Water Analysis in South Africa: Interlaboratory Comparison Studies. Part V: Trace Metal Analysis

R SMITH
[NATIONAL INSTITUTE FOR WATER RESEARCH OF THE COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, P.O. BOX 395, PRETORIA 0001]

Abstract

Part V of the programme of interlaboratory comparison studies involving South African laboratories engaged in water analysis is concerned with trace metal analysis. Evaluation of the results of the study showed that acceptable values were generally obtained for the nineteen trace metals being determined. Almost 95% of all the determinations were carried out by means of atomic absorption techniques. Variations among the different laboratories in the type of flame and interference suppressant used in the determination of specific metals by direct flame atomisation were noted.

Introduction

In continuation of the programme of interlaboratory comparison studies involving South African laboratories engaged in water analysis (Smith 1977; 1978 a, b; 1979) Part V is concerned with the analysis of trace metals. The results obtained and the analytical methods used by the fourteen laboratories who participated in the study are summarized and evaluated in this paper. Owing to the comparatively large number of analyses required, the study was carried out in two parts.

Sample Preparation

Part I

The calculated volumes of Hopkin and Williams' standard solutions (1 000 mg/dm^3) of cadmium, chromium, cobalt, copper and mercury (Samples 1 and 2) and iron, lead, manganese and nickel (samples 3 and 4) were diluted to the required volumes with deionized distilled water, and 500 cm^3 aliquots of each sample taken for each laboratory. The samples were preserved by the addition of 10 cm^3 of AR grade nitric acid per dm^3 of sample.

Part II

The calculated volumes of Hopkin and Williams' or Merck standard solutions (1 000 mg/dm^3) of zinc, aluminium, arsenic, and selenium (samples 1 and 2), beryllium, lithium, strontium and vanadium (sample 3), barium (sample 4) and silver (sample 5) were diluted to the required volumes with deionized distilled water; 500 cm^3 aliquots of samples 1 and 2 and 250 cm^3 aliquots of samples 3, 4 and 5 were taken for each laboratory. The samples were preserved by the addition of 10 cm^3 of AR grade nitric acid per dm^3 of sample.

The samples were contained in 500 cm^3 and 250 cm^3 polythene bottles, which, prior to the addition of the sample solutions, were treated, along with their plastic caps, as follows:

(1) Soaking for 24 h in a 10 times dilution of Contrad cleaning solution in deionized distilled water followed by rinsing with deionized distilled water.

(2) Soaking for 24 h in approximately 1 mol/dm^3 nitric acid solution, followed by rinsing with deionized distilled water.

(3) Rinsing with sample solution.

Analysis Requested

Part I

Samples 1 and 2: Mercury, cadmium, chromium, cobalt and copper.

Samples 3 and 4: Iron, lead, manganese and nickel.

Part II

Samples 1 and 2: Zinc, aluminium, arsenic and selenium.

Sample 3: Beryllium, lithium, strontium and vanadium.

Sample 4: Barium.

Sample 5: Silver.

Each laboratory was supplied with a table giving the concentration ranges of each constituent, and allowed complete freedom of choice as to the analytical procedures to be employed. It was requested that brief details of the methods used, or references to standard methods, should be submitted along with the results.

The following information was also requested for each of those constituents determined by means of atomic absorption: Make and model of instrument, type of flame, interference suppressant, dilution or concentration procedures used, and method of preparation of standard solution.

A period of one month was allowed for analysis of the samples and submission of the results. Each laboratory was allocated a code number, known only to that laboratory and the originator of the study.

Data Evaluation

Summaries of the results received, together with a statistical analysis of the results, are given in Tables 1 and 2. As in previous studies, all of the results received were first reviewed for outliers, using the ASTM procedure (ASTM, 1975), before analysing for mean, mean error, relative mean error, standard deviation and coefficient of variation. The results were then assessed (Table 3) according to the method of Greenberg *et al.* (1969), *viz.*:

(1) Results falling between the mean and ± 1 standard deviation are acceptable.

(2) Results falling between ± 1 and ± 2 standard deviations are acceptable but questionable.

(3) Results outside the limit of ± 2 standard deviations are unacceptable.

