical Committee Report Number 5. NWC, London, 1977.
2. CHEESEMAN, R.V., and WILSON, A.L. Manual on Analytical Quality - Control for the Water Industry. WRC Technical Report TR66, 1978.
3. MINISTRY OF AGRICULTURE, FISHERIES AND FOOD. Permissible Levels of Toxic Metals in Sewage Used on Agricultural Land. ADAS Advisory Paper 10. MAFF, London, 1971.

4. MINISTRY OF AGRICULTURE, FISHERIES AND FOOD. The Analysis of Agricultural Materials. Technical Bulletin 27. HMSO, London, 1973

5. DEPARTMENT OF THE ENVIRONMENT. Methods for the Examination of Waters and Associated Materials. Mercury in Waters, Effluents and Sludges by Flameless Atomic Absorption Spectrophotometry. HMSO, London, 1978.

6. DAVIS, R.D. Control of Contamination Problems in the Treatment and Disposal of Sewage Sludge. WRC Technical Report TR156, 1980.

7. DEPARTMENT OF THE ENVIRONMENT. Methods for the Examination of Waters and Associated Materials. Atomic Absorption Spectrophotometry, An Essay Review by K.C. Thompson. HMSO, London, 1979.

8. THOMPSON, K.C. Shape of the Atomic-Absorption Calibration Graphs for Chromium Using an Air-Acetylene Flame. Analyst, 1978, 103, 1258-1262.

9. THOMPSON, K.C. and WAGSTAFF, K. Determination of Chromium in Natural Waters and Sewage Effluents by Atomic-absorption Spectrophotometry Using an Air-Acetylene Flame. Analyst, 1978, 104, 224-231.

10. MUSSELWHITE, C. The Determination of Molybdenum in Sewage Sludge. Water Research Centre, LR 1201, 1980.

11. THOMPSON, K.C., and WAGSTAFF, K. Simplified Method for the Determination of Cadmium, Chromium, Copper, Nickel, Lead and Zinc in Sewage Sludge Using Atomic-Absorption Spectrophotometry. Analyst, 1980, 105, 883-896.

APPENDIX A

RESULTS OF HOMOGENEITY TESTS ON SAMPLES

Table A1. Preliminary tests, samples ground to pass 2 mm

Element	Mean and coefficient of variation	Sample A	Sample B	Sample C	Sample D
Cu	$\bar{x}$	259	943	779	15.4
	CV%	3.2	4.2	6.4	6.9
Zn	$\bar{x}$	2730	1555	664	85.6
	CV%	3.1	3.2	7.1	5.2

Units for mean = mg/kg (dry basis)

Each mean is derived from 10 results (n = 10)

Table A2. Final tests, samples ground to pass 0.5 mm

Element	Mean and coefficient of variation	Sample A	Sample B	Sample C	Sample D
Cd	$\bar{x}$	9.55	26.3	3.53	<0.25
	CV%	2.40	2.40	3.73	-
Cr	$\bar{x}$	108	444	41.6	25.9
	CV%	4.46	4.68	3.78	8.70
Cu	$\bar{x}$	277	838	758	15.3
	CV%	3.20	1.81	2.10	4.41
Ni	$\bar{x}$	153	186	25.6	17.1
	CV%	2.02	2.34	3.30	4.28
Pb	$\bar{x}$	287	229	266	28.7
	CV%	8.98	5.46	4.80	6.91
Zn	$\bar{x}$	2689	1484	690	87.7
	CV%	2.51	1.63	2.20	3.15

Units for mean = mg/kg (dry basis)

Each mean is derived from 20 results (n = 20)

APPENDIX B

INSTRUCTIONS SENT TO COLLABORATING LABORATORIES

COLLABORATIVE ANALYSIS OF SEWAGE SLUDGE AND SOIL

1. OBJECTIVES

To compare the results obtained using existing methods of analysis for metals in prepared samples of three sewage sludges and one soil, as a preliminary stage in the development of recommended methods.

2. SAMPLES

The Stevenage Laboratory of the WRC has prepared and tested three samples of sludge and one sample of soil. Sample A is of sludge treated with lime-copperas, Sample B is of digested sludge, Sample C is of raw sludge, and Sample D is of soil.

3. PROGRAMME OF WORK FOR PARTICIPATING LABORATORIES

3.1. MANDATORY

3.1.1. "Total" metals (strong acid extractable). Determine "total" concentrations of Cd, Cr, Cu, Pb, Ni and Zn by their currently used methods in the three samples of sludge and the soil sample.

3.1.2. "Available" metals. Determine "available" concentrations of Cu, Ni and Zn in the soil sample only, by the methods proposed by the SCA (details enclosed) and by their currently used methods if different.

3.1.3. Experimental design. Dry weight determinations, at 105°C for the sludges and 30°C for the soil, should be carried out on separate portions of the samples.

Participants are asked to carry out the analyses as duplicate determinations on 5 days spread over a period of 3-6 weeks. Each analytical result should be from an independent portion, weighing not less than 0.5 g, of the sample received. Each determination should be accompanied by a reagent blank taken through the same procedure as the sample i.e. blanks should also be carried out in duplicate on each of the five days. Thus, assuming the procedures for sludge and soil vary slightly, and that both the SCA and own method for "available"

metals in soil will use two extractants, batches of samples for analysis will consist of:

16 digested samples ([3 sludges + 3 blanks] x 2; [1 soil + 1 blank] x 2)

16 extracted samples ([1 soil + 1 blank x 2], by 2 methods each using 2 extractants) requiring a maximum of 32 Cu, Ni, Zn determinations and 16 Cd, Cr, Pb determinations for each of the five days on which the analysis is performed.

If convenient, it is acceptable to digest a batch of samples on one day and carry out the rest of the analysis on the following day. The order of analysis of the replicates in each batch should be randomised. Each result should be calculated using its associated blank value. In this way, each result will be independent which will permit a valid estimate of within-batch variability. Throughout the analysis, laboratories should follow the procedures they normally use and not expend an unusual amount of effort on the samples.

3.2. VOLUNTARY

In view of guidelines for the utilization of sewage sludge on agricultural land, those laboratories which have the appropriate facilities are urged to determine also "total" concentrations of as many as possible of Mo, As, Hg, B, Se and F in the four samples by their currently used methods. It is likely that analysis of the samples for these elements will be comparatively tedious. Therefore, analysis of five subsamples together with five reagent blanks, on a single occasion within the 3-6 week period is all that is required. Other details of experimental design are as for 3.1.3.

3.3. RESULTS

3.3.1. Format and time-scale. Laboratories are asked to submit results on the enclosed forms as soon as possible and certainly within 3 months of receiving the samples for analysis. Analytical results should be quoted to at least three significant figures whenever possible, and expressed on a dry weight basis.

3.3.2. Methods. Precise details of methods used should be sent with the results. Details of methods should include procedures for blank correction and preparation of calibration curves as well as the analytical process itself.

3.3.3. Destination. Results should be sent to Dr R D Davis, Water Research Centre, Elder Way, Stevenage, Herts SG1 1TH.

3.3.4. Completion. The identification of participating laboratories will be coded and each will be sent a copy of the results in completion of the exercise together with details of the sludges and soil used and their preparation.

DOE/WRC COLLABORATIVE ANALYSIS OF SLUDGES AND SOIL - RESULTS SHEET

Name:

Address:

Mandatory list

"TOTAL" METALS

Cadmium

BATCH	REPLICATE	SAMPLE			
		A	B	C	D
1	1				
	2				
2	1				
	2				
3	1				
	2				
4	1				
	2				
5	1				
	2				

Chromium

BATCH	REPLICATE	SAMPLE			
		A	B	C	D
1	1				
	2				
2	1				
	2				
3	1				
	2				
4	1				
	2				
5	1				
	2				

DOE/WRC COLLABORATIVE ANALYSIS OF SLUDGES AND SOIL - RESULTS SHEET

Name:

Address:

Voluntary list

"TOTAL" ELEMENTS

Molybdenum

REPLICATE	SAMPLE			
	A	B	C	D
1				
2				
3				
4				
5				

Arsenic

REPLICATE	SAMPLE			
	A	B	C	D
1				
2				
3				
4				
5				

Mercury

REPLICATE		SAMPLE		
	A	B	C	D
1				
2				
3				
4				
5				

COLLABORATIVE ANALYSIS OF SEWAGE SLUDGE AND SOIL

ADDITIONAL INFORMATION

SAMPLE E

At the request of some participating laboratories, an aqueous sample (Sample E) has been included in the mandatory part of the exercise. Sample E contains six metals in concentrations within the ranges likely to be found in sludge digests. Laboratories are asked to carry out duplicate determinations for metals (Cd, Cr, Cu, Pb, Ni, Zn) in Sample E on five occasions at the same time as they determine "total" metals in samples A-D.

RESULTS

Results for Sample E should be expressed in mg/l and reported on the enclosed sheet. Results for Samples A-D should be expressed as mg/kg dry weight and reported on the sheets circulated previously. If possible results should be submitted within 3 months of receipt of sample. More than 70 laboratories are taking part in the exercise and each will receive a copy of the final report of the results.

SHAKER

An enquiry has been received concerning the type of shaker to use in the SCA Methods for Extractable Metals in Soils. The shaker intended was the Griffin bottle shaker (A. Gallenkamp and Co. Ltd, Catalogue No. SGL-200) which shakes at about 275 strokes/min. This apparatus should be set in the 'medium throw' position in which the cradle travels 25 mm. Alternative equipment should be adjusted to give a similar rate of shaking.

COLLABORATIVE ANALYSIS OF SOILS AND SLUDGES

"AVAILABLE" METALS IN SAMPLE D

100 g. Sample D is enclosed for the determination of "available" Cu, Ni and Zn.

Important

1. As only 3 metals have to be determined by the SCA Methods please use
5 g Sample D per 25 ml 0.05 M EDTA extracting solution (EDTA Method Step 6.1)
2.5 g Sample D per 100 ml 0.5 M acetic acid extracting solution (Acetic acid Method Step 6.1)

2. Some participating laboratories have indicated that they cannot prepare standard solutions from pure metals as indicated in the SCA Methods. Where this is the case, it is acceptable to prepare standards from appropriate dilutions of proprietary standard solutions provided that this is reported in the details of methods used submitted with the results.

APPENDIX C

STATISTICAL METHODS USED IN THE ANALYSIS OF RESULTS

1. ESTIMATION OF ANALYTICAL ERRORS

Statistical analysis was first carried out on an individual laboratory sample set of results for one metal. The total variation estimated for each set was taken as a measure of PRECISION with which a laboratory could measure the metal level in that sample. The data were then pooled for all laboratories and individual laboratory means were compared with an estimated true value to determine laboratory BIAS.

2. PRECISION

It would be desirable that variation between batches on different occasions was approximately equal to that found between replicates in a single batch. This does not always occur and so these two sources of error were separated and compared. This was achieved by an 'Analysis of Variance' a well established technique described in statistical texts[1], see also Table C1. When variation between batches was significantly above that found within a batch, this extra variance was estimated (S_b^2) and allowed for when calculating the overall precision.

TABLE C1. Anova table; general form

Sources of variation	Sums-of-squares	Degrees of freedom	Mean - squares	F-statistic
Between-batch	SSB	m-1	BMS = SSB/m-1	BMS/EMS
Within-batch	SSE = SS-SSB	m(r-1)	EMS = SSE/m(r-1)	
(Total)	(SS)	(mr-1)		

where m = number of batches, and r = number of replicates within a batch

2.1. WITHIN-BATCH VARIATION

The variance within batches (S_w^2) was estimated as the mean square of the error (EMS) between replicates taken directly from the 'anova' table in the usual way, i.e. S_w^2 = EMS, see Table C1.

2.2. BETWEEN-BATCH VARIATION

The variance between batches, S_b^2, was estimated using the equation[1]:

$$BMS = r S_b^2 + S_w^2 \qquad (1)$$

where BMS is the mean square for between batch variability in the 'anova' table (Table C1)

r is the number of replicates in a batch.

As S_w^2 is equal to the error mean square in the analysis of variance, S_b^2 was calculated directly from the anova table values as:

$$S_b^2 = (BMS - EMS)/r \qquad (2)$$

2.3. TOTAL VARIATION

Two approaches were taken to estimate the overall variance, S_t^2, that is the precision of a single set of results. When between batch variation fell below the significant level ($P \geq 0.05$) as shown by the analysis of variance, S_b^2 was assumed to be zero. In these cases an estimate of S_t^2 was made on the basis that variation from batch to batch was approximately equal to that found within a single batch. This would be equivalent to ten replicate analyses and:

$$S_t^2 = \frac{SS}{(mr-1)} \qquad (3)$$

where $P \geq 0.05$ from an analysis of variance.

If, and only if, between batch variation was significant ($P < 0.05$), was S_t^2 estimated by combining separate estimates of between and within batch error:

$$S_t^2 = S_w^2 + S_b^2 \qquad (4)$$

where $P < 0.05$ as shown by an analysis of variance.

For more general comparison variances were expressed as coefficients of variation:

$$CV_n = 100S_n/\bar{X}_L \qquad (5)$$

where $\bar{X}_L$ is the mean of a sample set of results for a laboratory

S_n is the $\sqrt{}$ of the variance of interest i.e. within batches (S_w^2), between batches (S_b^2) or overall (S_t^2).

3. BIAS

3.1. "TRUE"VALUE

Before estimating the bias of a particular laboratory mean the 'true' value of each metal concentration in each sample has to be calculated. It was decided that a mean value of all individual laboratory means, excluding outliers, would be taken as the 'true value' (T),

$$T = 1/N \sum_{i=1}^{N} \bar{X}_{Li} \qquad (6)$$

where N is equal to the number of laboratories.

Outliers were identified in the first instance by analytical considerations, that is, determining whether the laboratory concerned used an atypical technique, and secondly by statistical examination. In the case of the latter an 'outliers-ratio', R, was calculated[2]:

$$R = \frac{\bar{X}_{LS} - \bar{\bar{X}}}{S} \qquad (7)$$

where $\bar{X}_{LS}$ is the suspect laboratory mean
$\bar{\bar{X}}$ is the initial value of T
S is the standard deviation of any laboratory mean.

When R exceeds the tabulated value for N laboratories, it may be considered with 95% confidence that the suspect mean came from a population different to that of the other laboratories[2,3].

3.2. DEVIATION

The bias was calculated in each case by expressing the deviation of a particular laboratory-mean from the "true" value as a percentage of the true value:

$$\text{Bias or Deviation } \% = 100(\bar{X}_{Li} - T)/T \qquad (8)$$

4. ACCURACY

4.1. CONFIDENCE LIMITS

A final estimate was made combining both precision within a single laboratory and its corresponding bias. This was the maximum probable deviation (MPD%) that a laboratory mean might reach, but not exceed, with 95% confidence.

This could be taken as a measure of overall accuracy of that mean value.

This involves calculation of the 90% confidence limits of a laboratory mean as follows; $\bar{X}_L \pm S_{\bar{X}} \cdot t_{0.1}$ where $S_{\bar{X}}$ is the standard deviation (standard error) of the laboratory mean, and $t_{0.1}$ the 'student's t statistic' at a probability level of 0.1 and n-1 degrees of freedom.

4.2. STANDARD ERROR OF A LABORATORY MEAN

This value was calculated in either of two ways as was S_t^2, that is, depending on whether a significant between-batch variation was found. If S_b^2 could not be reliably estimated then; $S_{\bar{X}} = S_t/\sqrt{n}$ $(P \geq 0.05)$ in the usual way, however, when S_b^2 proved significant this was modified to*:

$$S_{\bar{X}} = \sqrt{\left(\frac{S_b^2}{m} + \frac{S_w^2}{mr}\right)} \qquad (9)$$

where m is the number of batches

r is the number of replicates in a batch.

4.3. MAXIMUM PROBABLE DEVIATION

This was calculated as a single laboratory means deviation (bias) from the "true" value T plus its 90% confidence limit taken in the direction which maximises that deviation[4]:

$$\text{If } \bar{X}_L < T \quad MPD\% = 100\,(\bar{X}_L - T - S_{\bar{X}} \cdot t_{0.1})/T \qquad (10)$$

$$\text{If } \bar{X}_L > T \quad MPD\% = 100\,(\bar{X}_L - T + S_{\bar{X}} \cdot t_{0.1})/T \qquad (11)$$

5. SAMPLE DISTRIBUTIONS OF LABORATORY MEANS

Each sample of laboratory means from which a "true" value was estimated (one metal level in a given sample), was investigated statistically to discover the nature of its distribution. A normal distribution would be expected in most cases and the validity of the statistics in fact relies on this being so. To show that our assumption of normality was not far out a measure of skewness (departure from symmetry) was estimated:

* Personal communication from W.J. Brooker, Water Research Centre.

$$\text{Skewness} = M_3/(M_2)^{3/2} \tag{12}$$

Also an indication of the flatness or peakedness known as kurtosis:

$$\text{kurtosis} = M_4/(M_2)^2 \tag{13}$$

where M_2, M_3 and M_4 are the second, third and fourth moments respectively of the sample distribution (N elements);

$$M_n = 1/N \sum_{i=1}^{N} (\bar{x}_{Li} - T)^n \tag{14}$$

A normal distribution has values of skewness and kurtosis of -0.5 to +0.5, and 3, respectively. Kurtosis values of <3 indicate flattening of the curve and those of >3 indicate greater peakedness.

The estimates of skewness and kurtosis were made from grouped data to allow histograms to be drawn illustrating these values (Figures E-J). Little loss of accuracy was incurred by grouping the data because $\bar{x}$ and S values derived from the sets of grouped data (Tables E-J) compared closely with the corresponding values obtained from the original data (Tables 2, 4, 6, 8, 10 and 12).

REFERENCES

1. BROWNLEE, K.A. Industrial Experimentation 4th Edition. London, HMSO, 1956.
2. STEINER, E.H., and YOUDEN, W.J. Planning and Analysis of Results of Collaborative Tests. Association of Official Analytical Chemists. Arlington, 1979.
3. CHEESEMAN, R.V., and WILSON, A.L. Manual on Analytical Quality-Control for the Water Industry. Technical Report TR66, Water Research Centre, 1978.
4. WATER RESEARCH CENTRE. Accuracy of Determination of Ammoniacal Nitrogen in River Waters. Technical Report TR58, WRC, 1978.

PPENDIX D. - METHODS USED BY LABORATORIES TO DETERMINE "TOTAL" METALS

ABLE D1 METHODS, "TOTAL" METALS

ABORATORY NUMBER	METHOD	EXTRACT-ANT	TIME OF EXTRACTION	ADDITIVES	FILTRA-TION	BACKGROUND CORRECTION	STANDARDS	ADDITIONAL INFORMATION
1	AAS	$HClO_4/H_2O_2$		None	P541	None	Proprietary	
2	AAS	HNO_3/H_2O_2		$LaCl_3$	GF/C	"	"	
3	AAS	HNO_3/H_2O_2		$LaCl_3$	P40	Cd, Ni		A-C asned at 400°C overnight
4	AAS	HNO_3/H_2O_2					Proprietary	
5	AAS	HNO_3/H_2O_2		$LaCl_3$	P40	All elements		
6	AAS	HNO_3/H_2O_2	2h (soils 0.5h)	None	None	" "		
8	AAS	HNO_3/H_2O_2	0.75 h	$LaCl_3$	P540	As required		
9	AAS	HNO_3/H_2O_2		$LaCl_3$	P541	All elements	Proprietary	N_2O/C_2H_2 flame prCr
10	AAS	HNO_3/H_2O_2	0.75 h	$LaCl_3$	P540	As required		
11	AAS	HNO_3/H_2O_2		None	P540	None	Proprietary	
12	AAS	$HClO_4/HNO_3$		$LaCl_3$	GF/C			
13	AAS	HNO_3/H_2O_2		$LaCl_3$	GF/B			
15	AAS	HNO_3		$LaCl_3$	GF/C	All elements		
16	AAS	HNO_3/H_2O_2						Sample E digested HNO_3/H_2O_2
18	AAS	$HNO_3/H_2SO_4/H_2O_2$	Several h	$LaCl_3$	P1	All elements		
19	AAS	$HNO_3/HClO_4$			P543	All elements		
20	AAS	$HNO_3/HClO_4$	8 h		P543	Cd, Pb, Ni, Zn		
21	AAS	HNO_3		NH_4Cl	P42		Proprietary	Sample A asned at 420°C
22	AAS	HNO_3/H_2O_2		$LaCl_3$		None		
23	AAS	HNO_3/H_2O_2		$LaCl_3$	P40	Cd, Pb, Ni and Zn	Proprietary	$HNO_3/HClO_4$ digestion D and E
24	AAS	HNO_3		$LaCl_3$		Cd, Pb, Ni and		
25	AAS	$HNO_3/HClO_4$			P541			
26	AAS	HNO_3/H_2O_2		NH_4Cl	P1	All elements	Proprietary	
27	AAS	$HNO_3/HClO_4$		NH_4Cl for Cr	P1	" "	" "	E digested; N_2O/C_2H_2 flame Cr
28	AAS	HNO_3/H_2O_2	0.8on at 170°C		P540	" "	" "	
29	AAS	HNO_3/				All except Cr		N_2O/C_2H_2 flame Cr
30	AAS	H_2SO_4/				" "		" " "
31	AAS	H_2O_2*				" "		" " "
32	AAS	HNO_3/H_2O_2		$LaCl_3$	P541		Proprietary	
33	AAS	HNO_3/H_2O_2		$LaCl_3$				
34	AAS	HNO_3/H_2O_2		None		All elements	Proprietary	
35	AAS	HNO_3/H_2O_2		NH_4Cl for Cr		All except Cu, Cr	"	
36	AAS	HNO_3/H_2O_2			P542	None		
38	AAS	HNO_3/H_2O_2			P1	All elements	Proprietary	Reflux extraction
39	AAS	HNO_3/HCl		$LaCl_3$	P542		"	Asn at 420°C for 16 h then extract
40	AAS	HNO_3/HCl		$LaCl_3$	GF/A	All elements	"	Asn at 400°C for 16 h then extract
41	AAS	HNO_3/H_2O_2			P541	" "	"	
42	AAS	HNO_3/H_2O_2			GF/C	" "		

*DEPARTMENT OF THE ENVIRONMENT Analysis of Raw Potable and Waste Waters, p166, Method C HMSO, 1972.