TABLE 1
SUMMARY OF RESULTS (Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Zn, Al)

Constituent	Units	Sample number	Laboratory Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	True Value (µg/dm³)	Mean Value (µg/dm³)	Mean Error (µg/dm³)	Relative Mean Error (%)	Standard Deviation (µg/dm³)	Coefficient of Variation (%)
Cadmium	µg/dm³Cd	I-1	200*	93	115	100	90	90	100	120	95	125	89	100	-	100	95	101	6	6,8	12	12,0
		I-2	180*	74	85	74	80	67	73	100	69	100	71	70	–	73	70	78	8	11,4	11	14,6
Chromium	µg/dm³Cr	I-1	280	220	290	274	250	289	250	320	300	310	305	270	–	246	280	277	3	1,0	29	10,6
		I-2	220	170	200	196	230	222	200	270	220	280	222	270	–	212	220	224	4	1,8	32	14,4
Cobalt	µg/dm³Co	I-1	250	220	220	200	220	228	206	240	267	245	–	–	–	–	220	230	10	4,4	21	9,1
		I-2	170	170	150	147	180	178	147	200	200	195	–	–	–	–	170	174	4	2,2	21	12,0
Copper	µg/dm³Cu	I-1	420*	165	200	147	170	167	168	210	125	175	146	160	160	160	160	166	6	3,5	22	13,2
		I-2	290*	140	170	112	120	122	129	160	91	130	125	130	79	126	120	126	6	4,7	24	19,2
Iron	µg/dm³Fe	I-3	390	270	310	302	-	300	281	360	263	355	250	328	319	276	280	308	28	10,0	42	13,5
		I-4	280	225	270	240	-	245	219	280	166	265	219	240	244	217	220	239	19	8,7	31	13,1
Lead	µg/dm³Pb	I-3	540*	255	300	-		261	300	320	366	310	-	260	–	258	260	292	32	12,4	37	12,8
		I-4	320*	220	230	-	-	216	225	280	275	290	-	210	–	220	210	241	31	14,6	31	13,1
Manganese	µg/dm³Mn	I-3	365*	165	180	138	180	156	170	200	300*	220	200	150	180	170	160	176	16	9,8	23	13,1
		I-4	290*	140	150	101	140	128	136	160	254*	195	150	120	140	131	130	141	11	8,4	23	16,2
Nickel	µg/dm³Ni	I-3	200	250	260	208	200	233	241	240	225	230	-	270	–	248	240	234	6	2,6	23	9,6
		I-4	100*	200	200	151	200	178	185	200	190	200	-	175	–	188	180	188	8	4,4	15	8,2
Zinc	µg/dm³Zn	II-1	570*	355	400	340	420	360	340	345	325	340	348	350	–	359	360	357	3	0,8	27	7,5
		II-2	500*	250	310	247	330	260	251	230	258	230	221	260	–	261	260	259	1	0,3	32	12,2
Aluminium	µg/dm³Al	II-1	–	380	–	–	-	417	405	470	425	370	–	–	–	357	400	403	3	0,8	39	9,5
		II-2	–	300	–	–	-	350	333	370	333	500*	–	–	-	290	320	329	9	2,9	30	9,1

*Outlier

TABLE 2
SUMMARY OF RESULTS (Hg, As, Se, Be, Li, Sr, V, Ba, Ag)