TABLE D1 METHODS, "TOTAL" METALS

LABORATORY NUMBER	METHOD	EXTRACTANT	TIME OF EXTRACTION	ADDITIVES	FILTRATION	BACKGROUND CORRECTION	STANDARDS	ADDITIONAL INFORMATION
43	AAS	HCl/H_2O_2	2h at 100°C	$LaCl_3$	P542	All elements		
44	AAS	HNO_3/HCl			P540			Ash at 400°C for 18h then extract
45	AAS	HNO_3/H_2O_2						
46	AAS	HNO_3/H_2O_2	3h					
47	AAS	HNO_3			P54	Cd, Pb, Ni, Zn		N_2O/C_2H_2 flame for Cr
48	AAS	HNO_3/H_2O_2	0.5 h		GF/C			
52	AAS	HNO_3/H_2O_2	3 h		Sintered glass			
53	AAS	HNO_3/H_2O_2			P540	Cd, Cu, Pb, Ni, Zn		N_2O/C_2H_2 flame for Cr
56	AAS	HNO_3/H_2O_2						" "
57	AAS	$HClO_4/HNO_3$			P541			Cr, reference p. 183
58	AAS	HNO_3/H_2O_2						
59	AAS	HNO_3/HCl			P1	Cd, Pb, Ni and Zn		Ash at 400°C for 24h then extract
60(1)	AAS	HCl	Reflux 0.25 h	K^+ 2000 mg/l	None	Cd, Pb and Ni		N_2O/C_2H_2 flame for Cr
60(2)	AAS	HNO_3	" "	" "	"	" " "		" " "
60(3)	AAS	HCl/HNO_3	" "	" "	"	" " "		" " "
61	AAS	HNO_3						
62	AAS	HNO_3						
63	AAS	HNO_3/H_2SO_4		NH_4Ac for Pb	GF/C	Cd and Zn		N_2O/C_2H_2 flame for Cr
64(1)	AAS	HNO_3		$La(NO_3)_3$	P54		Proprietary	
64(2)	AAS	HNO_3		None	None		"	
65	AAS	HNO_3	Reflux 0.25 h	None	None		"	
66	AAS	HNO_3			P540			Ash at 450°C for 4 h
67	AAS	$HNO_3/H_2SO_4/H_2O_2$			P542	All elements		
68(1)	AAS	HNO_3/H_2SO_4			Sintered glass			
68(2)	AAS	HCl/ HNO_3/ H_2O_2	2 h		P541			
69	AAS		2 h			All except Cr	Proprietary	N_2O/C_2H_2 flame for Cr
70	AAS	HNO_3/H_2SO_4			None	None	"	
71	AAS	HNO_3/H_2O_2		$La(NO_3)_3$	P40	All except Cu, Cr	"	
72	AAS	HNO_3	Reflux 0.25 h	None	None	Cd, Ni and Pb		
73	AAS	HNO_3	"	"	"		Proprietary	N_2O/C_2H_2 flame for Cr
74	AAS	HNO_3	"	"	"			
75	AAS	$HNO_3/HClO_4$		"	P541	All elements	Proprietary	
76	AAS	$HNO_3/HClO_4$		"	"			
77	AAS	$HNO_3/HClO_4$		"	"		Proprietary	
78	AAS	HNO_3				Cd, Pb and Zn	"	
79	AAS	HCl						Ash at 550°C then extract
80	AAS	$HNO_3/HClO_4$			P44			
81	AAS	HNO_3/H_2O_2	Reflux 4 h		P42			

TABLE D1 METHODS, "TOTAL" METALS

LABORATORY NUMBER	METHOD	EXTRACTANT	TIME OF EXTRACTION	ADDITIVES	FILTRATION	BACKGROUND CORRECTION	STANDARDS	ADDITIONAL INFORMATION
82	AAS	HNO_3/H_2SO_4		NH_4Ac				
83	AAS	HNO_3/H_2SO_4		HN_4Ac	P1			
84	AAS	HNO_3/H_2O_2			P1	Cd, Pb, Ni and Zn	Proprietary	N_2O/C_2H_2 flame for Cr
85	AAS	HNO_3/H_2O_2		$LaCl_3$	P541			Ash A, B, C at 500° 3h then extract
86	AAS	HNO_3/H_2O_2/HCL		8HQ for Cr	P540			
87	AAS	HNO_3/H_2O_2			P540			
88	AAS	HNO_3/H_2O_2/HCL	3 h	$LaCl_3$	None			
89	AAS	HNO_3			"			
90	AAS	HNO_3		None	"	All elements		
91	AAS	HNO_3	1.5 h	None	None	All elements		N_2O/C_2H_2 flame for Cr
92	AAS	$HNO_3/HClO_4$		None	P541	All elements	Proprietary	
49	AAS	HNO_3/H_2O_2		$LaCl_3$	P540	" "	"	Ash at 400° C overnight then extract
50	AAS	HNO_3/H_2O_2		"	"	None		" "
51	AAS	HNO_3/H_2O_2		"	"	"	"	" "
54	AAS	HNO_3/H_2SO_4		NH_4Ac	P1	Cd, Ni, Pb		
55	AAS	HNO_3/HCL		$LaCl_3$	P52	All elements		Ash at 450° C overnight then extract
7	AAS	HNO_3/H_2SO_4			P541	None		

APPENDIX E - RESULTS FOR 'TOTAL' CONCENTRATIONS OF CADMIUM IN SLUDGES AND SOIL

TABLE E1. Summary of results for 'total' cadmium

n = 10 unless stated; †n = 8, ‡n = 3-6. * indicates significant between-batch error (P<0.05)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
1	f	10.1	58.4	67.7	4.5	12.9	15.8	10.4	61.2	70.9	23.5	65.1	87.6	5.7*	3.5	7.0
2	a	17.1	36.2	49.7	3.8*	4.9	7.9	14.7†	25.4	40.5	29.5*	-6.9	32.3†	10.4*	-3.5	11.7
3	k	15.1	-13.9	21.4	5.2*	-1.5	4.0	10.1	-5.4	11.8†				3.3*	-2.2	4.7
4	a	9.1	6.9	12.6	4.5*	15.1	19.7	40.8*	4.5	38.7				2.6	18.0	19.7
5	a	15.8	-4.1	12.9	5.7*	-4.9	9.2	18.2*	-1.1	14.9	5.3	-47.5	50.8‡	24.2*	-19.0	34.7
6	a	7.6	-4.4	8.6	3.1*	3.4	6.0	9.2	-7.5	12.1	76.3	-87.3	93.8†	2.3	-1.6	2.8
7	g	28.9*	-20.1	38.8	5.8*	-5.5	10.2	37.2*	-0.03	34.4†	28.3*	82.3	121.6	1.9	0.04	1.1
8	a	8.1	-14.2	18.3	6.4	-8.8	7.4	13.2	-10.8	17.7				4.6*	5.1	8.7
9	a	4.2*	-3.8	7.0	2.3	2.3	3.7	9.3	-5.3	10.4				1.8	1.2	2.3
10	a	7.8	0.2	6.2	6.2	14.1	18.2	28.3	-11.7	26.2	26.4	4.5	37.0‡	4.1*	9.4	13.0
11	a	9.1	62.9	71.5	3.8	11.1	13.6	13.3*	20.8	36.8	24.6	-18.0	29.6	18.4	6.7	18.0
12	d	28.9*	-4.3	25.6	4.0*	8.1	11.5	51.3*	-13.6	47.3				4.0	0.4	2.8
13	a	10.4	-3.2	9.1	5.0*	-5.4	9.2	16.0*	-22.0	32.2	37.3*	-75.3	82.8	3.8	-3.9	6.0
15	b	35.6*	-19.0	42.2	33.7*	-10.4	38.9	37.7*	14.0	54.5†				2.1*	7.7	10.3‡
16	a	6.4	-6.6	10.1	2.9	0.5	2.2	14.8	-2.8	11.1	37.3	51.9	118.6‡	3.6*	-4.2	7.1
18	j	19.6	-9.2	19.5	5.4	-2.6	5.6	38.9	13.4	42.7†				7.9*	4.3	11.0
19	d	3.0*	1.3	3.7	3.8*	3.3	6.4	24.0	-8.9	21.6				4.9*	2.0	6.0
20	d	4.1*	12.8	16.4	4.3*	3.3	6.9	9.3*	8.6	18.1†	13.6*	-9.6	19.7			
21	b (k for A)	3.9	-13.5	15.5	3.9	-10.9	13.0	4.8	-14.9	17.2	7.4*	-89.9	90.5	3.1*	2.3	4.9
22	a	19.9	21.6	35.7	8.9*	1.2	8.5	12.8	38.4	48.8	57.1	-0.8	33.5	3.8*	-4.3	7.2
23	a (d for D)	12.1	-13.4	19.5	11.3	-7.3	13.4	19.9	-3.0	14.2				13.2	3.9	11.9
24	b	4.8	-1.9	4.6	3.4*	4.1	6.9	12.3	-1.8	8.8				6.1*	10.6	16.0
25	d	7.0	-4.4	8.3	3.3	7.2	9.3	17.2	-5.0	14.4				2.6	-0.4	1.8
26	a	9.5	-10.5	15.5	2.6	-1.7	3.2	18.7	-2.3	12.9	41.1*	-66.2	76.9			
27	d	10.8	-13.7	19.1	7.1	-2.8	6.8	9.3	-15.0	19.6				17.5	-8.5	17.8
28	a	10.8*	0.01	8.6	4.1*	-3.8	7.1	0.0	8.9	8.9	30.7*	92.1	137.2	7.1*	-1.9	7.6
29	j	7.8*	-16.1	23.0	5.2*	-1.7	5.8							3.3*	2.4	5.0
30	j				8.1	-13.3	17.4							3.9	6.7	9.1
31	j				19.7	-41.0	49.7	12.0*	93.3	115.1†				7.3*	3.5	9.8
32	a	13.7*	-3.3	13.8	6.8*	4.0	9.6	24.4*	8.1	25.6				4.6*	6.3	10.2
33	a	63.2	6.0	83.3	24.2*	-19.7	34.7	42.9	22.1	83.8‡				36.3*	-11.9	41.9†
34	a	5.2	-3.1	6.5	3.6	2.1	4.6†	8.6	14.9	21.5†	21.1	-85.3	87.4†	5.4*	1.2	6.3†
35	a	9.9	-14.8	19.7	4.0	-2.0	4.3	16.9	-20.4	28.2				3.1	1.1	3.0
36	a	6.5	9.8	14.4	3.2	11.6	13.9‡	7.2	-1.8	6.8‡	40.5*	-49.9	77.1‡	26.9	-15.3	42.2‡
38	a	5.4	-9.1	12.3	4.5*	-2.5	6.4†	3.9	-7.0	9.4†	22.7	-86.4	88.5†	1.4	1.7	2.7†
39	k	34.7*	-4.7	30.5	25.6*	-10.2	28.2	130.0	28.2	140.1†				25.2*	7.8	30.0

TABLE E1 (Cont'd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
40	k	5.0*	-6.5	10.2	3.1*	-0.02	2.5	21.6*	7.6	26.3				6.0*	1.2	8.0‡
41	a	7.0*	27.2	34.0	6.2	4.0	7.8	18.9	22.5	35.9	154.8	102.0	283.2	3.0	-8.5	10.1
42	a	15.8	-4.3	14.0	5.8	11.8	16.1†	15.7	-18.3	26.9†	64.3	64.0	103.0‡			
43	e	19.0	4.7	16.2	6.9	2.8	6.9	25.8	10.4	26.9				9.8	3.9	9.9
44	k							13.4	20.7	30.0				2.2	-4.6	5.8
45	a	8.2	60.5	68.1	10.4	5.4	11.7	19.3	11.2	25.0				3.6	8.3	10.5
46	a	10.3	75.3	85.7	4.5*	-6.2	9.4	2.0	-2.2	3.3				2.6	-5.8	7.4
47	b				3.4	12.5	14.7							2.2*	-1.1	2.9
48	a	4.3	-2.7	5.1	5.9*	6.0	11.0	10.7*	10.0	19.6				4.2*	3.5	7.0
49	k	7.1	10.3	14.8										3.4	-4.2	6.2
50	k	12.4	24.6	33.5										8.3	6.7	11.8
51	k	5.6*	23.8	29.3										10.0	14.5	21.1
52	a	7.1	4.6	8.5	6.9*	-1.4	6.8	8.4	7.1	12.3	1.4	1.7	2.5	3.9*	1.2	4.4
53	a	19.9	22.0	37.7	4.0	22.1	24.9	24.7	18.5	35.4				5.1*	25.7	30.7
54	g				22.8*	-23.7	38.0							11.2*	-1.9	10.5
55	k				6.0*	-0.3	4.9	7.7	-72.1	73.8‡				1.9	-3.9	4.9
56	a	15.3*	7.7	20.6	21.2	-3.5	19.7	27.3*	14.4	39.8				4.6*	0.6	4.2
57	d							13.0	15.0	27.3‡				1.9	-1.4	6.7‡
58	a	11.7	54.1	64.6												
59	k	24.4*	-19.0	34.4	5.9*	3.2	8.1	26.1	-6.1	20.3				3.5	-2.3	22.1
60A	h	2.5	-7.6	9.0	1.3	-1.1	1.8	7.2	-6.7	10.6						
60B	b	2.9	-8.2	9.7	1.7	-1.5	2.4	7.2	-6.7	10.6						
60C	c	2.5	-7.6	9.0	1.9	-0.7	1.7	7.2	-6.7	10.6				2.2	-4.6	5.8
61	b	6.4	-2.4	5.8	2.8	-3.6	5.1	13.9	-5.5	13.2				1.8*	-2.7	4.0
62	b										17.2	105.8	126.3			
63	g	39.6*	-66.6	74.3	27.0*	-37.8	51.4	16.3	-42.6	48.9†						
64A	b	4.7*	-16.9	19.8	4.7*	-5.7	9.1	9.4*	-20.9	26.5				4.1*	-5.4	8.4
64B	b	12.5	-14.7	20.8	5.8	-1.9	5.2	20.9	-25.6	34.6						
65	b	15.6	-23.8	30.7	5.7*	-14.0	17.6	35.2*	-21.6	43.5				10.2*	1.6	10.0
66	k	15.7*	14.7	28.5	5.2*	-0.4	4.5	17.5*	0.6	14.5	30.2	9.5	31.6†	3.2	0.4	2.2
67	j				24.9*	-54.1	63.2									
68A	g	31.3	-56.8	64.6‡	15.7	-38.8	44.4	33.4	-30.9	44.3				6.1	3.9	7.6
68B	i	2.4	21.2	23.9	3.1	14.1	17.4	8.8	10.9	20.2†	38.3	-58.0	73.3			
69	i	4.7*	-7.1	9.6	3.5*	-5.4	7.9	15.1*	-6.7	17.3				2.2*	-1.1	2.9
70	g	22.9	21.9	42.1	32.5*	-20.5	41.5	44.7*	29.6	75.5	46.2	67.4	158.2‡	2.9	-3.5	5.1
71	a	3.4	-7.9	9.7	3.8	-2.1	4.3	13.2	17.7	26.7				<0.4	-2.7	2.7‡

TABLE E1 (Cont'd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
72	b	4.4	11.5	14.4	5.1	17.7	21.1	17.1	0.9	10.8	58.1	-23.5	107.6‡	4.6	-3.1	5.6
73	b	5.6	-0.1	3.4	3.5*	7.2	10.2	12.1	-7.5	14.0				7.4	10.9	15.7
74	b	3.6	-10.8	12.7	2.5*	-6.1	7.9	11.3	-4.2	10.4				3.1*	-2.2	4.6
75	d	4.2	-12.6	14.7	2.4*	-0.9	2.8	2.9	-5.5	7.2				2.2	-4.6	5.8
76	d	1.7	-14.2	15.1	1.7	-8.5	9.4	2.9	-21.3	22.6				1.2*	-11.9	12.7
77	d	3.6	-5.0	7.0	2.0*	5.1	6.7	12.1*	3.7	13.7				1.6*	-0.4	1.7
78	b	7.3	-9.8	5.2	3.8	11.1	13.6	10.7	-2.6	8.5				2.3	2.0	3.5†
79	k				40.3*	20.0	58.9	18.7	32.4	48.9	85.4*	273.3	572.4†	17.3	-0.7	10.7
80	d	7.9	4.9	9.7	7.1	3.5	7.8	11.4*	-12.9	20.9	82.7	-88.4	93.9	1.9	-1.8	2.9
81	a	7.5*	-27.5	31.6	3.4*	-22.6	24.7	10.3*	-27.0	33.0						
82	g	59.6*	-29.5	63.8	24.7*	-5.4	24.0	47.8	0.3	31.4						
83	g	8.7	-18.4	22.5	4.6	-6.6	9.1	14.8	-16.7	23.9						
84	a	4.9	-12.5	14.9	4.9*	-6.8	10.6	11.9*	-20.1	27.4				2.0	-5.4	6.5
85	k(a for D)	7.4	-6.4	10.4	8.2*	-1.5	8.0									
86	i	14.2	-6.1	14.1	3.6*	-10.2	12.8	37.6	34.0	63.2						
87	a	8.3	21.7	27.6	7.2*	1.3	7.1	16.0*	21.8	37.0						
88	i	11.9	25.4	31.2	9.4	16.8	23.2	40.8	13.4	40.2						
89	b	6.0	7.3	13.2	0.0	3.7	11.0‡	19.2	5.0	28.7‡				<0.4	-4.0	4.1†
90	b	6.1	-7.3	18.2	2.7*	-0.6	2.7	4.8*	-6.2	10.4†				3.6*	-3.0	6.2
91	b	0.2*	-12.1	12.2	10.4*	5.5	13.9	35.2	-16.5	33.5				<0.4	5.1	5.2
92	d	26.9*	4.9	27.8	9.0*	-4.4	11.4	19.6	-43.1	49.5	27.9*	-86.9	90.2	4.0	-8.8	10.9

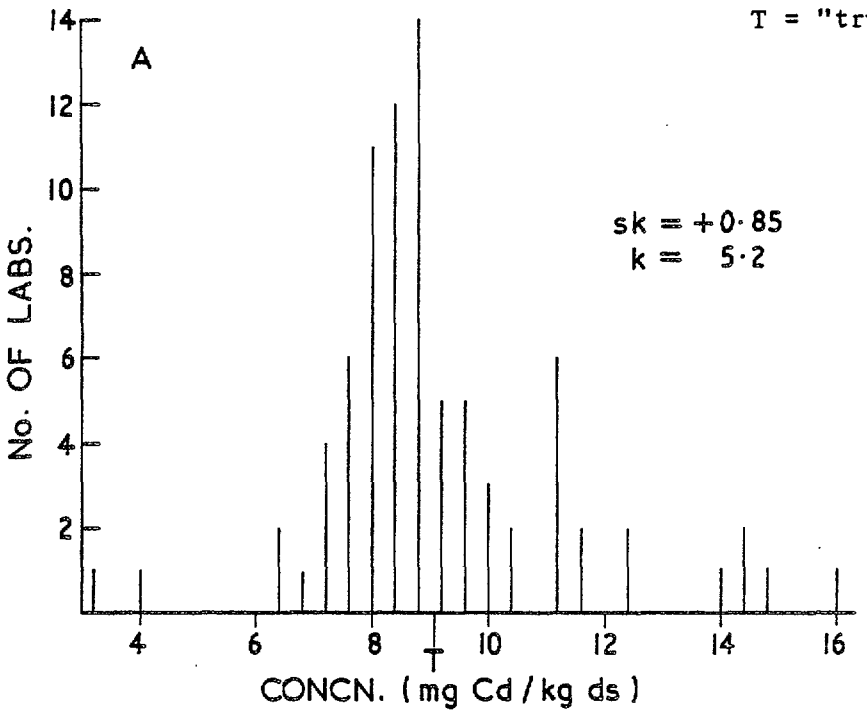
TABLE E2. Statistics of populations of grouped laboratory means: cadmium

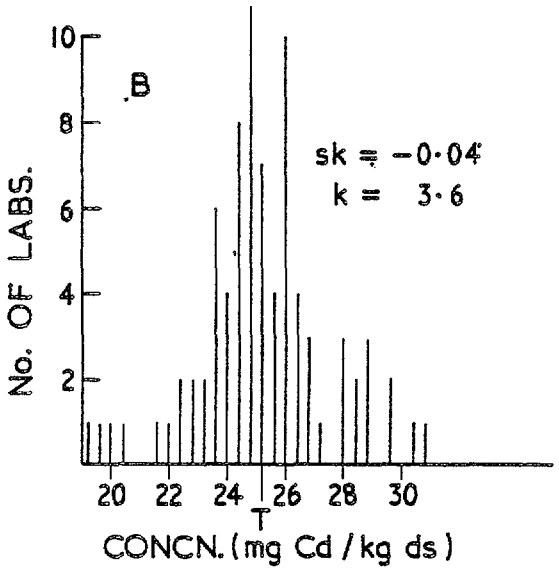
Sample	Mean, $\bar{x}$	Standard deviation, s	Number of groups	Skewness	Kurtosis
A	9.107	2.100	33	0.846	5.16
B	25.19	2.259	30	-0.041	3.64
C	3.591	0.586	30	0.149	2.81
D	0.971	0.818	N/A	1.309	5.04
E	0.2572	0.0158	32	-0.035	4.12

Units for $\bar{x}$ and s are mg/kg dry basis (A-D) or mg/l (E)

Figure E. Histograms of individual laboratory mean concentrations in samples A-E for cadmium

T = "true" value, sk = skewness and k = kurtosis





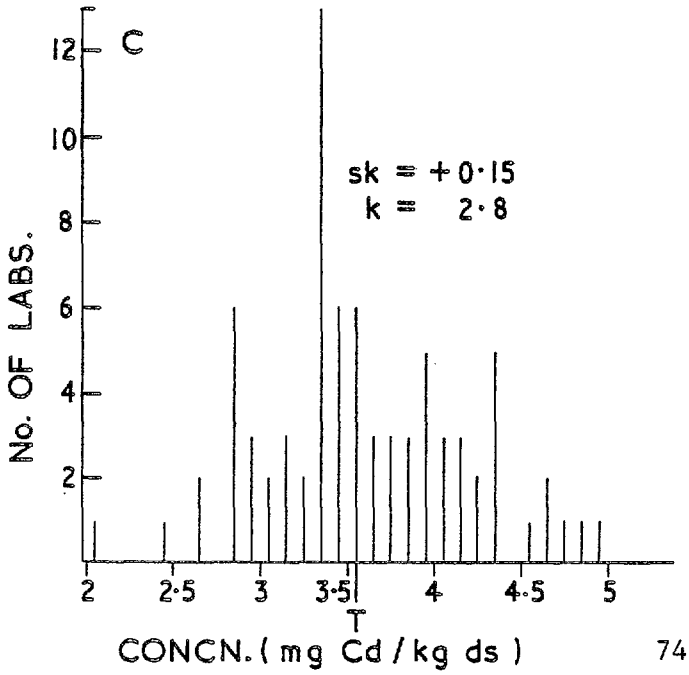
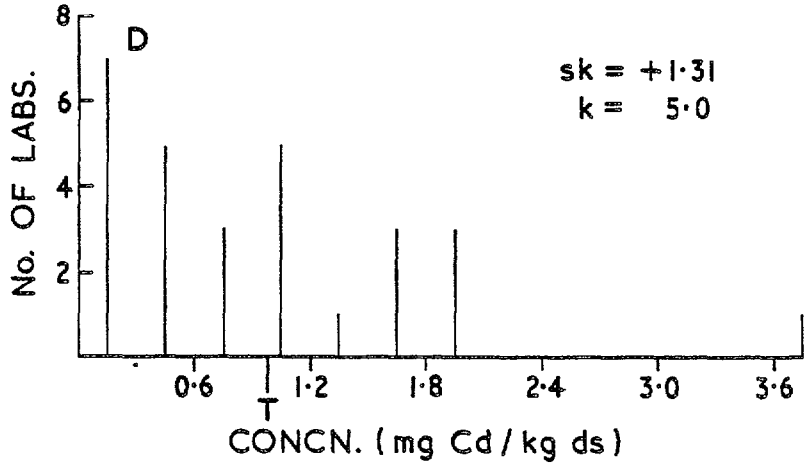
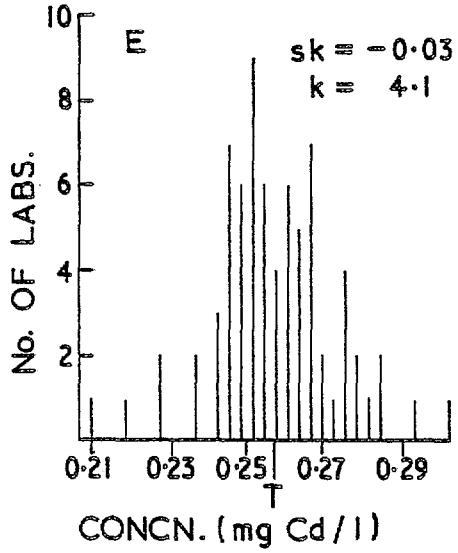


Figure E continued





APPENDIX F. RESULTS FOR TOTAL CONCENTRATIONS OF CHROMIUM

TABLE F1 Summary of results for "total" chromium

n=10 unless stated † n=8 ‡ n=3-6 *indicates significant between-batch errors (P=<0.05)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
1	f	7.7*	55.5	64.8	5.0*	12.3	15.6	12.4	63.7	75.5	17.4*	32.6	50.7	3.2	3.9	5.9
2	a	15.8*	-41.3	48.8	5.6*	-50.2	52.3	19.8	-54.4	59.7	9.4*	-53.4	56.9	2.5*	3.6	5.7
3	k	2.8	32.1	34.3	5.6	2.1	4.2	11.0	-8.8	14.6	6.0	-11.6	14.7	2.5	-18.3	19.4
4	a	21.9*	15.4	35.2	10.2	-30.3	35.1	28.9*	-14.5	33.4	40.8*	3.6	36.1	12.4*	23.6	36.1
5	a	25.6*	-39.5	51.6	13.8*	-33.3	40.7	30.4	-54.7	62.7	22.6*	-56.4	64.1	14.2*	-11.9	22.0
6	a	18.1*	-20.7	32.3	6.3	7.7	11.6	11.7*	-4.4	12.8	16.4*	11.5	26.2	11.9*	11.3	22.0
7	g	9..	13.1	19.0	14.7*	0.4	12.3	19.3*	54.9	81.0	27.0*	169.4	226.4	2.8*	5.1	7.4
8	a	7.6*	27.0	34.4	4.2*	-2.1	5.3	12.9*	-10.6	19.3	13.2*	3.6	14.3	10.0	-15.3	15.9
9	a	24.1*	-57.5	65.8	10.1*	-38.1	43.1	70.7*	-78.3	92.7‡	36.5*	-71.2	83.3‡	7.0	-30.1	33.0
10	a	3.5	48.1	51.1	3.0	10.1	12.0	6.3*	8.6	13.7	17.1	5.0	15.4	6.9	-5.2	8.9
11	a	17.6*	-64.1	69.3	7.8*	2.7	9.2	40.5	-5.3	27.6	31.4*	-68.2	75.9	13.3*	-3.7	13.4
12	d	18.2*	-13.2	25.9	5.1*	-3.5	7.2	32.6*	-24.1	44.3	15.5	-22.8	29.8	2.7*	-9.0	11.0
13	a	5.4*	-52.5	54.5	5.3	1.5	4.6	5.3	-65.0	66.0	8.8	-84.0	84.8	7.0	11.8	16.3
15	b	27.8*	-47.3	59.1	14.1*	-72.2	75.6	26.7	-49.0	56.9	33.8*	-33.6	51.9	19.8	-46.3	54.9
16	a	3.8	-28.3	29.7	3.3	2.8	4.8	6.3*	-12.5	16.8	8.5	-35.4	38.6	2.0*	3.5	4.6
18	j	23.5*	-18.1	33.8	10.0*	-24.7	30.8	16.2	-35.0	41.1	9.8	-12.3	17.3	5.9*	-4.4	8.9
19	d	4.0*	-10.7	13.3	7.1*	-8.4	13.6	8.0	-12.5	16.6	5.8	-23.8	26.3	4.3*	7.9	11.7
20	d	7.2	-22.9	26.2	3.6	12.8	15.1	4.2	15.5	18.3	6.2*	-5.9	10.5			
21	b (k for A)	2.2*	-8.7	10.2	2.3	-3.9	5.2	3.5	-17.3	19.0	3.6*	-19.2	21.4	2.1	17.2	18.5
22	a	38.1*	8.7	42.5	16.0*	-10.8	22.4	25.0*	-16.3	33.3	66.3*	12.4	73.5	10.8*	-7.4	15.6
23	a (d for D)	9.0	-6.4	11.3	9.2*	-19.3	26.0	11.2	-7.2	13.2	38.1*	-45.8	62.0	20.1*	-25.1	36.8
24	b	15.2*	-55.6	60.9	10.5*	-40.8	45.8	22.9*	-63.4	70.3	24.3*	23.8	57.7†	13.3	-20.2	26.2
25	d	4.4*	-7.8	11.0	7.6*	17.3	24.1	8.8*	7.6	14.8	15.5	-15.1	22.7	6.1	7.0	10.7
26	a	3.2	-26.6	28.0	2.8	2.1	3.8	3.5	7.9	10.1	14.2	17.3	26.9			
27	d	13.8	20.7	30.4	14.2*	9.6	22.3	14.6*	17.8	31.8	9.7*	34.1	44.6	20.1*	8.8	26.6
28	a	2.9*	38.5	41.6	1.3	2.8	3.6	5.2	1.9	5.0	4.7*	8.5	12.4	2.8	1.8	3.6
29	j	5.7*	48.2	54.9	2.4	9.9	11.4	4.3	27.5	30.7	18.0*	64.8	87.8	3.7*	-13.1	15.7
30	j	12.6*	57.5	73.6	13.0	21.9	31.1	55.1*	276.9	437.9	33.5	126.9	170.9	6.9*	-15.4	19.9
31	j	27.7*	-2.3	24.4	19.0*	-20.1	31.9	46.9*	27.9	76.8	31.4*	17.4	47.4	2.3	-9.9	11.0
32	a	16.7	-58.9	62.9	6.6	-55.4	57.1	35.6*	-58.9	70.7	27.1*	-70.4	76.8	12.6*	3.1	13.7
33	a	51.7*	6.4	51.3	44.8*	-31.6	56.2	6.9	-37.4	62.4	37.7	14.1	42.9	10.7*	6.8	17.6
34	a	16.8	-31.6	39.3	3.8	-8.3	10.7†	12.5	50.0	60.4†	20.1*	-48.0	57.8†	1.5	-1.4	3.1†
35	a	7.3	-18.9	22.3	12.3*	-33.9	40.4	27.5	-44.7	53.5	20.9*	-19.1*	32.4	3.2	12.2	14.3
36	a	40.8	-28.1	47.7†	33.3	-7.3	28.0†	45.2	15.5	25.2†	19.7	-34.7	45.2‡	5.8	-0.7	7.4‡
38	a	9.8*	-36.6	42.3	3.9	-7.3	9.6†	15.8	-13.3	22.2†	9.2*	-43.5	48.3†	7.5	-8.5	13.1†
39	k	31.8	1.1	19.7	7.0*	0.6	6.2	46.3	17.8	49.5	44.7*	46.1	98.6	4.0	17.4	20.1

TABLE F1 (contd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
40	k	3.2*	-32.1	19.7†	4.0*	12.8	16.9†	4.4	-7.9	11.1†	13.6	2.3	13.7‡	12.3*	14.6	37.7‡
41	a	10.3*	-22.4	28.6	27.4	11.3	29.0	17.0*	3.9	18.4	12.2	3.1	10.3	5.8*	-29.2	32.6
42	a	23.9	-17.4	30.7†	14.0*	38.2	43.1†	19.2	30.0	46.7†	16.7	-45.7	52.5‡	0.4	2.9	3.6‡
43	e	15.4*	28.1	44.1	4.8*	-0.2	3.8	14.6*	-2.4	13.5	20.6*	32.2	56.4	13.9*	-2.4	13.1
44	k							5.2	-8.4	11.2				4.1*	6.9	10.2
45	a	15.4*	-30.2	38.8	12.2*	-10.6	19.3	12.2*	-17.0	24.8				12.3*	17.2	29.0
46	a	5.5	-7.8	10.7	1.6	-3.9	4.8	2.0	-3.1	4.3				1.7	-1.6	2.5
47	b				1.3*	22.3	23.6							1.1*	4.5	5.4
48	a	7.9*	-25.4	30.2	5.6*	6.3	11.1	4.5*	2.4	6.1				6.9*	12.6	19.6
49	k	5.7*	20.9	26.5										1.7	-0.7	1.6
50	k	6.6	7.7	11.8										3.6	1.1	3.3
51	k	6.3	18.8	23.1										7.4	0.2	4.4
52	a	12.2*	1.5	11.5	3.1*	30.3	33.5	2.3	33.2	34.9	6.2*	60.6	68.3	1.2	1.8	2.6
53	a	2.9	68.7	71.6	2.8	22.3	24.3	5.5	19.1	23.3				1.7*	5.0	6.5
54	g				12.3*	33.1	46.4							3.5*	4.7	7.7
55	k				2.5*	4.0	6.0				5.6*	15.4	20.1	0.4	-6.5	6.6
56	a	18.9*	43.9	64.8	11.1	6.8	13.7	22.1	64.7	85.8	34.2*	-0.6	26.1	16.1*	1.4	14.5
57	d							12.9	6.2	17.5‡	12.3	33.4	46.9‡	2.0	1.9	3.4‡
58	a	8.5	15.9	21.6												
59	k	11.9*	316.2	356.4	7.1*	39.3	46.8	35.6	150.6	202.2	26.6*	434.9	548.2	1.6*	4.0	5.3
60A	h	0.8	34.9	35.6	1.5*	8.8	10.1	2.1	-0.9	2.1	2.2	-0.5	1.8			
60B	b	2.5*	40.4	43.0	1.2	9.6	10.4	3.2*	-5.4	7.7	2.8	-9.1	10.5			
60C	c	1.3	42.5	43.7	1.6*	9.6	11.0	2.0	2.4	3.6	2.5	2.6	4.1	1.5	-5.3	6.1
61	b	9.4*	-4.2	11.5	5.3	1.0	4.1	10.2*	-2.6	10.5				1.9	2.5	3.6
62	b										7.1*	-26.3	30.3			
63	g	5.8	30.9	35.2	6.5	2.2	6.1	11.7	6.6	13.8	28.5	36.4	58.9			
64A	b	9.5*	-73.9	75.9	29.4*	-30.2	47.0	4.1	-73.7	74.3	15.5*	-71.5	75.1	17.4*	-22.1	32.7
64B	b	9.0*	-49.4	53.0	8.3	-24.1	27.8	11.4	-33.6	38.0	15.0*	-67.0	70.8			
65	b	3.6	-26.6	28.1	5.3*	5.2	9.7	6.2*	1.1	6.1	9.9	-34.8	38.5	5.0*	1.8	6.0
66	k	1.6	51.3	52.8	2.6*	14.7	16.9	5.8	15.9	19.8	7.4	16.0	21.0	1.6	3.4	4.4
67	j	7.1*	39.2	47.1	13.1*	72.7	91.0	12.4*	54.0	68.9	10.0	125.8	139.0			
68A	g	16.5	3.3	18.0†	30.4	-17.1	31.8	21.9*	11.5	30.7	30.4*	59.5	99.2	7.2	7.7	12.3
68B	i	2.7	61.5	64.8‡	8.1	14.5	23.3‡	5.2	28.6	34.9	34.8	12.7	50.0			
69	i	2.5*	63.3	65.6	4.3	30.3	33.5	6.0	38.3	43.0	6.0*	46.4	53.5	1.6	3.3	4.3
70	g	18.7	-20.6	29.2	9.9	-13.7	18.6	19.4	17.3	30.5	26.8*	30.1	57.5	3.9	-13.1	15.1
71	a	14.3	-55.4	59.1	12.3*	-51.6	56.4	30.0*	-57.1	67.3	13.0*	-62.5	66.4	1.7	4.6	6.3

TABLE F1 (Contd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
72	b	6.8	-46.6	48.7	6.0	2.5	6.1	4.1	-8.1	10.3	9.2	-11.1	15.8	6.2	2.0	5.6
73	b	11.4	54.7	64.9	5.5*	11.1	15.8	13.7	19.5	29.0	12.1*	1.4	11.2	10.7*	12.5	22.2
74	b	6.7*	-36.9	40.4	6.4*	-7.9	12.8	6.0*	-19.7	23.5	22.7*	-35.1	47.2	7.9*	5.4	12.2
75	d															
76	d	3.7	53.8	57.1	2.9	21.7	23.8	3.5	42.2	45.1	4.7	44.1	48.0	4.7*	11.0	15.2
77	d				9.8*	7.3	15.8									
78	b	13.2*	-22.4	30.7				7.6*	1.1	7.1	20.5*	-24.0	36.6	6.7*	12.8	19.6*
79	k	18.0*	-21.1	32.7	11.5*	-27.8	34.2	15.7*	-16.4	26.4	44.7*	-29.0	53.6	7.2	-21.1	24.4
80	d	6.4	28.5	33.2	11.4*	9.1	19.1	9.2*	-4.8	11.7	7.8	-20.8	24.4	1.7*	9.6	11.1
81	a	3.6	-31.2	32.7	5.5*	10.4	15.4	4.1*	-9.6	12.5	5.1*	-16.9	20.2			
82	g	22.8*	-22.1	35.8	22.0*	35.7	60.1	24.9*	49.6	78.7						
83	g	4.2	47.7	51.3	6.7	5.1	8.0	5.7	35.8	40.2						
84	a	7.2*	56.7	65.5	5.8*	10.9	15.9	7.6	9.3	14.1	9.6*	13.2	21.7	1.3	1.8	2.6
85	k (a for D)	3.2	23.0	25.2	5.9*	-5.7	10.2	31.2	-19.7	34.2	14.1*	11.5	23.8			
86	i	11.3*	-1.1	10.1	15.2*	7.8	20.8	12.8*	22.5	35.2	15.6*	11.2	24.8			
87	a	4.8*	-16.1	19.2	5.7*	8.2	13.2	7.6*	-14.8	19.8						
88	i	27.0*	28.0	54.9	7.7*	4.7	10.9	28.8*	3.3	25.9						
89	b	11.3	180.6	218.2‡	3.6	40.3	48.6	9.3	449.1	509.2‡	25.0			0.5	-12.8	13.5‡
90	b	11.9*	-14.8	26.1	4.7*	2.5	6.9	11.2	0.3	6.8	5.2	48.3	52.8	13.9*	12.7	38.7‡
91A	b	11.8*	37.9	50.7	8.1*	4.6	11.3	14.5	9.7	18.9	17.0*	31.2	49.1	3.5*	3.7	6.6
91B	b													2.0	-3.9	5.0
92	d	6.7*	77.5	86.9	9.3*	6.2	13.9	7.9	29.6	39.2‡	5.7*	57.4	64.3	6.9*	-1.2	6.4

TABLE F2. Statistics of populations of grouped laboratory means: chromium

SAMPLE	Mean, $\bar{x}$	Standard deviation, s	Number of groups	Skewness	Kurtosis
A	111.4	40.39	32	0.108	1.947
B	393.5	91.10	37	-0.371	4.486
C	36.52	12.68	32	0.572	5.844
D	32.97	15.08	28	0.925	4.934
E	2.446	0.276	34	-0.684	3.202

Units for $\bar{x}$ and s are mg/kg dry basis (A-D) or mg/l (E)

Figure F. Histograms of individual laboratory mean concentrations in samples A-E for chromium

T = "true" value, sk = skewness and k = kurtosis

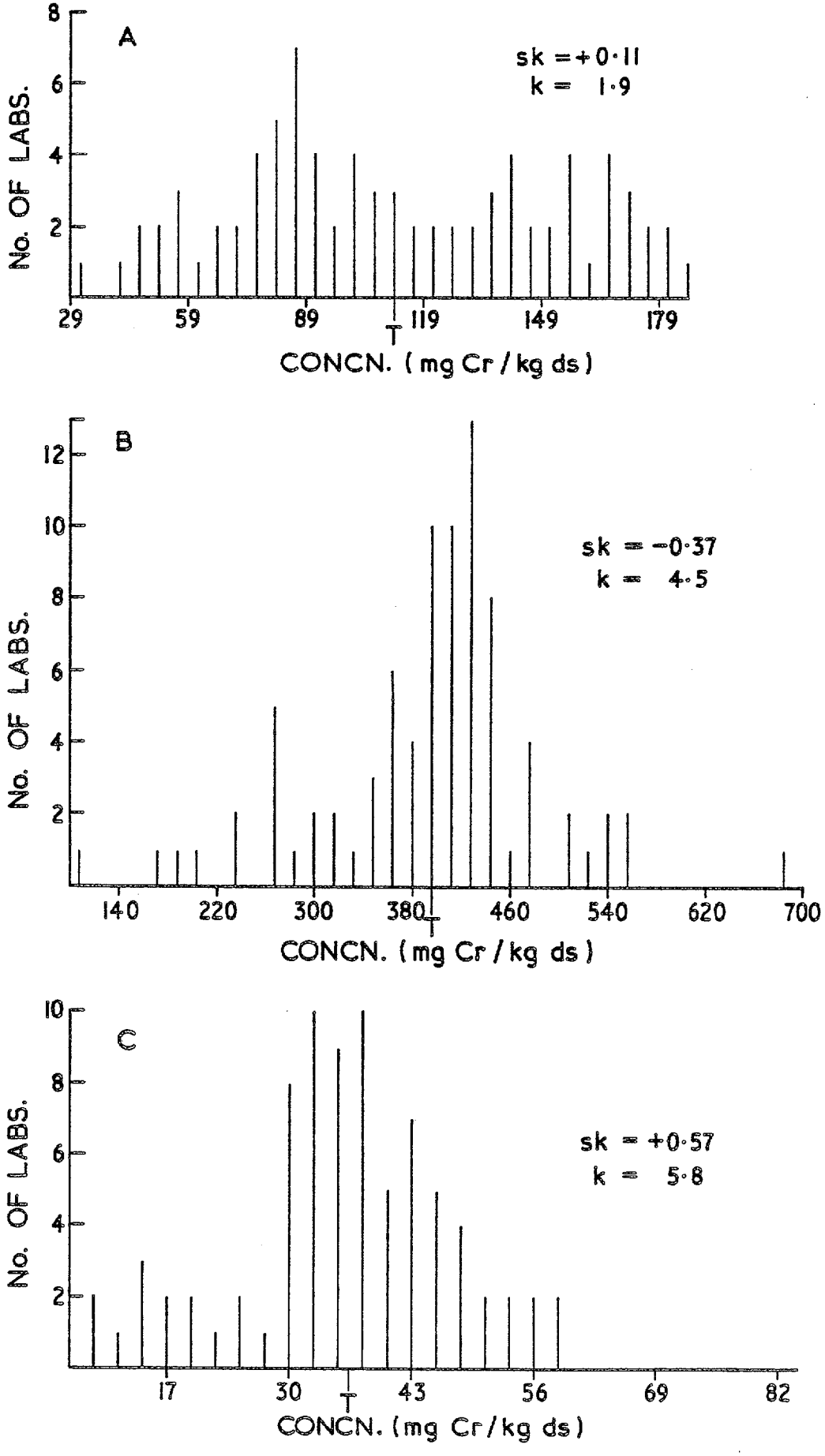
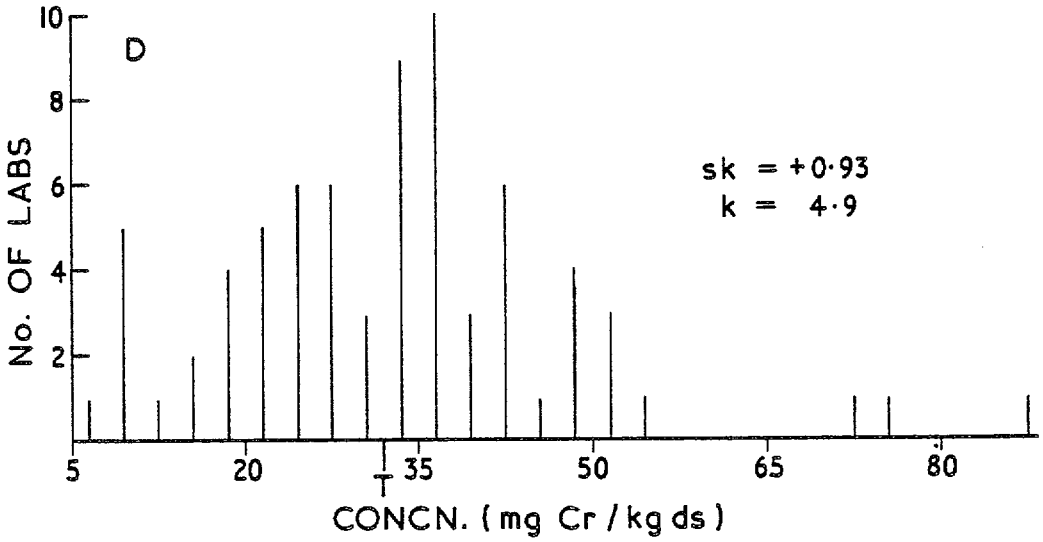
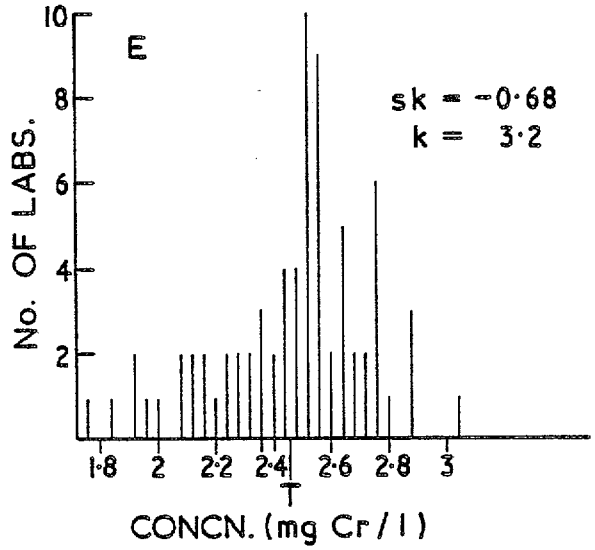


Figure F continued





APPENDIX G. RESULTS FOR TOTAL CONCENTRATIONS OF COPPER

TABLE G1 Summary of results for "total" copper

n=10 unless stated † n=8 ‡ n=3-6. * indicates significant between-batch errors (P=<0.05)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
1	f	4.7	-2.9	5.6	5.7*	-7.1	11.2	1.5	0.5	0.9	7.3†	8.0	12.6	1.9	1.4	2.4
2	a	4.1	2.8	5.2	4.2*	0.9	4.2	2.2*	1.3	1.7	12.6*	-6.5	15.6	3.5*	-2.2	4.8
3	k	5.3*	2.0	6.2	6.8*	-6.4	11.4	2.8	-4.9	6.4	7.9	-0.7	5.3	3.5	-1.8	3.2
4	a	8.1*	-0.7	7.3	5.8*	7.1	12.1†	6.4*	-6.9	11.7	34.0	-2.4	24.6†	1.9	1.2	2.3
5	a	7.2	2.0	6.3	6.2*	5.6	10.9	4.1*	4.1	7.4	27.9	1.6	18.0	22.4*	10.8	30.3
6	a	2.6	5.4	6.9	1.4	3.1	4.0	2.1	5.3	6.6	6.3	-7.3	10.7	1.9*	-1.7	3.1
7	g	7.4*	8.8	15.2	4.0*	0.1	3.8‡	13.4*	2.7	15.7‡	43.2*	43.2	93.9	4.4*	-0.6	4.1
8	a	24.0*	2.5	22.1	20.4*	-3.2	19.2	40.9*	8.6	42.2	22.3*	-6.8	23.6	18.1*	10.7	27.1
9	a	1.9*	3.1	4.6	2.9	-2.4	4.0	4.2	-0.9	3.3	5.8*	-12.0	16.1	1.1	0.9	1.6
10	a	4.2	7.4	10.0	2.1	6.8	8.1	6.6	8.1	12.2	8.2	-4.3	8.8	3.5*	8.4	11.2
11	a	3.0	8.4	10.3	3.0	0.9	2.7	3.5	0.3	2.4	11.1	-12.6	18.2	8.3*	-3.8	10.3
12	d	4.6*	3.9	7.8	1.3*	3.0	4.0	2.1	-0.8	1.9	15.0	-3.2	11.6	3.1*	-4.6	7.0
13	a	4.5*	-6.2	9.7	9.1*	-6.2	13.1	3.7	-6.6	8.6	2.7*	-7.7	9.6			
15	b	5.4	-1.0	5.3	6.3	3.4	7.2	9.4*	3.5	10.9	38.1*	19.8	56.9	2.4	3.6	5.6‡
16	a	2.4*	1.1	2.6	3.6	-0.1	2.2	1.5	-1.7	2.6	4.0	58.3	62.1	2.6	-3.2	4.6
18	j	16.9	4.8	18.3	5.5	-5.6	9.5	9.4	-3.5	8.7	33.5	3.2	23.2	23.3*	-9.6	27.5
19	d	2.6	6.3	7.9	3.1*	2.9	5.4	1.7	2.7	3.7	3.5*	-5.0	7.3	1.4*	2.8	4.0
20	d	1.7	6.8	9.6	3.3*	7.6	10.4	2.4	6.1	7.5	3.4*	-5.5	8.0			
21	b (k for A)	2.5	-11.4	12.7	2.9	-10.7	12.2	2.8	-13.3	14.7	2.6	-23.5	24.7	2.0	0.8	2.0
22	a	3.8	1.7	4.3‡	4.1*	2.4	5.7	2.6	5.0	6.5	3.3	11.6	14.1†	0.6	-0.5	0.9
23	a (d for D)	8.3*	-13.2	18.9	7.9*	-6.2	12.0	6.5*	-7.8	12.5	22.5*	0.9	18.9	6.6*	-8.0	13.3
24	b	4.4*	-1.5	4.8	2.4	1.2	2.6	2.2*	0.9	2.8	3.6	-5.9	7.9	3.9*	11.6	15.0
25	d	8.3	0.7	5.5	3.4	9.0	11.1	6.2	8.6	12.5	8.2	2.1	6.9	3.3	-0.7	2.6
26	a	2.6	-0.3	2.2	3.4	2.2	4.2	4.1*	4.5	7.7	5.8	-3.7	6.9			
27	d	3.8*	-9.5	12.1	7.5*	-9.9	15.2	7.4*	-8.0	13.2	6.4*	-4.4	9.3	10.3*	-8.8	16.0
28	a	4.6*	3.2	6.9	2.4	-6.3	7.6	3.1*	-3.9	6.3	24.0*	28.1	52.4	5.3*	5.2	9.5
29	j	8.2*	-1.4	7.7	3.9	13.3	15.9	8.6	11.0	16.6	8.8*	12.4	20.3	3.0	4.1	8.6
30	j	5.4*	-13.4	17.0	7.3	2.3	6.6	8.6	0.2	6.6	32.9	20.9	44.0	1.2*	0.9	2.7
31	j	6.7	-18.3	21.5	1.6	-16.7	17.5	2.4	-9.6	11.2	17.1*	4.8	18.9	5.2*	1.7	2.6
32	a	4.3	1.1	3.6	5.9*	-3.7	8.1	7.6	2.1	6.6	12.1*	-12.4	20.8	2.8	-0.6	2.9
33	a	14.3*	-9.1	19.2	4.2	-10.2	12.8	16.7*	-17.3	28.0	40.8*	-43.4	56.8	2.5*	-0.4	2.7‡
34	a	3.3	-4.3	6.4	2.7	0.5	2.3	4.0*	5.9	9.9‡	9.7*	-30.2	36.6†	2.3	2.0	4.2†
35	a	5.2*	-4.2	8.0	3.9	-4.5	6.7	2.0	-1.6	2.8	5.4	-8.5	11.4	2.9*	-1.4	3.7
36	a	9.9	-2.7	10.7‡	5.6*	-2.9	7.9	3.9	-6.2	8.7‡	44.7	-8.8	48.8‡	3.2	-4.8	7.6‡
38	a	7.4	-6.6	11.2†	3.0*	-2.0	4.6	5.5	-1.2	4.8‡	5.6	20.3	23.3†	<0.01	<0.01	<0.01
39	k	14.3	15.9	25.5	10.2*	3.5	11.7	4.9	2.9	5.8	82.9	-28.6	136.4	2.0	6.0	7.3