Constituent	Units	Sample number	Laboratory number 2	3	4	5	6	7	8	9	11	13	True value ($\mu g/dm^3$)	Mean value ($\mu g/dm^3$)	Mean error ($\mu g/dm^3$)	Relative mean error (%)	Standard deviation ($\mu g/dm^3$)	Coefficient of var. (%)
Mercury	$\mu g/dm^3Hg$	I-1	21	–	18	22	18	–	–	–	–	16	16,0	19,0	3,0	18,8	2,4	12,9
		I-2	14	–	10	18	14	–	–	–	–	12	11,0	13,6	2,6	23,6	3,0	21,8
Arsenic	$\mu g/dm^3As$	II-1	–	–	–	–	64	–	–	34	–	–	60	–	–	–	–	–
		II-2	–	–	–	–	47	–	–	30	–	–	50	–	–	–	–	–
Selenium	$\mu g/dm^3Se$	II-1	–	–	–	42	32	–	–	32	–	–	35	–	–	–	–	–
		II-2	–	–	–	47	26	–	–	25	–	–	28	–	–	–	–	–
Beryllium	$\mu g/dm^3Be$	II-3	75	–	–	–	74	–	80	–	–	–	80	–	–	–	–	–
Lithium	$\mu g/dm^3Li$	II-3	300	310	–	–	–	354	290	–	–	–	300	314	14	4,5	28	8,9
Strontium	$\mu g/dm^3Sr$	II-3	290	430*	–	–	325	247	290	–	–	–	300	288	12	4,0	32	11,1
Vanadium	$\mu g/dm^3V$	II-3	–	405	–	–	–	547	–	–	–	–	400	–	–	–	–	–
Barium	$\mu g/dm^3Ba$	II-4	650	–	–	–	565	601	470	–	–	–	600	571	28	4,7	76	13,3
Silver	$\mu g/dm^3Ag$	II-5	300	390	–	–	320	288	–	300	333	–	300	322	22	7,3	37	11,5

*Outlier

TABLE 3
ASSESSMENT OF RESULTS

Laboratory number	Cadmium	Chromium	Cobalt	Copper	Iron	Lead	Manganese	Nickel	Zinc	Aluminium	Mercury	Lithium	Strontium	Barium	Silver	Totals		
	a b c	a b c	a b c	a b c	a b c	a b c	a b c	a b c	a b c	a b c	a b c	a b c	a b c	a b c	a b c	a	b	c
1	- - 2	2 - -	2 - -	- - 2	- 2 -	- - 2	- - 2	- 1 1	- - 2	- - -	- - -	- - -	- - -	- - -	- - -	4	3	11
2	2 - -	- 2 -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	1 - -	1 - -	- 1 -	1 - -	23	3	-
3	1 1 -	2 - -	1 1 -	- 2 -	2 - -	2 - -	2 - -	1 1 -	- 2 -	- - -	- - -	1 - -	- - 1	- - -	- 1 -	12	8	1
4	2 - -	2 - -	- 2 -	2 - -	2 - -	- - -	- 2 -	- 1 1	2 - -	- - -	1 1 -	- - -	- - -	- - -	- - -	11	6	1
5	2 - -	2 - -	2 - -	2 - -	- - -	- - -	2 - -	1 1 -	- - 2	- - -	- 2 -	- - -	- - -	- - -	- - -	11	3	2
6	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	- - -	- 1 -	1 - -	1 - -	24	1	-
7	2 - -	2 - -	- 2 -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	- - -	- 1 -	- 1 -	1 - -	1 - -	20	4	-
8	- 2 -	- 2 -	1 1 -	- 2 -	- 2 -	1 1 -	1 1 -	2 - -	2 - -	- 2 -	- - -	1 - -	1 - -	- 1 -	- - -	9	14	-
9	2 - -	2 - -	- 2 -	- 2 -	- 1 1	- 2 -	- - 2	2 - -	1 1 -	2 - -	- - -	- - -	- - -	- - -	1 - -	10	8	3
10	- 2 -	- 2 -	2 - -	2 - -	1 1 -	1 1 -	- 1 1	2 - -	2 - -	1 - 1	- - -	- - -	- - -	- - -	- - -	11	7	2
11	2 - -	2 - -	- - -	2 - -	1 1 -	- - -	1 1 -	- - -	1 1 -	- - -	- - -	- - -	- - -	- - -	1 - -	10	3	-
12	2 - -	1 1 -	- - -	2 - -	2 - -	2 - -	1 1 -	1 1 -	2 - -	- - -	- - -	- - -	- - -	- - -	- - -	13	3	-
13	- - -	- - -	- - -	1 1 -	2 - -	- - -	2 - -	- - -	- - -	- - -	1 1 -	- - -	- - -	- - -	- - -	6	2	-
14	2 - -	1 1 -	- - -	2 - -	2 - -	2 - -	2 - -	2 - -	2 - -	1 1 -	- - -	- - -	- - -	- - -	- - -	16	2	-
TOTALS	19 5 2	18 8 -	12 8 -	19 7 2	18 7 1	14 4 2	17 6 5	17 5 2	18 4 4	10 3 1	6 4 -	3 1 -	2 2 1	2 2 -	5 1 -	180	67	20

a = Results between mean and ± 1 standard deviation
b = Results between ± 1 and ± 2 standard deviations
c = Results outside ± 2 standard deviations