TABLE G1. (Contd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
40	k	2.1	-5.9	7.0	3.7*	-0.2	3.2	3.9*	-0.3	3.4	8.7*	-9.3	16.2	1.8	-3.2	5.2‡
41	a	6.3	-6.2	9.7	6.2*	-5.7	10.3	7.7	-6.5	10.7	11.2*	0.6	9.4	4.2*	0.1	3.5
42	a	6.5*	20.9	28.0†	3.6	18.6	21.5	2.1	23.6	25.6	8.1	-6.4	12.6‡	1.9	4.0	133.8‡
43	e	3.9	19.1	11.6	5.4	10.9	14.4	7.5†	13.2	19.9	3.5	-1.2	98.8	2.8	8.5	10.3
44	k							3.3	-4.4	6.3				1.8*	-6.2	7.6
45	a	6.3	-6.2	9.6	3.7	6.0	8.3	12.6*	-11.3	19.9				1.2*	5.0	5.9
46	a	1.6*	-0.9	2.1	1.0*	-4.4	5.1	0.9*	-4.9	5.6				1.0*	-6.4	7.1
47	b				1.3*	6.5	7.6							1.4*	2.4	3.6
48	a	3.3*	9.1	12.0	2.3	9.9	11.4	5.1*	5.1	9.2				2.4*	7.2	9.5
49	k	4.9*	3.2	7.1										1.4	1.8	2.6
50	k	8.8*	-5.6	12.3										3.0*	-1.5	3.8
51	k	2.8*	-4.7	6.9										<0.1	<0.1	<0.1
52	a	5.7	-4.4	7.5	2.2	-11.3	12.5	1.8	-8.7	9.7	18.6	-22.4	30.8	0.7‡	-0.2	0.8
53	a	3.5*	0.5	3.2	4.3*	3.6	6.9	3.6*	0.4	3.3				2.2*	2.2	4.0
54	g				3.6	-6.6	8.6							4.7*	-7.2	10.8
55	k				3.9	2.2	4.5				8.1	-12.9	17.0	1.0*	0.9	1.7
56	a	7.4*	-19.1	23.6	12.7*	-17.4	25.5	8.7*	-19.2	24.6	26.9*	-20.4	37.5	7.4*	-2.6	8.4
57	d							1.8	2.1	3.6‡				1.7	1.6	2.9‡
58	a	5.0	-13.5	16.0												
59	k	3.6	1.8	3.9	6.2*	1.0	5.9	2.8	-5.6	7.2	27.7	10.7	28.5	1.4*	-2.3	3.4
60A	h	1.3*	-2.8	3.8	0.7*	2.1	2.7	0.6*	-0.4	0.9	3.2	0.5	2.4	<0.1	-2.0	2.1
60B	b	0.9	0.7	1.2	0.7*	2.4	2.9	0.7	0.9	1.3	3.4	-6.2	8.0			
60C	c	1.7*	<0.1	1.4	0.7	2.9	3.3	1.0*	1.7	2.5	3.2	0.5	2.4			
61	b	5.5	8.5	12.0	3.1	4.8	6.7	3.1	5.0	6.9				3.0*	1.0	3.4
62	b										12.9	-9.7	16.4			
63	g	6.5	-12.5	15.8	10.3	-14.6	19.7	6.2	-13.0	16.1	27.3	-24.5	36.5			
64A	b	6.3	-3.5	7.0	6.0*	-5.0	9.5	5.9*	-9.1	13.3	6.1	-11.6	14.7	8.5*	0.1	7.1
64B	b	3.6	-2.3	4.3	5.9	-0.5	3.9	4.0	-2.1	4.4	11.7*	-15.2	22.9			
65	b	4.8*	-2.5	6.2	2.6*	0.6	2.7	1.9*	7.5	9.0	12.7*	4.5	14.4	1.6*	-1.6	2.8
66	k	3.3*	-5.9	8.3	2.2	-6.7	7.9	2.5*	-6.1	8.0	9.7*	-5.6	12.9	2.4*	0.4	2.3
67	j	3.1	-2.6	4.4	4.6*	9.9	13.8	5.5*	10.4	15.0	8.5*	6.0	12.9			
68A	g	2.7	8.1	9.8	2.0*	3.9	5.5	4.2	3.5	6.0	39.1*	-34.4	54.0	6.0	7.3	11.0
68B	i	2.8	12.5	15.5	2.8	5.3	8.1	2.7	5.9	8.6‡						
69	i	2.4	-12.7	11.4	5.4*	1.3	5.7	6.5*	-1.9	7.0	3.3	-5.0	6.8	1.7*	0.1	1.4
70	g	14.0†	-2.9	13.4	7.0	-14.6	18.1	9.3	-15.9	20.4	11.2	30.9	39.5	3.5	-3.8	6.5
71	a	8.0†	-2.6	8.6	6.1*	-4.2	8.8	2.8	-0.6	2.2	7.0*	-11.9	16.8	3.8	-6.0	9.8‡

TABLE G1. (Contd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
72	b	4.9	13.3	14.5	5.2	14.4	17.9	6.0	15.4	19.4	18.7*	-3.8	18.0	1.0	-7.9	8.4
73	b	2.7	9.4	11.1	2.6	6.0	7.5	3.7	4.0	6.2	5.4*	-7.4	11.2	3.0*	-5.2	7.4
74	b	3.0	-5.5	7.2	2.4	-4.1	5.4	3.1	-2.6	4.4	5.8	-12.9	15.8	0.5	-3.0	3.3
75	d	5.7*	6.9	11.5	1.2*	6.2	7.2	1.9	6.0	7.2	4.4	29.4	32.6	1.4	-1.7	2.5
76	d	2.9*	2.4	4.7	0.9	6.9	7.5	1.4	0.4	1.2	1.5	-0.2	1.1	3.3*	2.7	5.4
77	d	5.7*	5.1	9.6	3.5	4.4	6.5	3.2*	4.8	7.4	7.8	39.5	45.8	3.2*	-0.5	3.2
78	b	3.5	11.4	13.7	2.9	6.2	8.0	2.6	8.2	13.7	6.1	-3.5	6.9	1.6	-1.6	2.6†
79	k	9.1	-12.7	17.3	12.7	-22.2	27.9	11.8	-20.1	25.6	41.2*	16.9	54.2	11.0*	-16.3	23.3
80	d	9.7	8.6	14.7	4.1	7.4	10.0	7.5	3.4	8.0	4.4	-3.8	6.2	9.0*	6.8	14.6
81	a	7.5*	-10.8	16.0	2.5*	-2.7	4.6	13.2	1.2	9.0	7.9*	-8.7	14.4			
82	g	9.2*	3.1	10.6	3.9	0.2	2.5	6.3*	1.1	6.1						
83	g	2.3	-0.8	2.2	2.1	1.5	2.7	2.8	-0.9	2.5						
84	a	4.1	9.4	9.4	5.6*	-0.9	5.2	5.8*	-0.2	4.8	8.7	-8.4	13.0	1.3	-0.4	1.1
85	k (a for D)	5.6	-0.9	4.1	4.7	-3.1	5.7	2.9*	-8.1	10.1	7.7*	6.0	12.4			
86	i	6.5	5.0	8.9	5.9*	5.9	10.9	3.5	9.0	11.2	24.7*	21.3	38.6			
87	a	4.8*	-3.7	7.4	2.3*	-1.8	3.6	1.9	-4.3	5.4						
88	i	2.4	2.4	3.8	11.6*	11.1	21.4	6.5	12.7	17.0						
89	b	8.0	12.7	23.2*	6.6	6.9	18.7*	5.3	5.0	11.5*	18.9	20.1	47.6*	4.5	2.7	10.5
90	b	4.9	0.3	3.2	2.9	-1.6	3.2	2.0	1.1	2.3	5.1	3.8	6.9	3.0*	-2.4	5.1
91	b	18.0	7.8	18.6	4.4	0.8	3.4	3.1	4.5	6.4	4.4	8.2	11.0	5.8*	-1.6	6.1
92	d	2.8	-7.4	2.9	4.3	-3.3	6.2	4.3	-3.4	5.8	7.0	-18.7	22.0	1.9	-3.2	4.6

TABLE G2. Statistics of populations of grouped laboratory means: copper

Sample	Mean $\bar{x}$	Standard deviation, s	Number of groups	Skewness	Kurtosis
A	244.9	18.7	20	-0.077	3.078
B	799.2	58.1	22	-0.393	3.406
C	716.7	54.5	32	-0.194	3.813
D	16.52	3.04	34	0.821	4.209
E	2.50	0.122	24	-0.133	3.987

Units for $\bar{x}$ and s are mg/kg dry basis (A-D) or mg/l (E)

Figure G. Histograms of individual laboratory mean concentrations in samples A-E for copper
T = "true" value, sk = skewness and k = kurtosis

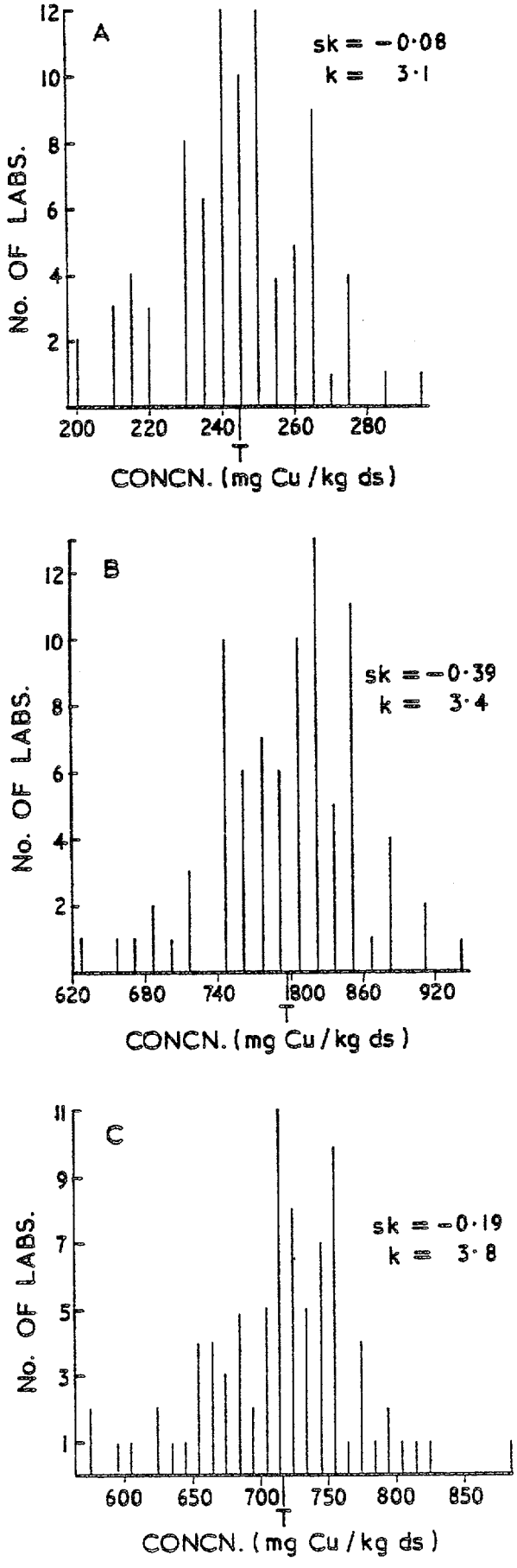
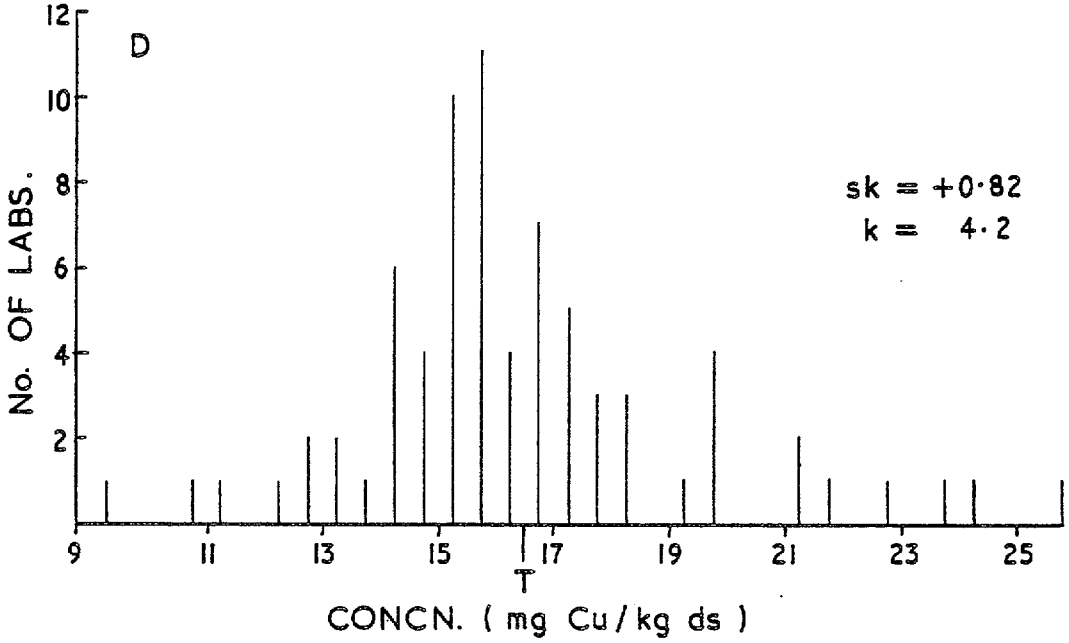
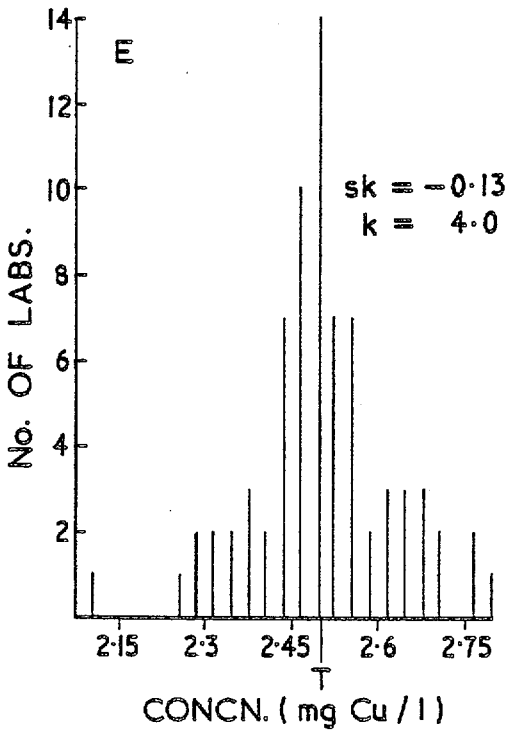


Figure G continued





APPENDIX H. RESULTS FOR TOTAL CONCENTRATIONS OF NICKEL

TABLE H1. Summary of results for "total" nickel

n = 10 unless stated. †n = 8. ‡n = 3-6. *indicates significant between-batch errors(P = <0.05)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
1	f	3.0*	10.3	12.7	8.1*	-0.5	6.7	6.6	19.5	24.1	5.8	42.7	47.5	2.2	-3.0	4.3
2	a	2.9*	7.4	9.8	5.2*	2.5	6.7	20.2*	-13.4	27.5	8.7*	-10.1	16.3	4.3*	-0.9	4.3
3	k	12.7	-7.9	14.7	7.8	-8.9	13.1	43.4	16.5	50.3†	23.4	-15.4	16.7†	8.7*	-6.1	12.7
4	a	17.1	-6.4	15.7	3.4	4.2	6.6†	24.6	-9.4	24.3†	1.6	-25.7	48.3‡	2.8*	4.3	7.0†
5	a	7.0	3.9	8.1	4.1*	-2.5	5.6	12.8	-28.7	34.0	1.3	-26.1	34.4	7.6*	-15.8	20.9
6	a	5.6	2.5	5.8	6.6	-0.02	3.8	9.6	-3.6	9.0	11.4	-8.3	14.3	3.6*	1.5	4.4
7		11.9*	28.5	40.8	10.8*	12.4	21.7	23.5*	51.0	83.1†	38.8*	165.3	248.2	2.2*	6.6	8.5
8	a	9.1*	-4.7	11.2	6.4	-2.1	5.7	22.9*	-5.1	21.9	12.8	-6.9	13.8	5.7*	10.2	15.3
9	a	5.0*	-3.4	7.3	3.0	-4.9	6.6	6.3	-19.7	22.7	12.2*	-26.4	33.6	1.7	1.6	2.6
10	a	3.7	12.1	14.5	3.4	14.8	17.1	16.9	18.8	30.5	16.0*	8.3	21.5	2.6	18.1	19.8
11	a	2.3	39.3	41.2	2.4	18.9	20.5	17.3*	31.4	49.6	9.0*	37.3	47.1	9.7	4.4	10.1
12	d	2.8	9.6	11.4	3.5	7.8	10.0	9.2	3.7	9.2	11.8*	15.4	26.0	1.6	-2.4	3.2
13	a	2.2*	1.6	3.4	2.3	5.0	6.4	5.6	-4.3	7.4	5.4	-6.4	9.3	2.9*	-5.9	8.1
15	b	11.6*	-11.8	20.0	11.1*	-7.5	15.7	9.8	-13.0	17.9	16.7*	-22.5	32.5	1.9*	0.2	2.3‡
16	a	3.1	-1.6	3.3	2.8*	0.6	2.8	4.5	-13.4	15.7	9.4	-30.7	34.5	1.9	-1.0	2.1
18	j	5.1	-12.6	15.3	4.3	-8.8	11.1	30.2*	-32.9	48.3	28.4*	-26.3	42.8	8.4*	-11.7	17.4
19	d	2.6*	-2.2	3.6	1.1	2.0	2.6	3.3	2.2	4.1	4.8*	6.2	10.3	2.7*	2.2	4.5
20	d	3.3*	8.9	11.9	4.4*	7.5	11.1	10.5*	12.6	22.0	6.8*	20.8	27.3			
21	b (k for A)	5.2	-17.2	19.3	3.3*	-7.6	10.0	10.5	-11.5	16.9	3.4	-26.9	28.4	1.9	3.9	5.4
22	a	9.3	21.2	27.8	4.2*	9.0	12.6	11.3	24.5	32.7	13.3	47.9	59.3	3.8*	2.7	5.9
23	a (d for D)	3.2	-10.6	12.5†	3.5	-12.3	14.1	4.4	-4.3	6.8	7.5*	5.5	11.7	4.8*	-8.8	12.3
24	b	4.6*	-9.5	12.7	4.3	-2.4	4.8	10.8*	-7.7	15.7	2.8*	-6.1	8.1	1.9*	11.2	13.0
25	d	10.0*	1.3	9.4	8.7*	7.6	15.2	8.3	8.1	13.2	5.4	22.3	26.1	4.0	-4.3	6.6
26	a	2.8	6.3	8.0	2.7	-0.5	2.0	5.4	-3.5	6.5	7.0	15.4	20.1			
27	d	2.4	-14.0	15.2	2.8	-19.5	20.9	6.5	-2.8	6.4	8.4	4.7	9.8	8.3*	-10.2	16.0
28	a	3.2*	-6.9	9.3	3.4*	-8.2	10.7	4.9	-12.2	14.7	7.3	-11.2	15.0	5.6*	-0.2	4.6
29	j	5.2*	-7.7	11.6	6.0*	11.2	16.4	9.5*	29.8	39.3	6.5	35.5	40.6	7.1*	-2.2	7.7
30	j	11.1*	-7.1	13.0	13.3*	4.2	15.3	25.7	49.1	71.2	35.0*	26.0	61.3	4.9*	-0.7	4.5
31	j	5.7*	-31.3	34.3	11.9	-25.9	31.0	9.5*	-17.8	23.6	32.5	-1.2	19.8	1.8*	2.0	3.5
32	a	5.2	3.0	6.1	7.2	-7.1	10.5	28.9	-25.7	38.1	21.3	-13.2	23.9	3.9*	2.9	6.2
33	a	9.4	-16.5	21.1	7.2	-13.3	16.9	98.3	-33.6	77.4†	84.2	-23.9	66.9†	5.7	-0.9	4.2
34	a	7.0	-6.6	11.0†	7.6	-2.4	7.4†	9.8	8.3	15.7†	2.8	-33.9	35.1†	5.7*	0.2	5.6†
35	a	3.7	-9.0	10.9	5.2	-9.4	12.1	14.2	-10.1	17.5	3.8	-10.0	11.9	1.5	-5.6	6.4
36	a	7.2	0.7	5.6†	8.4*	1.8	9.8†				23.3	14.4	36.3‡	6.4	-0.4	7.9‡
38	a	6.0	-12.1	15.7†	3.0	-8.7	10.5	7.3	-13.6	17.7†	5.1*	-9.5	13.7†	7.0	1.7	6.5†
39	k	11.5*	24.7	33.0	11.1*	5.4	14.2	22.1	10.9	25.1	16.2	94.5	112.8	7.9*	3.4	9.8

TABLE H1 (continued)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
40	k	2.9*	-5.3	7.5	2.1*	-1.0	2.6	6.4	-8.2	11.6	7.6*	-0.2	7.0†	2.3	4.0	5.9‡
41	a	3.0*	-10.9	12.4	4.1	-9.6	11.8	7.3	-0.07	4.3	6.4	16.4	21.4	1.8	-13.1	14.0
42	a	3.7	-3.4	5.8†	13.0	15.2	25.2†	12.4	8.4	17.4†	6.5	-7.5	12.5†	<0.01	0.2	0.3‡
43	e	7.7*	2.6	7.0	4.3*	6.5	10.1	19.8*	16.5	34.3	8.5	4.7	9.9	6.9*	12.7	19.0
44	k							7.8	13.4	19.3†				1.1*	-3.0	3.9
45	a	5.6	-2.3	5.5	6.6	-5.3	8.9	12.0	-7.6	16.7‡				3.2*	0.9	3.5
46	a	2.6	24.5	26.4	3.5	5.0	7.1	2.0	0.04	1.2				0.7	-3.6	4.0
47	b				2.3*	7.3	9.2							4.4	5.0	7.7
48	a	6.2*	6.7	12.1	7.0*	5.1	11.0	13.5*	17.1	29.9				5.0*	3.8	8.7†
49	k	2.2*	-0.8	2.5										2.3	-0.7	2.0
50	k	9.7*	6.4	14.5										3.4	-1.9	3.8
51	k	1.7	2.2	3.2										4.3	4.4	7.0
52	a	3.8*	-14.3	16.9	3.7*	-10.4	13.0	14.1*	-19.8	28.5	8.8	-27.5	31.2	0.9*	-1.0	1.7
53	a	10.6	9.4	16.1	3.0	6.8	8.6	8.3	-0.6	5.3				1.7*	2.9	4.4
54	g				15.1	-18.9	26.0							3.9	-1.4	3.7
55	k				2.7*	8.5	10.8				11.7	2.1	9.0	0.5*	7.7	8.1
56	a	10.2*	-3.5	11.2	9.0*	-9.5	15.7	22.5	7.9	22.0	23.0*	8.0	22.4	7.3*	-1.8	7.6
57	d							5.3	26.9	32.4‡				2.7	1.3	3.5‡
58	a	6.1*	-3.1	7.6												
59	k	4.0	1.9	4.3	4.9	6.0	9.0	25.3	13.2	29.8	18.8	16.0	28.6	1.8*	-1.8	3.3
60A	h	2.5*	-6.3	8.2	2.0*	2.4	4.0	3.4	-7.7	9.5	3.5*	-20.0	22.3	<0.01	0.2	0.3
60B	b	1.5	-3.8	4.6	1.0	-2.1	2.7	3.2	-12.3	13.9	3.2*	-27.1	29.0			
60C	c	2.3*	-4.9	6.7	1.3*	1.2	2.3	2.4*	-4.8	6.4	3.6	-18.4	20.2			
61	b	5.3*	-6.8	10.8	4.8*	-6.6	10.0	6.2	-11.1	14.3				2.7	1.7	3.3
62	b										8.7*	5.2	12.6			
63	g	8.7	-1.7	6.6	9.6	-0.7	6.2	21.7	-4.1	16.2	51.0	-0.3	29.8			
64A	b	3.0	-6.6	8.2	4.7*	-2.8	6.2	6.2	-13.1	16.2	4.7*	-14.2	17.4	12.2*	4.2	14.6
64B	b	11.7*	-8.6	16.8	5.0	-2.0	4.8	6.8	-15.4	18.7	15.0*	-38.8	46.1			
65	b	15.4*	-5.3	17.3	5.0*	-6.7	10.2	37.6*	-4.9	34.0	26.3*	-26.1	41.1	14.4*	-0.4	12.1
66	k	8.3*	-2.5	9.1	3.9	1.2	3.5	8.6*	9.8	16.9	23.2*	15.4	36.9	2.1*	-0.3	2.0
67	j	6.3	-3.9	7.4	9.5*	3.4	11.4	9.0	-15.4	19.8	23.2*	-13.6	28.8			
68A	g	5.2	-6.8	9.6	11.3*	-8.9	17.1	32.4	-25.6	39.5				6.7	7.5	11.7
68B	i				3.5	18.4	22.3‡	15.6	35.2	55.3‡	10.9	35.5	49.6‡			
69	i	3.8*	-1.4	4.7	3.5*	-2.1	4.7	11.3*	1.0	10.2	3.8	-5.6	6.7	0.8	-0.7	1.2
70	g	10.7	-4.5	10.4	12.6*	-13.1	21.3	73.3*	51.9	141.5	39.2	-32.8	48.1	3.5*	-2.4	5.1
71	a	7.1*	-1.0	6.3	6.0	1.9	6.5	10.3	-11.3	16.6	3.9	-18.4	20.3	18.6	8.2	34.5‡

TABLE H1 (Contd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
72	b	1.9	27.7	29.3‡	3.0	20.4	22.5				10.9	913.3	987.0‡	1.6	2.6	3.6
73	b	6.7*	8.6	14.4	3.6*	1.7	4.5	6.4*	-7.7	12.2	11.0	-8.2	14.0	5.3*	-5.8	9.7
74	b	25.2	18.7	30.6	1.8*	-14.0	15.2	17.6*	21.4	32.6	14.2*	-26.6	34.6	3.5*	-5.2	7.8
75	d	2.4	-4.9	6.3	3.9	0.6	2.9	3.1	0.3	2.1	5.7	-1.5	5.8	1.7*	-0.2	1.4
76	d	2.3	4.0	5.3	3.9	9.1	11.6	7.8*	9.2	15.7	2.8	13.4	15.2	0.6*	7.1	7.6
77	d	1.9*	-8.4	9.8	3.8	5.7	8.0	5.6	-3.2	6.3	12.3*	18.0	29.2	2.4*	1.6	3.5
78	b	10.4	26.1	33.7	7.7*	15.3	22.6	11.7*	21.9	32.9	6.4	12.0	16.1	4.2*	-0.6	4.3‡
79	k	12.6	-0.3	7.5	26.1*	-20.1	36.6	23.3	-7.1	19.7	36.2	37.5	66.3	10.6*	-16.2	23.4
80	d	12.7	9.7	17.8	8.4*	8.3	15.5	11.0	-4.3	10.3	6.1	14.9	19.0	8.0*	5.8	12.4
81	a	9.4*	-7.4	14.3	7.8*	-10.5	16.2	11.7*	-14.1	22.2	8.4*	13.2	20.9			
82	g	3.6	1.4	3.6	11.6*	7.3	16.7	12.1	-5.1	11.7						
83	g	5.2	-7.1	9.9	2.3*	0.7	2.5	6.2	-4.3	7.7						
84	a	6.2*	-5.6	10.3	8.2*	-4.3	10.6	9.2*	-13.1	19.6	8.8*	-17.6	23.2	2.3	-0.2	1.4
85	k (a for D)	5.6	-5.3	8.4	5.2	2.9	6.0	9.7*	-8.5	15.3	10.0*	-4.6	12.1			
86	i	4.1	-2.3	4.6	6.7*	4.5	10.2	29.2*	25.7	55.7	16.0*	13.3	27.7			
87	a	3.3*	3.1	5.8	1.9	-1.2	2.3	10.0	0.2	5.9						
88	i	6.1	16.1	21.9	8.8*	5.8	12.9	22.5	4.7	18.4						
89	b	3.5	17.4	22.2	7.7	24.0	40.1‡	7.6	27.0	38.3‡	21.8*	48.5	102.3‡	0.08	0.2	0.3‡
90	b	7.0*	-5.5	8.6	3.3*	-2.3	4.8	10.4	-11.7	17.1	7.7*	-2.5	8.2	5.0*	-5.9	11.4‡
91	b	5.7*	-6.4	10.6	3.2	-5.6	7.3	18.7	-28.3	36.1	11.8	-18.2	23.7	9.8*	-3.4	11.1
92	d	8.3*	-12.3	18.0	2.8	-3.1	4.7	12.7	-16.6	22.8	6.2	-2.5	6.0	3.1*	0.3	2.7

TABLE H2. Statistics of populations of grouped laboratory means: nickel

SAMPLE	Mean, $\bar{x}$	Standard deviation, s	Number of groups	Skewness	Kurtosis
A	146.0	16.92	52	1.081	4.25
B	172.6	16.07	43	0.011	3.24
C	26.29	4.797	47	0.827	3.66
D	19.51	4.623	44	1.086	5.13
E	2.494	0.144	32	-0.112	4.59

Units for $\bar{x}$ and s are mg/kg dry basis (A-D) or mg/l (E)

Figure H. Histograms of individual laboratory mean concentrations in samples A-E for nickel

T = "true" value, sk = skewness and k = kurtosis

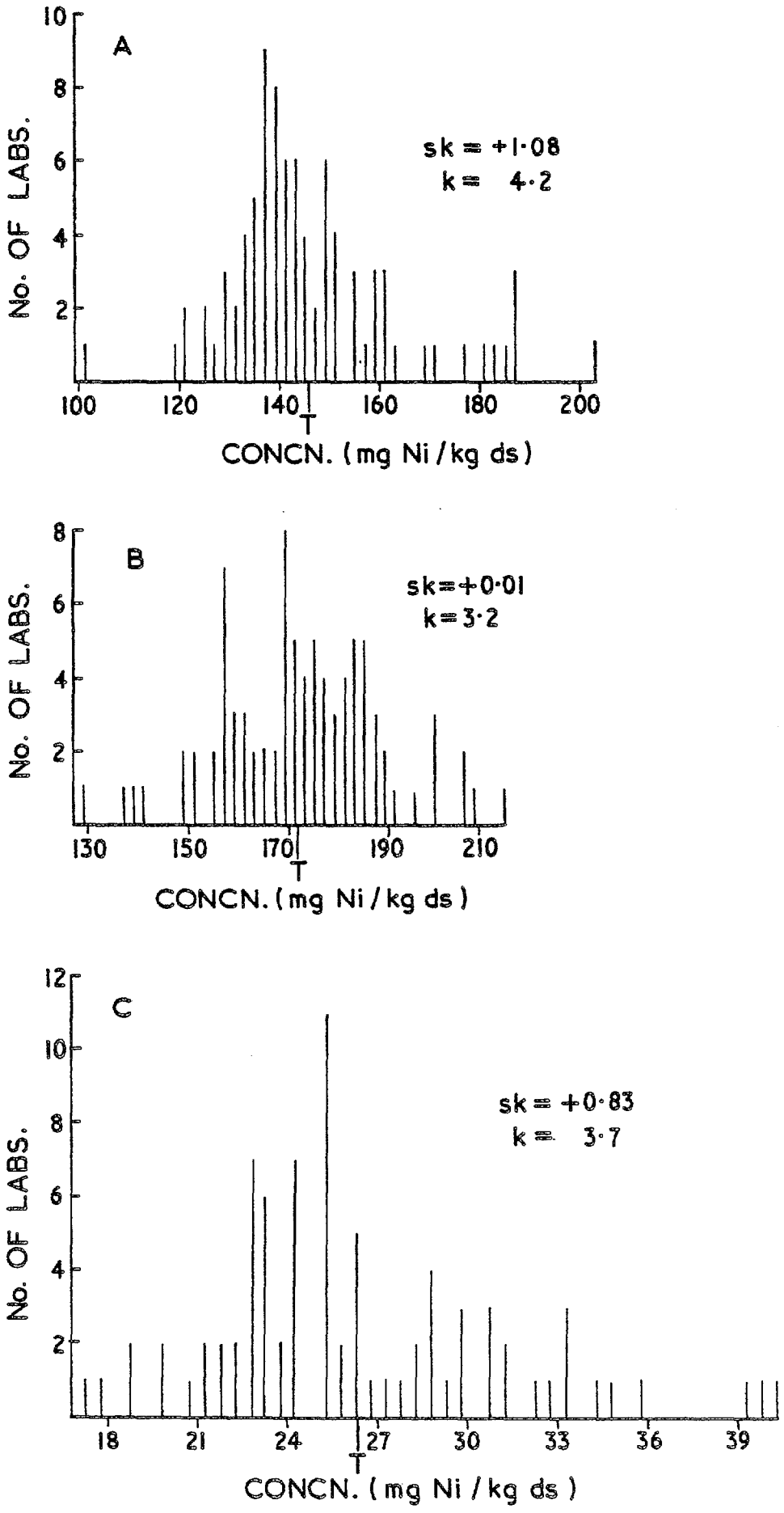
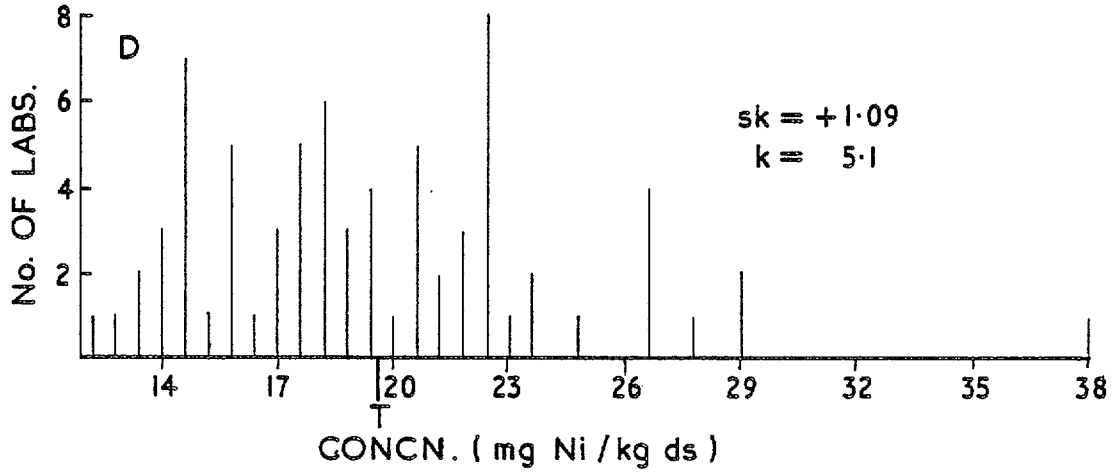
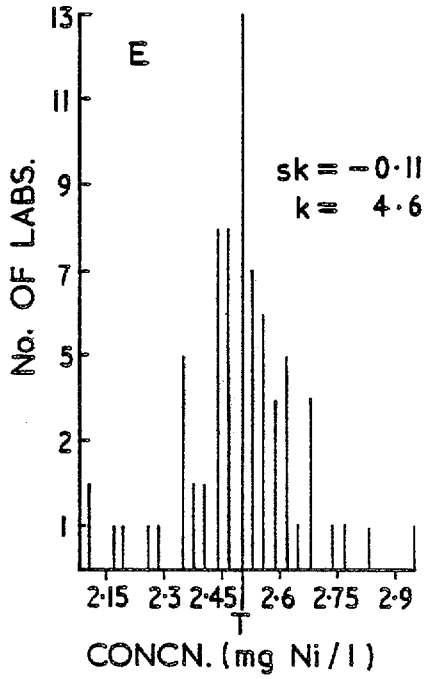


Figure H continued





APPENDIX I. RESULTS FOR TOTAL CONCENTRATIONS OF LEAD

TABLE I1 Summary of results for "total" lead

n=†O unless stated † n=8 ‡ n= 3-6 *indicates significant between-batch errors (P=<0.05)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
1	f	7.4	-0.3	4.6	6.5*	-0.2	5.1	7.2	5.5	9.9	11.9	49.9	60.2	2.0*	-1.4	3.0
2	a	2.6	3.2	4.7	4.5*	17.2	21.3	4.0	12.0	14.6	5.9	11.5	15.3	5.0*	-5.0	8.8
3	k	7.1*	3.8	9.5	5.5*	- 2.3	4.8	4.9	-4.1	7.2†	23.9	4.5	19.0	7.6*	-10.0	15.6
4	a	5.1	0.4	3.4	3.0	1.5	3.6†	11.8	2.5	9.5	21.9	0.9	18.2‡	2.7*	1.9	4.0
5	a	9.8	1.4	7.1	5.5	-2.2	5.3	10.2	-6.0	11.5	29.2*	-41.2	54.8			
6	a	4.7	6.3	9.2	8.4	7.7	12.9	10.8	9.3	16.1	6.1	1.2	4.7	1.5	1.1	2.0
7	a	86.9*	-72.0	91.8	68.4*	-61.4	86.3	40.1*	-42.0	60.4	40.3*	26.9	66.4	4.8	4.0	6.9
8	a	7.9	4.2	9.0	7.0	1.9	6.0	8.8*	3.0	10.1	24.0*	14.4	23.0	3.2	11.6	13.7
9	a	4.6*	0.2	3.9	5.8*	-4.4	8.8	4.9*	-4.9	8.6	5.2	-6.4	9.2	2.5*	-3.4	5.2
10	a	4.0	7.2	9.6	7.2	4.5	8.9	7.1	7.8	12.2	3.6	11.0	34.3	3.9	11.1	13.6
11	a	2.1	21.2	22.6	3.1	13.7	15.7	6.5*	12.8	18.6	6.4	19.4	23.9	11.6	1.0	7.8
12	d	3.9	-6.4	8.5	4.5	-5.4	7.9	3.5	-11.0	12.8	13.9	4.5	12.9	1.9	-3.8	4.9
13	a	10.0	-10.9	16.0	3.1*	-12.2	14.3	3.9	1.9	4.2	4.1*	6.5	9.9	3.0*	<0.1	2.5
15	b	9.9*	-9.3	16.3	8.7*	-7.8	14.0	33.6	3.3	23.4	24.1*	4.1	24.3	5.1*	-2.9	8.4‡
16	a	1.4	14.1	15.0	2.3	8.4	9.8	6.0	10.2	14.0	7.6	-2.6	15.2	3.8	1.6	3.9
18	j	41.9	-63.9	72.7	46.1	-45.8	60.3	31.3	-43.9	54.1	39.1*	2.4	33.5	4.9*	-2.7	6.6
19	d	4.4	5.1	7.7	3.1	5.3	7.2	2.2*	1.8	3.6	3.8	2.8	5.1	4.2*	0.4	3.5
20	d	7.8*	4.8	11.3	6.1*	4.9	9.9	2.3	6.5	8.5	9.2*	21.8	30.6			
21	b (k for A)	3.1	-10.2	11.8	2.6*	-10.9	12.7	3.4	-10.3	12.1	4.3*	-8.2	11.3	1.8	0.6	1.6
22	a	9.7	30.1	37.4	5.7	11.2	14.8	4.3	11.3	14.1	11.5	13.0	21.7†	6.3	2.4	6.1
23	a (d for D)	49.2	-47.3	62.3	22.0*	-27.7	40.1	5.9*	-12.7	16.6	5.2	-8.9	11.6	11.3*	-6.9	15.0
24	b	4.5	-1.6	4.2	4.3*	0.8	4.2	9.7	4.4	10.3	12.6*	-2.8	12.1	2.3*	9.2	11.3
25	d	5.2	-9.0	11.7	2.4	6.3	7.8	3.7	4.6	6.9	11.7	0.5	7.4	4.4	0.3	2.8
26	a	2.7	8.5	10.3	4.2	4.1	6.7	5.8	0.8	4.7†	10.5	20.6	28.0			
27	d	5.5	-5.5	9.4	5.5	-3.2	6.3	6.7	1.2	5.1	6.8*	-1.0	6.3	4.6*	-1.6	3.7
28	a	4.4	-3.5	6.0	2.1*	-8.4	9.9	4.0*	-6.6	9.6	17.4*	-16.6	27.9	6.5*	-2.0	6.9
29	j	25.9	-69.5	74.1	16.9	-58.2	66.3	26.3	-57.8	64.2	40.1*	-41.5	54.5	3.5*	-1.0	3.7
30	j	29.6	-79.5	83.0	39.3	-62.2	70.8	26.8	-59.0	66.1				7.3*	-4.6	10.1
31	j	32.4	-70.6	76.1	50.3	-80.7	86.3	17.6	-25.8	33.4	3.0	-13.2	28.1	4.4	3.0	5.7
32	a	6.8*	5.9	11.6	5.5*	7.3	12.0	7.1	7.9	12.3	7.8	-4.4	8.7	3.5*	4.2	7.2
33	a	11.8*	-13.2	21.4	18.1	-6.7	16.5	21.6	-19.0	29.1	48.6*	-12.0	59.5‡	7.4	-4.7	9.4
34	a	7.3	-11.2	15.6†	5.7	-1.3	5.1†	6.1*	-0.9	6.5†	4.5	-17.8	20.3†	0.0	<0.1	<0.1
35	a	4.8	-9.6	12.1	4.4	-10.0	12.3	4.3	-8.1	10.4	9.5	-14.0	18.7	3.7*	-9.7	12.4
36	a	33.3	-38.0	51.4	47.3	-56.3	69.7	36.0	-40.0	54.0	53.3	-21.6	52.9			
38	a	16.9*	-12.1	25.6	4.4	-5.5	8.2	6.4	-5.9	9.9†	8.5*	-14.9	21.4	2.1	<0.1	1.5†
39	k	10.7	-2.9	8.9	6.7	2.3	6.3	19.3	6.4	18.3	69.3	28.6	80.3	6.1*	-1.6	7.9

TABLE I1 (Contd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
40	k	10.0*	14.4	23.6	6.3*	9.7	15.3	6.8	10.4	16.1	15.7*	25.2	43.2	8.4*	1.4	8.2
41	a	3.8	-4.5	6.6	4.1	2.9	5.3	3.3	1.2	3.1	5.9	25.7	30.0	0.4	0.5	0.7
42	a	4.3	-3.1	5.9	4.8	-1.3	4.4	5.5	4.5	8.4†	5.6	-2.4	6.5			
43	e	2.5	15.0	16.7	4.5	15.7	18.8	3.9	14.1	16.7	15.0	24.6	35.5	3.0	11.6	13.6
44	k							7.6	-0.1	4.5				1.4	-5.8	6.6
45	a	3.8	1.8	4.1	3.5	-0.4	2.4	5.4	-8.0	10.9				5.4*	-0.9	5.2
46	a	1.5	40.9	42.0	4.3*	24.4	28.6	4.4*	8.9	11.5				3.4*	<0.1	2.6
47	b				1.9	6.0	7.1							4.2	4.4	7.0
48	a	4.5*	9.7	13.6	6.0*	6.0	10.8	4.9	5.2	8.2				5.8*	8.2	13.2
49	k	2.2	4.1	5.4										2.3*	-4.1	5.4
50	k	6.4*	2.3	7.2										3.5*	0.6	3.2
51	k	1.2	1.3	2.0										5.0	1.6	4.6
52	a	3.6	-11.4	13.2	3.6	-10.9	12.8	4.7	-12.3	14.7	13.5	-25.6	31.5	0.6	-0.6	1.0
53	a	4.3*	7.3	11.0	3.5	5.1	7.3	6.7	3.7	7.7				1.6*	0.8	2.0
54	g				36.4*	-40.9	58.2							3.8*	0.8	3.8
55	k				2.4	4.7	6.2				15.6	-5.3	15.2	2.2	-2.0	3.2
56	a	8.4*	-16.7	22.3	6.2	16.1	19.0	6.1	-17.1	20.0	7.9	5.6	10.5	4.1*	-7.2	10.0
57	d							3.1	5.1	7.8†				2.4	4.8	6.8†
58	a	9.0	0.1	5.3												
59	k	7.5*	-2.4	8.0	6.6	3.2	7.2	2.9	-0.8	2.5	13.9	-9.3	16.6	0.9*	-1.0	1.6
60A	h	1.7	-1.7	2.7	1.4	-0.4	1.2	1.7*	-3.1	4.4	2.1*	-8.5	9.6	1.0	-1.4	1.9
60B	b	1.8*	0.1	1.4	1.5	-3.0	3.9	2.4*	-2.2	4.1	2.6	-14.7	16.0			
60C	c	1.8*	-1.4	2.8	1.4	-1.2	2.0	2.6*	-2.4	4.5	2.4	-10.1	11.4			
61	b	5.6	-10.8	13.7	11.0*	-5.3	10.2	8.8*	2.3	9.5				2.2	1.8	3.1
62	b										15.0	-20.8	27.7			
63	g	19.0	-34.3	41.6	29.0	-16.6	30.6	60.1	-7.3	40.2	60.5	73.7	144.1			
64A	b	7.5	-10.2	14.0	6.4*	-4.1	9.0	7.5	-10.1	14.5	11.8	-10.0	18.0	7.3	2.9	7.2
64B	b	10.8*	-8.3	15.8	8.6	-5.3	10.0	8.1	-4.5	9.0	28.2	-25.9	38.0			
65	b	13.1*	-17.2	25.8	7.9	13.5	17.5	10.8*	-12.1	19.5				1.3*	-5.3	6.3
66	k	5.9*	-1.5	5.9	2.3	-3.1	4.4	4.0	-1.3	3.6	20.4	29.4	44.7	3.8	-1.2	4.2
67	j	40.5	-88.8	91.8	52.4	-84.9	30.0	72.2*	-81.6	93.7	13.1	-56.1	59.8			
68A	g													7.0	4.8	9.1
68B	i	0.9	22.5†	23.6	7.8	25.1	23.7	7.5	12.5	20.5†	41.0	7.9	50.1			
69	i	4.1*	-0.2	3.4	1.9	-2.1	3.2	1.4	-5.9	6.7	3.8*	-2.6	5.7	1.6	1.2	2.1
70	g	62.9*	-82.8	91.1	42.9*	-70.7	80.7	40.0	-69.2	76.3	52.5*	-17.6	50.6	4.3*	<0.1	3.3
71	a	7.7*	-1.7	7.8	9.6*	2.3	9.9	6.4*	-2.0	6.8	6.7*	19.6	23.8	5.3	0.8	6.0†

TABLE I1 (Contd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
72	b	6.5	24.0	28.6	4.0	15.1	17.8	3.9	17.5	20.1	27.0	18.6	37.2	1.4	-0.8	1.6
73	b	3.5	10.6	12.9	8.8*	9.8	17.2	6.5	12.0	16.2	8.6	-1.0	5.9	5.6	16.0	19.8
74	b	1.7	-10.5	11.4	3.8	-10.9	12.9	4.8	-7.6	10.2	32.6*	-14.7	37.2	2.9	-2.6	4.2
75	d	4.4	8.8	11.6	3.5*	3.8	5.8	2.7	-1.1	2.7	2.9	10.9	12.8	2.3*	-3.0	4.7
76	d	2.3	7.5	8.9	2.2	2.2	3.5	2.7	10.1	11.8	7.6	21.1	26.4	5.7*	7.1	12.1
77	d	9.0*	-2.3	9.5	7.1*	4.9	10.7	6.0*	6.2	11.3	9.6*	15.3	23.9	1.4*	2.0	3.1
78	b	6.2*	10.1	15.6	5.1*	7.6	11.9	5.2	9.3	12.6	7.5	17.8	22.9	1.7*	-1.2	2.7
79	k	15.6*	-10.3	21.1	13.2	-8.7	15.7	12.3	-9.7	16.2	68.0*	29.0	100.6	10.3*	-19.6	24.5
80	d	43.2*	-38.6	59.5	24.0	-24.9	35.3	27.2*	-43.4	31.2	6.9	-5.0	8.7	4.0	-2.0	4.2
81	a	6.3*	- 6.2	10.9	3.1	-14.9	16.4	2.7	-18.1	19.3	5.8	-17.3	20.1			
82	g	13.2	-35.7	40.6	20.3*	-28.6	40.2	13.5*	-20.1	28.4						
83	g	10.0*	-33.7	39.0	8.5*	-17.0	22.6	6.4*	-9.2	13.6						
84	a	6.8	- 1.8	5.7	9.6*	-4.1	11.4	9.0	-0.9	6.0	7.4	-8.2	12.1	1.7	-0.8	1.7
85	k (a for D)	6.0*	-8.2	12.5	8.1*	-5.6	11.6	8.7	-6.4	11.1	6.6*	-3.5	8.4			
86	i	5.1	2.8	5.8	4.2*	5.3	8.6	4.0*	1.3	5.0	16.7*	1.8	15.0			
87	a	2.7	3.0	4.6	4.2*	0.8	4.0	4.5	-2.9	5.4						
88	i	3.8*	2.6	5.7	7.1	0.1	4.3	4.3*	-3.7	7.0						
89	b	11.9*	14.4	36.7#	5.7	10.2	20.8	18.2	-1.0	30.4#	7.9	35.3	47.9#	<0.01	4.0	4.2#
90	b	5.3*	-8.0	11.7	2.3	-0.7	2.0	4.6	1.3	4.0	4.8	17.7	21.0	9.0*	-1.6	11.8#
91	b	4.7	0.7	3.5	15.1*	-7.4	18.3	4.2	-1.6	4.0	15.0	-25.3	31.8	2.3*	-3.8	5.6
92	d	5.1	-11.7	14.3	4.9*	-7.2	9.9	16.1	-8.5	20.4	7.4	9.1	13.8	9.7*	-14.7	21.2

TABLE I2. Statistics of populations of grouped laboratory means for lead

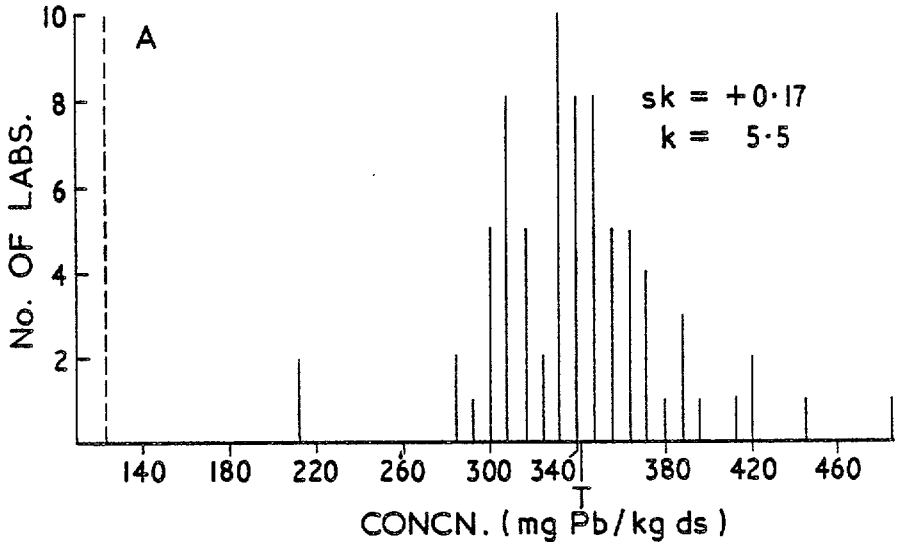
Sample	Mean, $\bar{x}$	Standard deviation, s	Number of groups	Skewness	Kurtosis
A	340.1	42.2	35	0.171	5.53
B	226.4	20.8	40	-0.222	3.70
C	243.1	19.9	30	-0.186	2.47
D	24.0	4.57	33	-0.103	3.42
E	2.50	0.14	31	-0.147	5.41

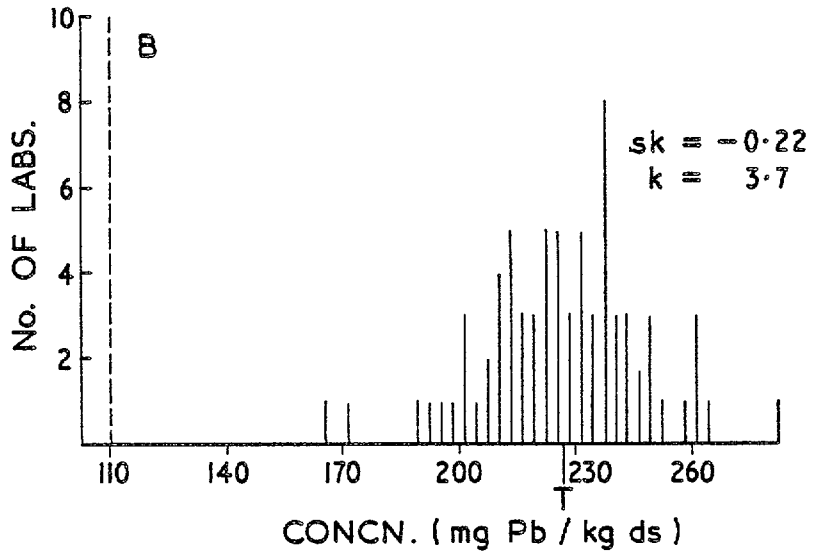
Units for $\bar{x}$ and s are mg/kg dry basis (A-D) or mg/l (E)

Figure I. Histograms of individual laboratory mean concentrations in samples A-E for lead

- - - - - indicates average value obtained by laboratories using digestion methods involving H_2SO_4 (g or j)

T = "true" value, sk = skewness and k = kurtosis





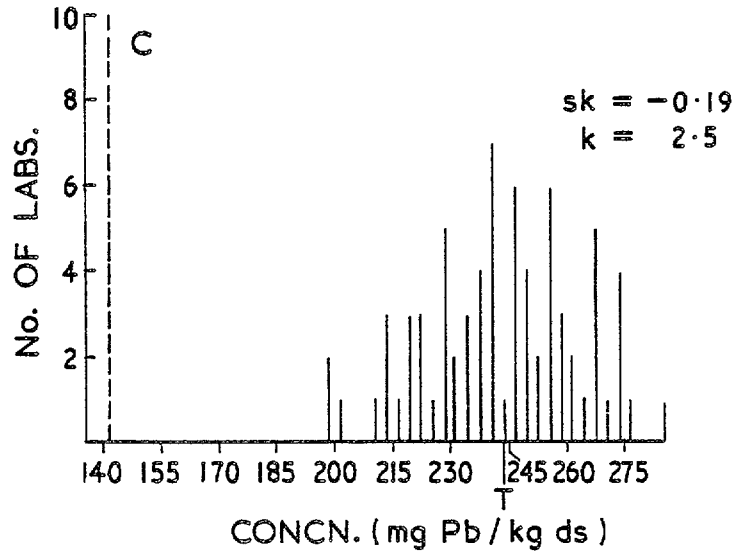
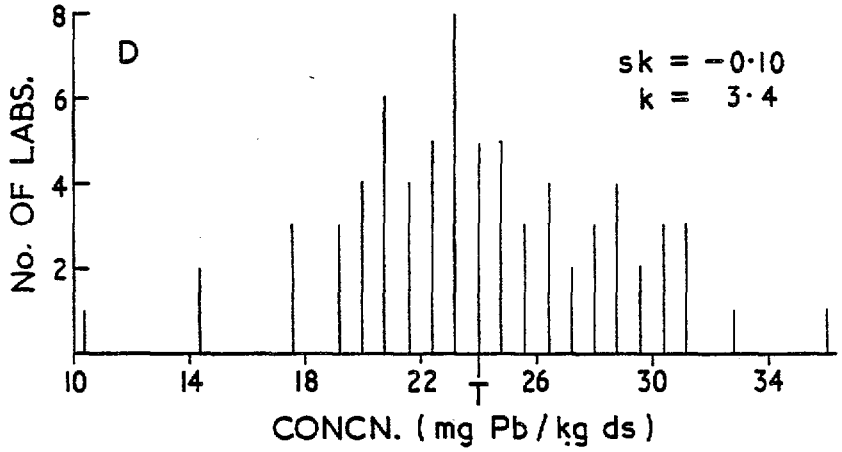
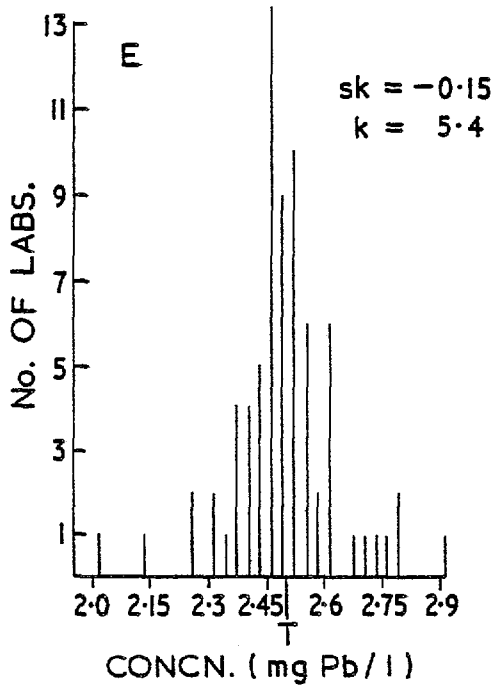


Figure I continued





APPENDIX J - RESULTS FOR 'TOTAL' CONCENTRATIONS OF ZINC IN SLUDGES AND SOIL

TABLE J1 Summary of results for "total" zinc

n = 10 unless stated; † n = 8, ‡ n = 3-6 * indicates significant between-batch error (P<0.05)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
1	f	3.5	-25.5	27.0	7.7*	-25.0	24.5	11.1*	-9.1	17.3	8.9*	11.3	19.1	1.5	-3.3	11.5
2	a	2.5	-1.3	2.7	4.9*	-2.4	6.2	2.5*	-6.1	7.9	7.1*	-9.5	14.4	8.2*	-1.6	9.8
3	k	4.0	5.7	8.1	5.5	1.2	4.4	5.2	0.7	3.7	7.4*	1.6	7.3	1.9	-1.8	2.9
4	a	5.8*	-8.7	13.0	5.7	-2.7	6.3	11.1*	-7.8	15.9	19.4	-11.3	25.5‡	1.8	-1.1	2.3†
5	a	5.8	8.3	11.9	8.8*	2.7	10.0	7.9*	2.4	8.7	6.2	0.9	4.5	2.6*	-1.5	3.6
6	a	2.1	5.2	6.5	6.1	3.3	7.0	3.1	3.8	5.7	2.3	-2.9	4.2	1.7	-3.0	3.9
7	g	8.4*	-10.1	16.2	8.2*	-17.6	22.9	15.8*	-11.0	24.2	31.8*	-6.0	30.1	1.8*	-3.3	4.7
8	a	7.7	-8.0	12.1	8.0	-11.2	15.3	12.2*	-6.7	15.3	8.1*	-3.7	9.8	4.5*	-0.2	3.8
9	a	6.8*	-5.2	10.4	5.5*	-7.9	11.9	3.8	-3.6	5.7	3.8*	-15.9	18.3	1.7	5.1	6.1
10	a	9.1*	-4.5	11.2	6.6	-4.6	8.2	14.3*	-0.5	11.9	16.3	-4.8	13.7	5.1	-0.5	3.4
11	a	2.6*	2.5	4.5	2.7	0.4	2.1	5.8*	3.1	7.7	6.5	5.3	9.3	2.5	0.8	2.4
12	d	6.1*	0.1	5.0	6.6*	1.0	6.1	4.7	10.8	13.7	5.0	10.7	13.8	0.8	2.1	2.6
13	a	3.4*	3.2	6.0	5.6	1.5	4.0	9.0	-13.0	17.6	8.8*	-9.9	16.3	3.9*	-7.2	10.0
15	b	6.1*	-4.6	9.0	4.4	-1.3	3.8	4.8	2.1	4.9	6.0	-7.8	11.1	5.3*	-2.1	8.0‡
16	a	3.3	-3.1	4.9	3.5	-0.2	2.2	4.5*	-2.9	6.3	6.4*	-9.9	14.2	3.1*	-7.9	10.1
18	j	6.9	9.2	13.5	24.6*	-6.3	24.7	34.5*	-12.4	36.8	6.8	16.0	20.6	6.6	5.2	9.1
19	d	2.2	6.5	7.8	2.6*	5.1	7.4	5.7	8.0	11.6	5.8*	5.8	10.7	1.0*	0.9	1.8
20	d	4.0*	1.4	4.5	4.8*	1.6	5.4	6.3*	-0.8	5.8	3.8	-1.7	3.8			
21	b (k for A.)	2.2	1.7	3.0	1.1	-2.6	3.2	2.2	-3.6	4.8	2.1	-15.2	16.3	2.6*	5.6	7.8
22	a	8.8	-4.1	9.0	3.7	-4.0	6.0	8.8	-4.3	9.2	4.3*	-7.6	10.7	0.9*	-0.5	1.2
23	a (d for D)	9.9*	-5.6	12.7	6.9*	3.3	8.8	8.2	8.1	13.2	9.6*	21.7	30.8	5.6*	8.9	13.8
24	b	2.7	2.5	4.0	3.3*	2.4	5.2	9.0*	7.0	14.9	3.6*	9.8	12.9	3.5	15.1	17.4
25	d	6.8	3.0	7.1	3.2*	11.0	13.7	2.9	10.8	12.7	9.9*	14.4	23.3	5.1*	-4.9	8.7
26	a	4.1	4.0	6.5	3.8	7.5	9.9	3.9	15.4	18.0						
27	d	4.1*	-0.2	3.4	2.5	-4.1	5.5	2.5	-4.6	6.3	5.1	2.4	5.4	4.8	-8.3	10.8
28	a	2.0*	-5.9	7.4	1.4*	-4.7	5.8	3.2*	0.6	3.2	4.4*	0.6	4.2	1.5*	1.4	2.6
29	j	4.4*	0.7	4.2	4.5*	-0.3	3.8	6.0	1.8	5.3	8.1	13.9	24.5	8.8*	-2.8	9.7
30	j	7.6	3.3	7.8	33.6*	26.9	59.1	7.9	9.4	14.4	26.2*	18.9	42.9	12.0*	7.4	17.5
31	j	4.0	-22.7	24.5	5.3*	-26.4	29.5	3.5	-14.4	16.2	2.1	-0.9	2.1	6.5*	6.1	11.6
32	a	11.2	5.6	12.5	3.5*	2.8	5.7	5.4	-0.3	3.5	8.2*	-6.7	12.9	1.4	1.7	2.5
33	a	3.2*	-5.6	8.0	19.0	-4.4	14.9	11.4	-10.5	16.4	28.1	-28.5	40.1	2.3*	3.6	5.6
34	a	3.7	-2.7	3.4†	7.8*	2.4	9.9†	6.7	1.7	6.3†	8.4*	-26.4	32.2‡	1.2*	-0.6	2.6†
35	a	2.2	-5.4	6.6	2.8	-5.1	6.6	2.9	-4.7	6.3	3.5*	-1.4	3.9	1.8	-3.7	4.7
36	a	2.9	3.2	3.7†	2.1	4.6	6.1†	7.0	2.5	7.3†	3.7	10.1	13.5‡	3.4	7.8	12.0‡
38	a	6.6	-4.3	5.9†	3.3	-2.8	4.9†	11.0*	-3.6	13.5†	12.3*	-7.3	18.0†	0.4	0.3	0.5†
39	k	11.8*	0.7	9.8	16.7*	-2.1	19.0	15.9*	-3.8	16.2	28.9	-0.6	17.3			

TABLE J1 (cont'd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
40	k	3.0*	5.7	8.2	2.5	6.1	7.6	6.6*	7.5	12.9	3.3	14.3	16.8†	3.0	0.8	4.3‡
41	a	8.5	-9.6	14.1	4.0	-8.6	10.7	8.9	-8.1	12.8	5.6	2.9	6.3	4.0*	-11.7	14.6
42	a	3.9	24.4	27.7†	7.9	28.4	34.9	12.2	26.5	36.8†	8.9	38.4	48.6‡	8.3	20.5	161.1‡
43	e	8.8	-3.6	8.5	15.6	-12.0	19.2	22.2*	-20.8	34.8	14.8	-0.4	9.0	21.6	3.8	16.7
44	k							3.2	0.2	2.0				3.3*	-3.7	6.3
45	a	6.2	1.5	5.2	5.6	-0.7	3.3	6.6	-8.9	12.4				1.9*	1.4	2.9
46	a	0.7	-4.6	5.0	2.0	-7.6	8.7	1.2*	-9.4	10.2				0.9	-9.3	9.8
47	b				3.0*	5.6	8.1							2.2*	0.4	1.8
48	a	3.3	7.4	9.5	3.4*	12.1	15.1	4.6*	24.0	28.4				4.9	9.0	12.4
49	k	3.6*	1.7	4.5										1.5*	0.8	2.1
50	k	4.3*	-3.7	7.0										3.0*	-4.9	7.1
51	k	1.4	-2.5	3.3										2.3	-4.2	5.5
52	a	5.3	-7.5	10.3	3.5	-9.2	11.5	3.5*	-17.0	19.3	7.3*	-0.9	6.6	0.2	-0.4	0.5
53	a	8.0	-0.2	4.8	5.9	4.8	8.3	5.5	-1.8	4.9				3.8*	-1.9	5.0
54	g				15.3*	-26.4	35.6							3.9*	-23.3	25.7
55	k				4.1*	7.1	10.7				7.8*	24.7	32.3	0.5	5.2	5.5
56	a	14.9*	-21.1	30.5	15.1*	-22.7	31.8	7.0	-17.4	20.8	11.5	-33.3	37.8	2.4*	0.7	1.5
57	d							9.5	-3.8	11.3‡				0.9	1.6	2.3‡
58	a	6.6	5.7	9.8												
59	k	3.3	4.6	6.7	3.5	7.8	10.0	2.9	1.0	2.7	9.9	2.0	6.7	1.1*	1.8	2.7
60A	h	1.0	-1.5	2.1	1.7*	3.9	5.4	1.6*	3.2	4.5	2.1	-4.7	5.9	0.5	0.4	0.7
60B	b	1.3*	0.9	1.9	1.6*	3.9	5.1	1.6*	2.9	4.2	1.9*	-13.4	14.6			
60C	c	1.4	1.6	2.4	1.6	3.9	4.9	1.2	4.4	5.1	1.5*	-7.1	8.2			
61	b	4.8*	2.3	6.3	2.5	0.4	1.9	3.8	3.0	5.3				1.6*	-0.6	1.3
62	b										10.0	-5.1	10.6			
63	g	4.3	-3.7	6.1	12.2	-6.9	13.5	11.3	-10.4	16.3	24.9	-13.1	26.2			
64A	b	6.8*	-3.1	8.2	7.5*	-2.9	8.7	6.4*	-9.4	14.0	9.7*	-10.2	17.0	6.0*	-2.7	7.4
64B	b	7.3*	-0.1	5.8	6.9	0.8	4.9	7.7	-4.4	8.7	12.4*	-36.4	42.5			
65	b	1.2	4.1	4.8	5.5*	-3.5	7.6	1.8	3.0	4.0	25.9	-1.5	16.3	2.6*	-2.2	4.1
66	k	3.5*	1.3	4.1	1.8	-1.1	2.1	2.7	1.4	2.9	4.3	-1.0	3.5	1.3*		
67	j	6.7	8.9	13.1	8.0*	15.3	22.6	6.1	0.2	4.5	20.3*	-3.3	19.1			
68A	g	8.6*	6.9	13.9	7.7*	6.1	12.7	10.0*	7.1	15.6	45.4*	-54.9	71.0	10.7	7.2	13.8
68B	i	3.6	10.8	14.7‡				2.8	3.9	6.7‡	4.2	8.3	12.6‡			
69	i	3.9	-8.5	10.5	3.2*	5.6	8.2	8.8	2.7	8.0	3.6	-0.6	2.7	1.3	2.2	3.0
70	g	15.9*	-16.1	26.6	13.2	-18.4	24.6	16.6*	-14.9	25.6	22.4*	-18.7	33.2	2.0	-0.7	1.9
71	a	5.2	5.0	7.9	7.7*	1.5	7.4	4.4	6.8	9.5	4.3	-6.2	8.5	2.0	1.2	3.2‡

TABLE J1 (Cont'd)

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
72	b	2.5	20.0	21.8	3.6*	20.5	23.8	2.7	21.4	23.2	9.3*	5.4	12.7	1.3*	0.4	1.5
73	b	8.6	15.5	21.3	4.5*	10.1	14.1	5.7	15.8	19.6	6.4*	3.0	8.4	2.3	1.2	2.7
74	b	3.4*	-3.6	6.1	2.4*	-5.7	7.4	2.9	-3.1	4.7	2.0	-10.1	11.2	1.0	1.3	1.8
75	d	2.2	-3.8	5.1	4.3*	4.2	7.7	1.8	4.5	5.5	1.9	15.1	16.4	0.8	0.6	1.1
76	d	1.4	3.9	4.8	1.9	10.4	11.7	2.3	6.6	8.1	2.8	14.3	16.1	2.2*	7.3	9.2
77	d	4.6*	3.2	6.9	4.6*	3.8	7.5	17.0	1.2	11.3	4.5	11.5	14.5	6.6*	0.4	5.5
78	b	5.4*	5.6	10.1	4.6*	3.7	7.2	3.4*	2.5	5.3	6.8*	1.3	6.8	1.8	-3.8	5.0
79	k	28.8	-16.0	32.2				11.2	-20.0	25.9	37.8	21.8	52.6	12.0	-19.0	25.6
80	d	9.1	11.2	17.0	9.9	7.2	13.4	12.2*	9.1	20.0	7.5	15.3	20.4	2.7	4.3	5.9
81	a	3.4	-4.3	6.2	4.4*	-6.1	9.3	5.4*	-4.0	8.1	3.5*	-0.9	3.6			
82	g	4.1	-2.6	4.9	6.4*	-4.9	9.5	10.8*	-7.5	15.4						
83	g	2.2	-0.9	2.2	2.0	-0.3	1.4	2.5	4.1	5.6						
84	a	4.8*	2.0	5.6	9.4*	0.9	8.5	6.9*	2.6	8.2	8.1*	-2.2	8.3	0.7	0.1	0.5
85	k (a for D)	6.8*	2.1	7.3	3.4	5.8	7.9	4.8*	2.1	6.0	6.9	7.5	11.8			
86	i	11.0*	-0.3	9.3	6.6*	8.8	14.5	10.3*	10.3	19.6	13.2*	29.7	42.9			
87	a	4.3	2.9	5.4	8.5*	2.4	9.5	9.9*	0.7	8.8						
88	i	10.5*	3.3	12.0	11.5*	1.4	10.8	15.3*	1.8	14.2						
89	b	9.8*	2.4	19.0+	3.5	2.9	9.0+	4.3	1.4	6.4+	3.9	11.9	17.0+	8.6	1.5	2.9+
90	b	3.7	0.8	2.0	4.2	-1.7	4.0	3.8	1.0	3.2	3.4	10.1	12.3	2.1	0.3	2.7
91	b	3.3	13.9	16.1	5.9	3.5	7.0	3.9*	13.0	16.5	5.8	16.1	19.9	1.6*	0.4	1.3
92	d	1.8	-5.9	6.9	3.7	-3.2	5.2	6.1	-5.3	8.7	4.1*	-2.5	5.6	3.8*	2.3	5.3

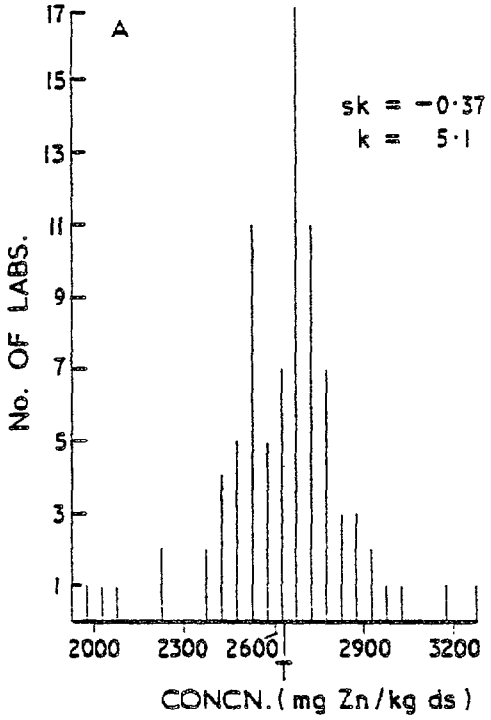
TABLE J2. Statistics of populations of grouped laboratory means: zinc

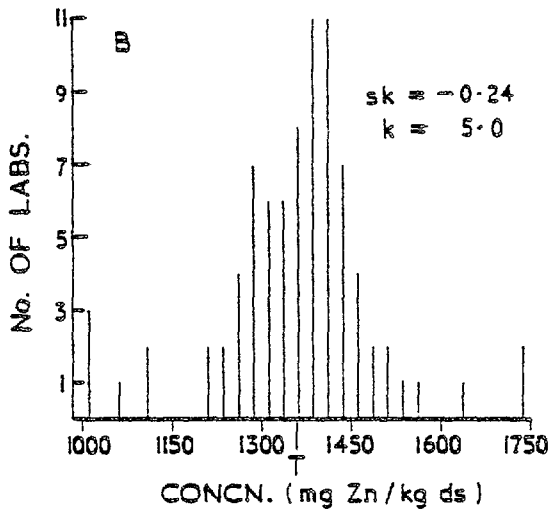
Sample	Mean, $\bar{x}$	Standard deviation, s	Number of groups	Skewness	Kurtosis
A	2,635	209	27	-0.367	5.13
B	1,362	129	30	-0.242	4.96
C	603.8	56.8	30	0.368	3.75
D	80.03	12.05	38	-0.595	4.71
E	9.958	0.613	45	-0.449	7.16

Units for $\bar{x}$ and s are mg/kg dry basis (A-D) or mg/l (E)

in samples A–E for zinc

T = "true" value, sk = skewness and k = kurtosis





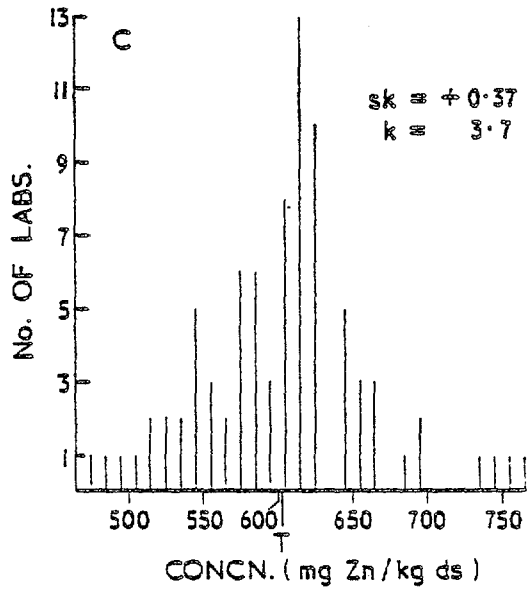
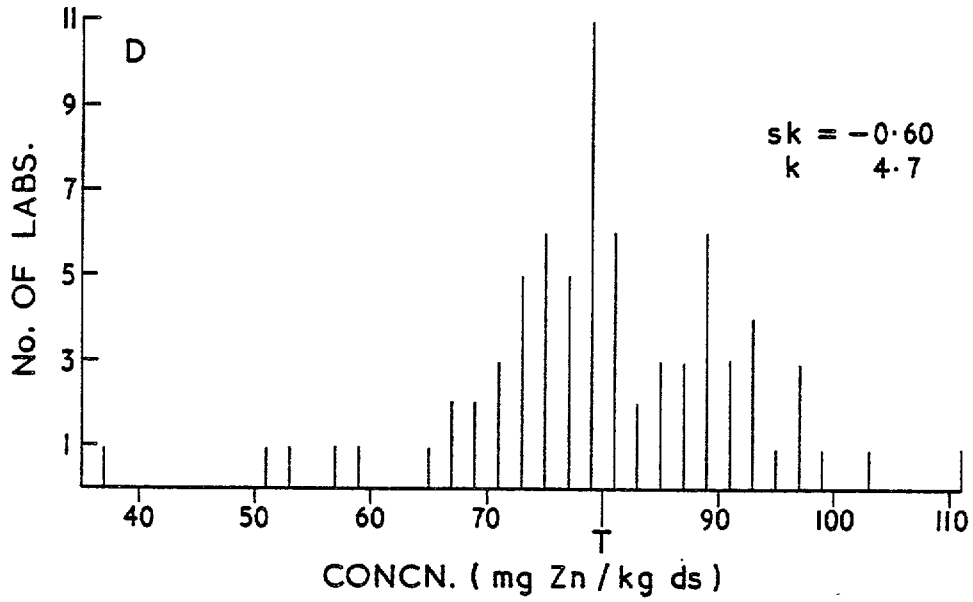
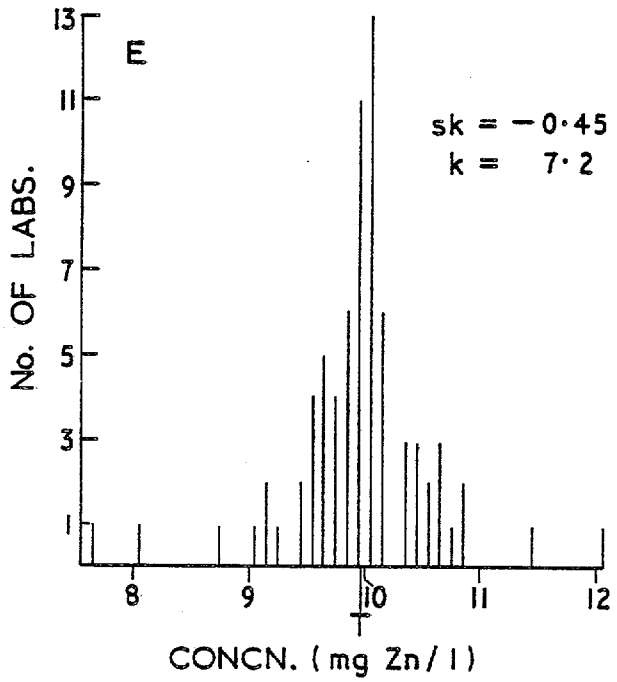


Figure J continued





APPENDIX K

STANDING COMMITTEE OF ANALYSTS METHODS FOR EXTRACTABLE METALS

THE DETERMINATION OF EXTRACTABLE METALS IN SOILS, SEWAGE SLUDGES AND RELATED MATERIALS

INTRODUCTION

The total content of trace elements in soils provides a general indication of their status and potential availability to plants but no information on their forms of occurrence. Trace elements may be present in the soil solution or held as readily exchangeable ions, as more firmly bound ions, as chelated ions, incorporated in precipitated oxides or insoluble salts and fixed in the crystal lattices of secondary or primary minerals. Water soluble and exchangeable ions are generally held to be readily available to plants but often represent only a very small proportion of the total content.

Some form of extraction is normally employed for the arbitrary assessment of the availability of soil constituents to the plant and an ideal extractant would simulate plant behaviour in so far as the uptake of all elements is concerned. Such an extractant is not available. The varied forms of combination of different elements in the soil and the fact that plant contents of trace elements vary depending upon species, part of the plant sampled and seasonal changes during growth are all factors which have to be considered in relating the trace element content of soil extracts to plant uptake. The extractant used must be both analytically convenient and diagnostically acceptable and will depend on the nature of the soil and the properties of the element in question.

For much investigational work a dilute acid extractant is used to assess the availability to plants of elements such as Cd, Co, Ni and Zn, present in soils in exchangeable cation form. Some trace elements occur in soils as metal-organic complexes that appear to be available to plants and for Cu it has been found that EDTA provides a more satisfactory diagnostic correlation with plant uptake than does a dilute acid extractant. For calcareous soils dilute acid extractants may be unsatisfactory as they could be neutralised by free lime present in the soil and in such cases EDTA may therefore be preferable. 0.05 M EDTA and 0.5 M acetic acid are widely used in assessing the availability of a number of trace elements in soils and the methods for the determination of these

are described below. Whichever extractant is employed it must be emphasised that it is necessary to establish experimentally the relationship between soil content and plant or animal behaviour under local conditions. All determinations of extractable trace metals described here are carried out on air-dry, <2 mm sieved samples.

Many cultivated surface soils, after air-drying and sieving have a density of around 1.0, notable exceptions being peats or soils with very high organic matter contents. With light peaty soils it may be useful therefore to express concentrations of metals on a W/V basis rather than a W/W basis to facilitate the interpretation of the amounts of elements available in the rooting zone of plants. For the majority of cultivated surface soils however differences between the two are probably small. It is recommended therefore that concentrations of metals in soils, sewage sludges and related materials be determined and expressed on W/W basis. In those cases where it may be necessary to express levels on a W/V basis, a conversion factor can be applied, following determination of the sample density.

THE DETERMINATION OF CADMIUM, CHROMIUM, COPPER, LEAD, MANGANESE, NICKEL AND ZINC EXTRACTABLE BY 0.05 M EDTA IN SOILS, SEWAGE SLUDGES AND RELATED MATERIALS

1. PERFORMANCE CHARACTERISTICS OF THE METHOD

1.1.	Substances determined.	Extractable Cadmium, Chromium, Copper, Lead, Manganese, Nickel and Zinc.
1.2.	Type of sample.	Soils, sewage sludges and related materials.
1.3.	Basis of the method.	Extraction of the sample with 0.05 M EDTA followed by determination of the extracted metals by atomic absorption spectrophotometry.
1.4.	Range of application.	
1.5.	Calibration curve.	
1.6.	Standard deviation. (a)	
1.7.	Limit of detection.	
11.8.	Sensitivity.	
1.9.	Bias.	
1.10.	Interferences.	See Section 3.
1.11.	Time required for analysis.	For 18 simultaneous extractions the analytical time is 4 h. and the operator time 3 h 15 m.

Sixteen soils	Range mg/kg	SD	Mean RSD
Copper	0.45-2.39	0.08-0.18	11.8
Manganese	8.8-48.6	0.5-4.2	6.6
Zinc	0.47-2.80	0.0-0.13	5.9

(a) From A.M. Ure and M.L. Berrow, Anal. Chim. Acta, 52 (1970) 247-257.

2. PRINCIPLE

The metals are extracted from the sample with 0.05 M ammonium ethylenediamine tetracetate solution (EDTA) at pH 7.0. The concentration of the metals in the extract is determined by atomic absorption spectrophotometry.

3. INTERFERENCES

Spectral interference can occur when undissociated molecular species in the atomiser absorb light at the same wavelength as (dissociated) atoms of the element of interest, particularly in the wavelength region below about 250 nm. Additional "apparent" absorption arising from other effects, such as scattering of light from the line source by high concentrations of inorganic salts, may also occur. These "non-atomic" effects are corrected for in most recent instruments by use of a suitable background correction system.

4. REAGENTS

All reagents and standard solutions should be kept in polyethylene bottles unless otherwise stated. Analytical reagent grade chemicals are suitable unless otherwise specified.

4.1. WATER

The water used to prepare the extracting and standard solutions should have metal contents that are negligible relative to the lowest concentration to be determined in the samples. Water distilled from an all glass apparatus is normally suitable but deionized water may contain traces of metals depending upon the local water supply.

4.2. AMMONIA SOLUTION (d_{20} 0.92)

Ammonia gas from a commercial liquid ammonia cylinder, controlled by a mild steel needle-valve, is gently bubbled into 1500 ml glass distilled water contained in a borosilicate vessel within a fume cupboard. The volume increases during the dissolution period and on cooling should be slightly greater than 2000 ml. When bubbles of ammonia gas reach the surface of the liquid the solution is saturated. This is normally after a period of 10 h. An appropriate safety trap between the needle-valve and the receiver prevents suck-back of the solution into the cylinder. Store in a polyethylene container in a cool place.

4.3. EDTA, AMMONIUM SALT SOLUTION, 0.05 M

4.3.1. Add 146.12 ± 0.05 g EDTA free acid to 800 ± 20 ml water and partially dissolve by stirring in 130 ± 5 ml ammonia solution (d_{20} 0.92). Continue the addition of further ammonia solution drop by drop until all the EDTA has just dissolved. Filter through a suitable filter paper (porosity 1.4-2.9 microns) into a 10 litre polyethylene container. Make up to 9 ± 0.5 litres. Adjust pH

value to 7 ± 0.05 by addition of a few drops only of ammonia solution or hydrochloric acid, make up to 10 ± 0.1 litres and shake well. (Prepared by this procedure, the solution is virtually free from copper contamination.)

4.3.2. Alternatively dissolve 190 ± 0.05 g EDTA, diammonium salt in water, dilute to 10 ± 0.1 litres and shake well. Store in a polyethylene container. (Prepared by this procedure, the extracting solution may contain unacceptably high concentrations of metals.)

4.4. 50% V/V HYDROCHLORIC ACID

Dilute 500 ± 5 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

4.5. 50% V/V NITRIC ACID

Dilute 500 ± 5 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

4.6. STANDARD CADMIUM SOLUTIONS

4.6.1. Solution A 1 ml is equivalent to 100 µg Cd

Weigh 100.00 ± 0.5 mg of cadmium wire (greater than 99.9% purity) and dissolve with gentle heating in a mixture of 7.0 ± 0.5 ml of nitric acid (d_{20} 1.42) and approximately 20 ml of water. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

4.6.2. Solution B 1 ml is equivalent to 20 µg Cd

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

4.7. STANDARD CHROMIUM SOLUTIONS

4.7.1. Solution A 1 ml is equivalent to 1 mg Cr

Weigh 1.000 ± 0.005 g chromium metal (greater than 99.9% purity) and dissolve with gentle heating in a minimum volume of 50% V/V hydrochloric acid. Quantitatively transfer the solution to a 1 litre calibrated flash, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

Alternatively, dissolve 2.829 ± 0.005 g of $K_2Cr_2O_7$ in distilled water, add

20 ml nitric acid (d_{20} 1.42). Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

4.7.2. Solution B 1 ml is equivalent to 20 µg Cr

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

4.8. STANDARD COPPER SOLUTIONS

4.8.1. Solution A 1 ml is equivalent to 1 mg Cu

Weigh 1.000 ± 0.005 g copper metal (greater than 99.9% purity) and dissolve with gentle heating in a minimum volume of 50% V/V nitric acid. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

4.8.2. Solution B 1 ml is equivalent to 20 µg Cu

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

4.9. STANDARD LEAD SOLUTIONS

4.9.1. Solution A 1 ml is equivalent to 1 mg Pb

Weigh 1.000 ± 0.005 g lead wire (greater than 99.9% purity) and dissolve with gentle heating in a mixture of 7.0 ± 0.5 ml of nitric acid (d_{20} 1.42) and approximately 20 ml of water. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

4.9.2. Solution B 1 ml is equivalent to 20 µg Pb

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

4.10. STANDARD MANGANESE SOLUTIONS

4.10.1. Solution A 1 ml is equivalent to 1 mg Mn

Weigh 1.000 ± 0.005 g of manganese metal (greater than 99.9% purity) and dissolve with gentle heating in a minimum volume of 50% V/V nitric acid.

Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

4.10.2. Solution B 1 ml is equivalent to 20 µg Mn

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

4.11. STANDARD NICKEL SOLUTIONS

4.11.1. Solution A 1 ml is equivalent to 1 mg Ni

Weigh 1.00 ± 0.005 g of nickel metal (greater than 99.9% purity) and dissolve with gentle heating in a minimum volume of 50% V/V nitric acid. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

4.11.2. Solution B 1 ml is equivalent to 20 µg Ni

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be fresly prepared before use.

4.12. STANDARD ZINC SOLUTIONS

4.12.1. Solution A 1 ml is equivalent to 1 mg Zn

Weigh 1.000 ± 0.005 g of zinc metal (greater than 99.9% purity) and dissolve with gentle heating in 40 ml of 50% V/V hydrochloric acid. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

4.12.2. Solution B 1 ml is equivalent to 20 µg Zn

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

4.13. Dilute the appropriate standard solutions B with 0.05 M EDTA solution to prepare a range of working standards covering the anticipated concentrations of each element in the extracts.

5. APPARATUS

5.1. LABORATORY WARE

On each occasion all laboratory ware (extraction bottles, beakers, filter funnels etc.) used in the procedure should be cleaned with 1:1 hydrochloric acid, rinsed with distilled water, cleaned with 0.005 M EDTA solution and finally rinsed with distilled water. Rubber stoppers and plastic materials containing zinc or cadmium should not be used in this determination.

5.2. EXTRACTION BOTTLES

250 ml borosilicate with glass stoppers. Polypropylene or polyethylene bottles and caps are also suitable.

5.3. A mechanical shaking apparatus.

5.4. FILTER STANDS AND FUNNELS

Filter stands should preferably be made from polypropylene and filter funnels from polyethylene to reduce metallic contamination.

6. ANALYTICAL PROCEDURE

Step	Experimental procedure	Notes
6.1.	Transfer 15 ± 0.1 g (notes a and b) dry sample prepared as described in (1) into the extraction bottle. Add 75 ± 1 ml 0.05 M EDTA extracting solution and immediately shake for exactly 1 h, preferably at a temperature of 20°C. Immediately filter through an 18.5 cm filter paper, (porosity 0.4-1.1 microns) and retain the filtrate for the determination of metals by atomic absorption spectrophotometry (note c). Carry out blank determinations with each set of analyses. It is convenient to allow the extracts to filter overnight.	(a) The subsample required for analysis is obtained by placing the whole sample on a polyethylene sheet and coning and quartering until approximately the required weight is reached. (b) If the concentration is to be expressed on a W/V basis, multiply the value obtained in 6.1 by the laboratory density.

Step	Experimental procedure	Notes
6.2.	Determine the laboratory density by weighing 20 ml (scoop filled and struck off level without tapping) of dry sample prepared as described in (1) and divide the weight in grams obtained by 20.	(c) Some extracts may require dilution with 0.05 M EDTA solution to bring their metal concentrations within the working ranges.

7. REFERENCES

1. The Sampling and Initial Preparation of Sewage and Waterworks' Sludges, Soils, Sediments and Plant Materials Prior to Analysis 1977. Published by HMSO.

THE DETERMINATION OF CADMIUM, NICKEL AND ZINC EXTRACTABLE BY 0.5 M ACETIC ACID IN SOILS, SEWAGE SLUDGES AND RELATED MATERIALS

1. PERFORMANCE CHARACTERISTICS OF THE METHOD

1.1.	Elements determined	Extractable Cadmium, Nickel and Zinc.
1.2.	Type of sample	Soils, sewage sludges and related materials.
1.3.	Basis of the method	Extraction of the sample with 0.5 M acetic acid followed by determination of the extracted metals by atomic absorption spectrophotometry.
1.4.	Range of application	
1.5.	Calibration curve	These performance characteristics are
1.6.	Standard deviation	dependent on the analytical technique and
1.7.	Limit of detection	instrumentation used for the final deter-
1.8.	Sensitivity	mination.
1.9.	Bias	
1.10.	Interferences	See Section 3.
1.11.	Time required for analysis	For 18 simultaneous extractions the analytical time is 4 h and the operator time 3 h, excluding the overnight shaking period.

2. PRINCIPLE

The metals are extracted from the sample with 0.5 M acetic acid. The concentration of the metals in the extract is determined by atomic absorption spectrophotometry.

3. INTERFERENCES

Spectral interferences can occur when undissociated molecular species in the atomiser absorb light at the same wavelength as (dissociated) atoms of the element of interest, particularly in the wavelength region below about 250 nm. Additional "apparent" absorption arising from other effects, such as scattering of light from the line source by high concentration of inorganic salts, may also occur. These "non-atomic" effects are corrected for in the most recent instruments by use of a suitable background correction system.

4. REAGENTS

All reagents and standard solutions should be stored in polyethylene bottles unless otherwise stated. Analytical reagents grade chemicals as suitable unless otherwise specified.

4.1. WATER

The water used to prepare the extracting and standard solutions should have metal contents that are negligible relative to the lowest concentrations to be determined in the samples. Water distilled from an all glass apparatus is normally suitable but deionised water may contain traces of metals depending upon the local water supply.

4.2. ACETIC ACID, 0.5 M

Dilute 30 ± 1 ml of glacial acetic acid (d_{20} 1.049) with water to 1 litre in a measuring cylinder.

4.3. 50% V/V HYDROCHLORIC ACID

Dilute 500 ± 5 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder.

4.4. 50% V/V NITRIC ACID

Dilute 500 ± 5 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a measuring cylinder.

4.5. STANDARD CADMIUM SOLUTIONS

4.5.1. Solution A 1 ml is equivalent to 100 µg Cd

Weigh 100.0 ± 0.5 mg of cadmium wire (greater than 99.9% purity) and dissolve with gentle heating in a mixture of 7.0 ± 0.5 ml of nitric acid (d_{20} 1.42) and approximately 20 ml of water. Quantitatively transfer this solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

4.5.2. Solution B 1 ml is equivalent to 20 µg Cd

Dilute 20.0 ± 0.1 ml of solution A with 0.5 M acetic acid solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

4.6. STANDARD NICKEL SOLUTIONS

4.6.1. Solution A 1 ml is equivalent to 1 mg Ni

Weigh 1.000 ± 0.005 g of nickel metal (greater than 99.9% purity) and dissolve with gentle heating in a minimum volume of 50% V/V nitric acid. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

4.6.2. Solution B 1 ml is equivalent to 20 µg Ni

Dilute 20.0 ± 0.1 ml of solution A with 0.5 M acetic acid solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

4.7. STANDARD ZINC SOLUTIONS

4.7.1. Solution A 1 ml is equivalent to 1 mg Zn

Weigh 1.00 ± 0.005 g of zinc metal (greater than 99.9% purity) and dissolve with gentle heating in 40 ml of 50% hydrochloric acid. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

4.7.2. Solution B 1 ml is equivalent to 20 µg Zn

Dilute 20.0 ± 0.1 ml of solution A with 0.5 M acetic acid solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

4.8. Dilute the appropriate standard solutions B with 0.5 M acetic acid solution to prepare a range of working standard solutions covering the anticipated concentrations of each element in the extract.

5. APPARATUS

5.1. LABORATORY WARE

On each occasion all laboratory ware (extraction bottles, beakers, filter funnels etc) used in the procedure should be cleaned with 1:1 hydrochloric acid and finally well rinsed with distilled water. Rubber stoppers and plastic materials containing cadmium or zinc should not be used in this determination.

5.2. EXTRACTION BOTTLES

250 ml borosilicate with glass stoppers. Polypropylene or polyethylene bottles and caps are also suitable.

5.3. A mechanical shaking apparatus

5.4. FILTER STANDS AND FUNNELS

Filter stands should preferably be made from polypropylene and filter funnels from polyethylene to reduce metallic contamination.

6. ANALYTICAL PROCEDURE

Step	Experimental Procedure	Notes
6.1.	Transfer 5 ± 0.05 g (note a) dry sample prepared as described in (1) into the extraction bottle. Add 200 ± 2 ml 0.5 M acetic acid extracting solution and shake, first by hand for a few minutes, frequently releasing any pressure arising from the liberation of carbon dioxide, and then on the mechanical shaking machine continuously for a 16 h period preferably at 20°C. Filter through a 18.5 cm filter paper (porosity 0.4-1.1 microns) and retain the filtrate for the determination of metals by atomic absorption spectrophotometry (notes b and c). Carry out blank determinations with each set of analyses.	(a) The subsample required for analysis is obtained by placing the whole sample on a polyethylene sheet and coning and quartering until approximately the required weight is reached. (b) If the concentration is to be expressed on a W/V basis, multiply the value obtained in 6.1. by the laboratory density. (c) Some extracts may require dilution with 0.5 M acetic acid solution to bring their metal concentrations within the working ranges.
6.2.	Determine the laboratory density by weighing 20 ml (scoop filled and struck off level without tapping) of dry sample prepared as described in (1) and divide the weight in grams obtained by 20.	

7. REFERENCES

1. The Sampling and Initial Preparation of Sewage and Waterworks' Sludges, Soils, Sediments and Plant Materials Prior to Analysis 1977. Published by HMSO.

APPENDIX L. LABORATORIES' OWN METHODS FOR EXTRACTABLE METALS

TABLE L1 METHODS, "EXTRACTABLE" METALS

LABORATORY NUMBER	OWN METHOD 1	OWN METHOD 2
2	Digest SCA extracts with HNO_3 before analysis	For Zn in HAc, extract 0.5h
3	Extract with 0.5M HAc overnight(Ni)or 0.5 h (Zn), use 10/200 (w/v)	Extract with 0.05M EDTA for 1h, use 2/50 (w/v)
12	Cu, as SCA EDTA method but use EDTA at pH4.	
13	As ADAS 10*	
15	As ADAS 10* but use 100.1 HAc/5ml soil	
21	As MAFF Bulletin 27†	
23	As ADAS 10*	
24	As ADAS 10*	
25	HAc as MAFF Bulletin 27†	
31	As MAFF Bulletin 27†	
35	As MAFF Bulletin 27†	
41	Cu as ADAS 10*	
43	As MAFF Bulletin 27†	
52	HAc 0.5h extraction as MAFF Bulletin 27†	
58	EDTA as MAFF ANAL/C/5‡ (0.05M EDTA, pH7)	HAc as MAFF ANAL/C/46‡ (0.5M HAc)
60(1)	As ADAS 10*	
64(1)	As ADAS 10*	
67	EDTA at pH 4.0	
68(1)	As ADAS 10*	
70	As MAFF Bulletin 27†	
92	As MAFF Bulletin 27† (HAc but 10.1 extraction ratio	

*MINISTRY OF AGRICULTURE FISHERIES AND FOOD, ADAS Advisory Paper 10, HMSO 1971
† " " " " " " , Technical Bulletin 27, HMSO 1973
‡ " " " " " " , Conference of Analysts, Analysts' Publication Committee (Unpublished)

APPENDIX M. RESULTS FOR EXTRACTABLE CONCENTRATIONS OF METALS IN SOIL

TABLE M1. Summary of results for extractable copper, nickel and zinc (SCA methods)

n = 10 unless stated; †n = 8; ‡n = 3-6; * indicates significant between-batch error ($P<0.05$)

LAB. NO.	COPPER						NICKEL						ZINC					
	EDTA			HAc			EDTA			HAc			EDTA			HAc		
	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
1	3.5	3.9	6.0	13.6	16.9	26.2	5.4	31.7	35.9				8.3	-1.4	6.1	4.4	-50.0	51.2
2A	6.4*	-7.0	12.6†							50.8†	13.2	59.7				16.3	-6.9	15.7
2B	8.9*	-4.3	11.1							19.0	-2.1	12.9				16.3	-9.4	18.0
3	37.5*	-19.7	44.4	41.1	48.1	60.5	28.4*	-17.3	36.4				17.4*	-9.2	18.3	11.2*	-15.5	23.0
5	2.8	-7.1	8.7	40.4*	12.4	45.2†	8.7*	-15.8	21.8	12.3*	-13.8	21.8	27.6*	20.3	46.8	44.8*	25.6	68.3
7	2.2	2.6	4.4‡							49.5*	72.8	172.3†				10.2*	8.0	20.1‡
8	11.6						14.0*	3.6	15.0	52.8*	62.0	128.5	24.4	15.7	32.1	33.1	29.2	53.9
9	8.4*	-2.8	9.2	19.1*	-7.5	21.0	11.1*	-13.6	21.3	26.2	-6.4	22.8†	10.6*	-9.1	16.7	5.0	-14.8	17.3
10	20.6	20.9	35.3				18.5*	11.4	27.6	36.8	0.1	21.5	11.6*	22.2	33.3	24.2	1.1	15.3
11	9.6	1.3	6.9				8.7	20.6	26.7	6.6	-10.3	13.7	5.1*	-4.5	8.3	6.3	-11.2	14.5
12	8.5*	11.6	19.1				10.5	-11.2	16.6	28.8	-61.7	68.1	8.5			10.9*	82.1	98.2
13	3.5*	-13.2	15.4				7.2*	-12.7	17.7	20.3	-14.6	24.7	15.6	11.0	21.0			
15	5.7	3.8	7.8†				4.9	-10.7	14.3	51.2*	36.8	93.4	10.0	35.5	46.6‡	4.7	-33.0	36.7‡
18										35.3	-27.4	44.6†				34.9	14.1	37.2
19	8.3*	3.6	10.6	13.7	-17.2	23.8	6.0*	-4.5	8.9				30.3	15.4	35.6	13.8	3.1	12.7 †
20	2.8	2.3	3.9				4.8*	3.3	7.4	26.3	15.9	33.5	2.1*	6.3	7.9	5.5*	-8.6	12.4
21	2.5	-9.7	11.0	8.8	-18.3	22.4	3.3	-3.3	5.2	11.6	-20.9	26.2	2.2	5.6	6.9	2.0	-7.5	8.6
22	9.3	-5.3	10.4	43.5	56.5	96.0	71.2*			61.5*	19.1	76.6	40.7*	9.5	45.9	23.5*	41.1	68.1
23	6.9*	-0.6	6.1	67.3	-33.9	59.7	11.4*	18.0	29.0	23.0*	-13.7	29.2	15.3	9.0	18.7	9.8*	8.4	16.8
24	7.3*	1.5	7.6				6.3*	24.4	31.6†	40.0*	-12.9	41.5	7.2*	1.6	8.5†			
25	14.2*	3.1	15.2	17.5	-23.6	31.4	11.6*	9.6	19.5	41.9*	-6.2	37.6	9.9*	-2.7	10.3	7.0	-12.3	15.8
26	0.7	2.7	3.1	14.8	-9.7	17.5	3.1	16.5	18.6	15.0	-10.3	18.1	9.9	-2.4	8.0	2.6	-0.3	1.8
27	5.5*	-6.7	11.4†	25.2	-10.5	25.7†	9.3*	-12.3	19.8†	37.4*	15.4	53.1†	4.7	-3.1	6.2†	5.6	-2.8	7.3‡
28	5.6*	8.1	12.9	10.2*	-15.1	21.7	3.8*	-2.2	5.1	11.2*	-16.0	23.7	2.5	4.5	6.0	4.2*	-5.1	8.3
29	2.1	-10.9	12.0				5.2*	-11.7	15.1				4.1*	-14.7	17.0	11.0	-11.7	17.3
30	13.7*	-3.1	13.6				18.2*	-6.3	19.6				49.3*	-21.3	53.0	18.5*	-25.5	41.3‡
31	3.8	-3.9	6.9‡	21.5	66.5	96.0‡	12.5*	-26.4	36.8‡	9.5	-26.7	32.4‡	8.7	-6.3	13.0‡	10.3	0.7	9.3‡
32	16.5*	-18.5	29.2	50.4	6.5	37.6	9.2	-10.0	14.8	37.5*	3.7	35.3	7.6*	-4.1	9.7	9.7	-1.8	7.3
33	9.9	-0.4	6.2				22.1	1.6	14.6	70.0	4.5	64.6‡	22.4*	10.9	31.2	11.2	15.4	30.5‡
39	49.2	5.2	35.3				16.3	5.5	15.5	8.3	46.3	53.4	22.7	10.0	24.5	35.5	50.5	81.4
41	6.4*	13.4	19.1	16.8	-5.9	15.1	7.6*	5.5	11.8	25.4*	26.9	52.9	8.0	1.2	5.9	6.8	-8.3	11.9
43	21.1*	-0.5	17.6	58.7*	-6.6	50.9	16.9*	4.0	17.5	32.8*	-2.7	28.4	14.6*	-1.3	12.2	20.0*	-10.3	2.1
52	9.4	4.0	9.7	19.1	41.2	56.7	4.5	20.1	23.3	5.4	51.5	56.2	7.5	-1.3	5.6	6.5	-21.9	24.9
56	4.5	-7.9	10.3	24.3			12.5	17.5	25.9				17.2*	-14.4	25.8			
60C										41.3*	-32.5	78.6‡				7.4	-14.8	22.3‡
64C	26.5*	-0.8	30.9	59.0	-30.6	78.8	12.6	0.1	10.6‡	18.0*	2.8	23.5‡	12.5	-0.2	10.5‡	13.1	-16.8	29.6‡

TABLE M1 (Contd)

LAB. NO.	COPPER						NICKEL						ZINC					
	EDTA			HAc			EDTA			HAc			EDTA			HAc		
	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
65	6.4*	18.4	24.5	9.5	18.6	25.1	13.4*	-9.1	18.2	1.4	5.4	6.3	9.9*	-5.9	13.4	4.7	17.5	20.8
66	4.3	-1.7	4.1				6.7	10.3	14.5	9.7	-3.3	8.8	4.0	1.2	3.6	6.2	-6.8	10.2
67	16.2	15.8	28.4‡				16.0	8.1	19.7†				12.4	14.0	23.4†	27.9	18.8	41.0†
68	3.6	14.1	17.5‡	11.0	1.9	11.3‡	3.3	10.6	13.6‡	15.5	24.1	39.9‡	7.9	-0.3	6.8‡	5.1	15.7	20.6‡
69	4.9	16.4	19.7	10.2	-7.5	13.0	5.3*	12.2	17.0	15.2*	-11.2	21.7	1.8	-1.0	2.0	2.5	2.7	4.2
70	3.7	-8.2	10.2	22.2	-67.8	111.6‡	5.4	-6.0	8.9	24.6	-9.8	22.7	4.9*	-20.6	23.6	14.6	32.7	44.0
71	13.4*	11.4	23.1				18.8	-6.0	16.2				7.8	-4.9	9.3			
72	8.2	3.0	7.9	16.4	21.1	32.6	8.2‡	-5.7	11.7	10.6	7.6	14.2	7.1	-1.9	5.9	15.8	-10.3	18.5
73	6.2	-9.0	12.3	24.3	4.4	19.1	4.1	-9.8	11.9	12.7	-7.7	14.5	6.3	1.4	5.1	7.5	-0.5	4.8
74	8.6*	-2.2	9.9†	17.4	2.9	13.3	9.3	-4.0	12.1†	33.9*	-23.3	43.2	3.5	-12.0	14.0†	6.8	-9.9	13.4
75	6.0	-14.6	17.5	8.2	-32.9	36.1	4.5	-17.2	19.3	11.8	12.4	20.1	2.6	-23.0	24.2	3.4*	-21.2	23.3
76	1.6	-2.0	2.9	8.6	-6.0	10.7	1.9	-0.6	1.7	3.2	2.6	4.5	1.5	-8.4	9.2	0.9*	2.8	3.6
77	6.1*	3.8	10.1‡				10.1*	-0.1	11.8‡	8.3	-47.7	54.1‡	2.2	-8.3	10.0‡	6.7	-8.8	13.9‡
78	3.2	-7.0	8.7	13.1	-2.8	10.2	4.8	16.0	19.2				3.6	-0.7	2.8	4.6*	-6.1	9.5
90	3.5	-4.1	6.1	29.4	-16.5	30.7	9.8	-7.9	13.1				7.8	0.2	5.5†	23.2	-17.5	28.6
91	15.8	26.6	33.3	40.4	-19.6	38.4	4.8	-24.9	27.0	20.4	-41.4	48.3	8.5*	-21.1	26.5	3.0*	-9.9	12.0
92	8.8*	7.2	13.7															

TABLE M2. Statistics of populations of laboratory means: extractable metals (SCA methods)

ELEMENT	SCA method	Mean $\bar{x}$	Standard deviation s	Kurtosis	Skewness
COPPER	EDTA	5.654	0.521	2.854	0.220
	HAc	1.341	0.383	3.543	0.978
NICKEL	EDTA	2.095	0.277	2.512	0.258
	HAc	2.296	0.629	3.671	0.517
ZINC	EDTA	7.334	0.871	3.536	0.480
	HAc	8.920	1.983	6.010	1.242

Units for $\bar{x}$ and s are mg/kg (dry basis)

TABLE M.3 Summary of results for extractable copper, nickel and zinc (own methods)

n = 10 unless stated. †n = 8 ‡n = 3-6. *indicates significant between batch errors (P=<0.05)

LAB. NO.	COPPER						NICKEL						ZINC					
	EDTA			HAc			EDTA			HAc			EDTA			HAc		
	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%	CV_t%	D%	MPD%
3																18.2*	-8.2	23.5‡
12	9.8*	10.3	20.0†															
13	4.2*	-12.6	15.5				3.7	-13.6	15.4	15.2*	25.2	40.1	13.3	-11.3	18.1	29.2	154.4	203.5
15	7.3	7.1	16.3‡							37.5	-37.4	65.0‡						
21				6.7	-70.1	71.3				7.6	-34.4	37.3				1.7*	-20.1	21.2
23	8.4*	-5.4	14.5‡				19.1*	1.2	22.9‡				3.2	-1.2	3.8‡	18.3	-7.5	21.4‡
24	7.3*	4.9	11.1													6.2	-2.6	6.1
25				28.5	-10.7	25.5				46.6*	7.7	47.6				18.7*	-4.7	18.9
31A	3.3	-1.9	4.6‡	4.7	65.8	72.2	9.3	12.9	19.5*	37.7*	63.6	135.1‡				5.3*	-9.7	15.1‡
31B																20.6*	22.7	51.9‡
35	5.9	22.1	26.2													5.4*	21.2	26.3
41	6.5	10.3	14.5															
43				91.9	29.6	98.6				88.4*	-7.2	72.2				24.0	-6.4	19.4
52				35.5	33.3	60.7				22.3*	61.6	88.8				17.0	-55.1	59.6
60C	11.3*	-4.8	13.6							7.5	-33.0	36.0				6.0*	-18.9	22.9
62	7.7	-38.4	41.6†							10.9	-28.8	33.3				35.5	-18.3	37.8†
64A	6.8*	-1.5	9.0‡	60.4	-17.0	58.3	11.3	0.3	9.7‡	21.2	-15.3	30.1‡	6.2	-0.6	5.7‡	6.2	-18.0	22.1‡
67	12.6	18.4	28.4†				2.6	5.9					6.1	17.6	22.4†			
68A	2.3	-1.9	3.8‡	22.1	-30.9	43.4	19.9*	17.6	38.5	39.5	-1.8	33.7	8.6	-4.6	11.3‡	5.6	-14.3	18.3‡
70	4.8	-6.5	9.0				8.0	1.4	6.1							4.7	-14.6	16.9

APPENDIX N. COLLABORATING LABORATORIES METHODS FOR "VOLUNTARY" ELEMENTS

Table N1. Methods for "total" molybdenum

Laboratory number	Method
1	See Vogel A.I. A text book of quantitative inorganic chemistry pp. 793-794. 3rd edition, Longman's 1961. (Colorimetric dithiol method).
6	HNO_3/H_2O_2 digest; AAS; N_2O/C_2H_2 flame.
19	$HNO_3/HClO_4$ digest; plus AL 1000 mg/l; AAS; Air/C_2H_2 flame
25	$HNO_3/HClO_4$ digest; plus Na 1000 mg/l; AAS; N_2O/C_2H_2 flame without background correction.
32	HNO_3/H_2O_2 digest taken up in HCl 2M; colorimetric thiocyanate method.
60A	HCl digest; AAS; N_2O/C_2H_2 flame
60B	HNO_3 digest; AAS; N_2O/C_2H_2 flame
60C	HNO_3/HCl digest; AAS; N_2O/C_2H_2 flame
73	Ash 500°C HCl digest 0.25 h; plus $AlCl_3$; AAS; N_2O/C_2H_2 flame
77	See Min. of Ag. Fish and Food Technical Bulletin 27, HMSO 1973 (colorimetric thiocyanate method).
82	HNO_3/H_2SO_4 digest taken up in NH_4Ac; AAS; N_2O/C_2H_2 flame
84	HNO_3/H_2O_2 digest; colorimetric thiocyanate method.
85	Ash (A-C) 500°C 3 h; HNO_3/H_2O_2 digest (A-D); colorimetric thiocyanate method as MAFF Bull. 27 (see 77).
90	XRF

Table N2. Methods for "total" mercury

Laboratory number	Method
3	$H_2SO_4/KMnO_4$ digest; plus hydroxylamine hydrochloride and stannous chloride; cold vapour AAS.
7	As 71 ($H_2SO_4/KMnO_4$ digest; cold vapour AAS)
15	HNO_3 digest: cold vapour AAS
25	$H_2SO_4/KMnO_4$ digest 2d at room temp.; plus hydroxylamine; cold vapour atomic fluorescence method.
38	HNO_3/H_2O_2 digest; plus HCl and stannous chloride; cold vapour AAS.
60 B	HNO_3 digest; cold vapour AAS
60C	HNO_3/HCl digest; cold vapour AAS
61	HNO_3/H_2SO_4 digest; plus persulphate, permanganate, hydroxylamine hydrochloride and stannous chloride; cold vapour AAS
71	See Methods for the examination of water and associated materials. Mercury in waters, effluents and sludges by flameless AAS. HMSO, London 1978. ($H_2SO_4/KMnO_4$ digest; cold vapour AAS.
73	HNO_3/HCl digest; plus HCl and stannous chloride; cold vapour AAS
82	HNO_3/H_2SO_4/vanadium pentoxide digest; cold vapour AAS.
83	HNO_3/H_2SO_4 digest taken up in NH_4Ac; cold vapour AAS
84	HNO_3/H_2O_2 digest; plus stannous chloride; cold vapour AAS
85	As 71 ($H_2SO_4/KMnO_4$ digest; cold vapour AAS).
86	HNO_3/HCl/H_2O_2 digest; cold vapour AAS

Table N3. Methods for "total" arsenic

Laboratory number	Method
19	$HNO_3/HClO_4$ digest; plus KI 0.05M, sodium ascorbate 0.5%, HCl 3-5M; hydride generation, AAS.
61	HNO_3/H_2SO_4 digest; plus KI, HCl, H_2SO_4, sodium borohydride; hydride generation, AAS
82	Hydride generation, AAS
83	" " "
84	HNO_3/H_2O_2 digest; hydride generation, AAS

Table N4. Methods for "total" selenium

Laboratory number	Method
77	Fluorimetric method with diaminonapthalene
82	Hydride generation, AAS
83	" " "

Table N5. Methods for "total" fluorine

Laboratory number	Method
10	Extract with $HClO_4$ IM 90°C; citrate buffer; ion selective electrode; standard additions
73	See Rea, R.E. Water Pollution Control 1979, 78, 139-142 (NaOH fusion taken up in buffered solution, ion selective electrode; standard additions)
84	KOH fusion taken up in citrate buffer (pH 5.8); ion selective electrode; standard additions.

Table N6. Methods for "total" boron

Laboratory number	Method
82	Ash with lime; extract with HCl; colorimetric carminic acid method.

APPENDIX O. RESULTS FOR "TOTAL" CONCENTRATIONS OF MOLYBDENUM, MERCURY, ARSENIC, SELENIUM, FLUORINE AND BORON

TABLE O1. Summary of results for "total" molybdenum

n = 5 unless stated. *n = 6-10. †n = 3-4 ‡n = 2

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		$\bar{x}$	CV%	D%	$\bar{x}$	CV%	D%	$\bar{x}$	CV%	D%	$\bar{x}$	CV%	D%			
1	Colorimetric	<10	-	-	<10	-	-	<10	-	-	<10	-	-			
6	AAS	23.5*	17.6	66.7	95.7*	14.0	17.8	22.8*	38.1	150	3.44*	53.8	-			
19	AAS	10.8	4.54	-23.4	27.8	5.32	-19.3	4.32	12.7	-52.7	0.86	5.81	-			
25	AAS	25.1	21.5	7.80	-	-	-	-	-	-	-	-	-			
32	Colorimetric	15.5	48.8	9.9	33.2	15.8	-3.66	12.2	43.5	33.6	-	-	-			
60A	AAS	16.5‡	-	17.0	12.0‡	-	-65.2	5.5‡	-	-39.8	<5‡	-	-			
60B	AAS	13.5‡	-	-4.3	29.0‡	-	-15.8	6.0‡	-	-34.3	<5‡	-	-			
60C	AAS	13.5‡	-	-4.3	15.5‡	-	-55.0	5.5‡	-	-39.8	<5‡	-	-			
73	AAS	14.5	7.72	2.8	28.1†	4.45	-18.5	6.26	20.0	-31.4	<2.5	-	-			
77	Colorimetric	7.9	13.0	-44.0	24.8	10.8	-28.0	4.14	24.9	-54.7	0.52	25.0	-			
82	AAS	ND	-	-	69.8	9.08	103	23.3†	76.8	155	-	-	-			
84	Colorimetric	10.4	10.0	-26.2	24.5	2.73	-28.7	6.64	4.67	-27.3	<1.5	-	-			
85	Colorimetric	9.3*	32.4	-34.0	26.1*	14.3	-24.0	<2*	-	-	<2.0*	-	-			
90	XRF	8.4†	-	-40.4	25.8‡	-	-24.9	3.75‡	-	-58.9	3.25‡	-	-			

TABLE 02. Summary of results for "total" mercury

n = 5 unless stated, *n = 4, †n = 3, ‡n = 2.

LAB. CODE NO.	ANALYTICAL METHOD	PRECISION AND BIAS														
		SAMPLE A			SAMPLE B			SAMPLE C			SAMPLE D			SAMPLE E		
		$\bar{x}$	CV%	D%	$\bar{x}$	CV%	D%	$\bar{x}$	CV%	D%	$\bar{x}$	CV%	D%			
3	AAS	0.95	14.7	-32.6	5.19	8.69	24.8	2.03	24.0	26.1	0.033	94	-74.6			
7		1.45‡	-	2.84	6.94‡	-	66.8	-	-	-	0.133‡	-	2.31			
15		1.42†	36.6	0.71	3.66†	16.3	-12.0	1.44†	35.4	-10.6	0.87†	26.6	569			
25	AAS	-	-	-	4.39	9.77	5.53	-	-	-	-	-	-			
38	AAS	1.43*	6.71	1.42	2.98*	10.74	-28.4	0.99*	4.06	-38.8	0.65*	26.2	-500			
60B	AAS	1.55‡	-	9.93	4.90‡	-	17.8	1.55‡	-	-3.73	0.095‡	-	-26.9			
60C	AAS	1.63‡	-	15.6	4.95‡	-	19.0	1.63‡	-	1.24	0.09‡	-	-30.8			
61	AAS	1.55	11.5	9.93	4.96	6.69	19.2	1.74	5.69	8.07	-	-	-			
71	AAS	0.65‡	-	-53.9	3.32‡	-	-20.2	-	-	-	-	-	-			
73	AAS	1.67	8.32	18.4	4.03	6.65	-31.3	<0.10	-	-	-	-	-			
82	AAS	0.1†	0.00	-93	0.125*	40.0	-97	0.5‡	-	-68.9	-	-	-			
83	AAS	0.98	8.57	-30.5	2.54	10.6	-38.9	1.48	5.68	-8.07	-	-	-			
84	AAS	1.46	34.7	3.55	4.03	14.9	-3.13	1.97	11.5	22.4	0.22	50	69.2			
85	AAS	1.32	25.2	-6.38	3.92	24.7	-5.77	1.34	18.4	-16.8	0.132	25.0	1.54			
86	AAS	3.63*	19.6	157	6.42*	4.45	54.3	3.08‡	-	91.3	0.27‡	-	108			

$\bar{x}$ = mean result obtained (mg/kg dry solids)

CV% = coefficient of variation of the mean (per cent)

D% = deviation of the mean from the "true value" (per cent)

Table 03 Summary of results for total arsenic, selenium, fluorine and boron

Arsenic

No	Laboratory method	Sample A $\bar{x}$	A R	A n	A CV%	B $\bar{x}$	B R	B n	B CV%	C $\bar{x}$	C R	C n	C CV%	D $\bar{x}$	D R	D n	D CV%
19	AAS	1.84	1.5–2.2	5	14.7	3.86	3.4–4.4	5	9.62	3.08	2.8–3.3	5	5.81	13.8	11.0–16.0	5	13.
61	AAS	2.35	2.27–2.42	5	3.0	5.38	5.07–5.81	5	6.64	4.42	4.12–4.71	5	5.16				
82	AAS	2.12	1.5–2.9	5	27.4	3.74	3.1–4.6	5	19.9	3.12	2.6–3.9	5	21.4				
83	AAS	<1.0	<1.0	5	-	3.0	2.7–3.3	5	7.45	3.02	2.7–3.3	5	7.55				
84	AAS	2.18	2.0–2.4	5	7.54	4.78	4.4–4.9	5	4.54	3.46	3.3–3.7	5	4.38	14.9	14.1–15.8	5	5.6

Selenium

No	Laboratory method	Sample A $\bar{x}$	A R	A n	A CV%	B $\bar{x}$	B R	B n	B CV%	C $\bar{x}$	C R	C n	C CV%	D $\bar{x}$	D R	D n	D CV%
77	Fluorimetric	0.73	0.65–0.85	5	10.4	4.7	4.2–5.2	5	9.27	4.0	3.5–4.4	5	11.6	0.30	0.28–0.32	5	5.6
82	AAS	0.25	0.1–0.4	2	-	1.58	0.8–3.9	5	82.4	0.86	0.5–1.5	5	53.7				
83	AAS	<1.0	<1.0	5	-	1.2	1.1–1.4	5	11.8	1.08	1.0–1.2	5	10.1				

Fluorine

No	Laboratory method	Sample A $\bar{x}$	A R	A n	A CV%	B $\bar{x}$	B R	B n	B CV%	C $\bar{x}$	C R	C n	C CV%	D $\bar{x}$	D R	D n	D CV%
10	ISE	132.2	128–136	5	2.70	289	260–302	5	5.90	239.2	210–267	5	9.74	33.7	32.0–37.1	5	6.3
73	ISE	86.4	80–90	5	4.74	356	344–380	5	4.25	222	206–236	5	5.32				
84	ISE	139	-	1	-	336	-	1	-	337	-	1	-	226	-	1	-

Boron

No	Laboratory method	Sample A $\bar{x}$	A R	A n	A CV%	B $\bar{x}$	B R	B n	B CV%	C $\bar{x}$	C R	C n	C CV%	D $\bar{x}$	D R	D n	D CV%
82	Colorimetric	42.6	31.0–53.0	5	19.7	73.6	50.0–81.0	5	18.9	49.2	36.0–65.0	5	23.1				

$\bar{x}$ = mean result obtained (mg/kg dry solids)

R = range of individual results (mg/kg dry solids)

n = number of individual results submitted

CV% = coefficient of variation of the mean (per cent)

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