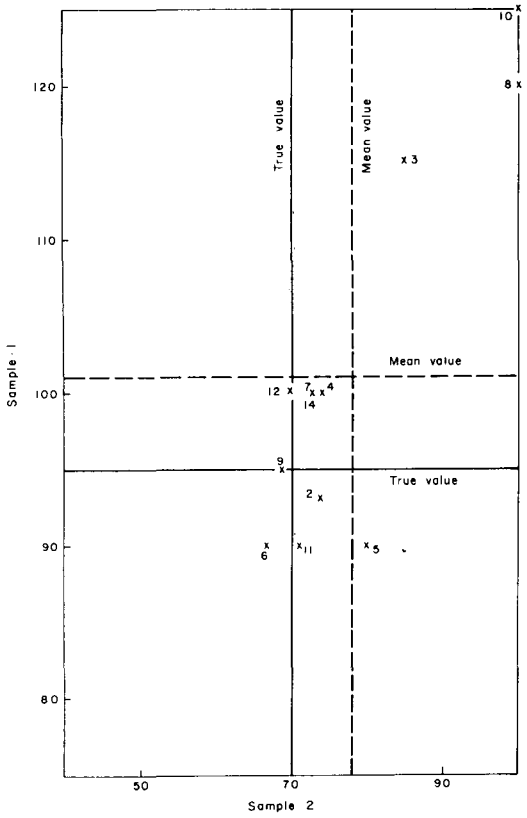

Figure 1
Cadmium (μg/dm³ Cd)

Of the results received, 67% were found to be acceptable, 25% were acceptable but questionable, while 8% proved unacceptable.

The results obtained for the cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, zinc and aluminium determinations (Table 1) were then evaluated by Youden's graphical technique, the procedure for which was fully described in Part III of this programme of studies (Smith, 1978b).

Insufficient results were submitted for the mercury, arsenic and selenium determinations to allow Youden evaluations to be carried out for these constituents.

Figure 1 to 10 represent Youden graphs of the result pairs obtained by each laboratory for the ten constituents shown in Table 1. Most of the plotted points were found to fall in the upper right or lower left quadrants of the graphs, indicating a predominance of systematic errors. Particularly widespread values were obtained for the iron and lead determinations.

The "true" values given in Tables 1 and 2 and also shown on Figures 1 to 10 are based on the theoretical values calculated from the amounts of the reference metals added.

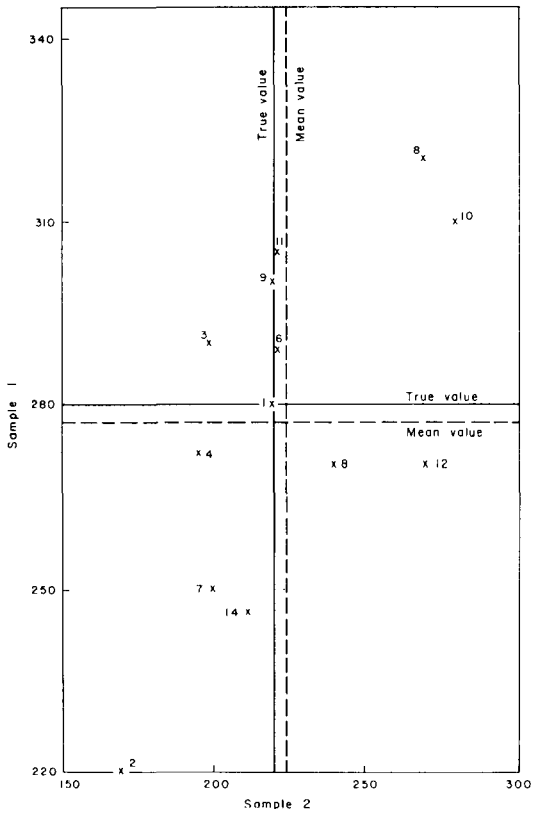

Figure 2
Chromium (μg/dm³ Cr)

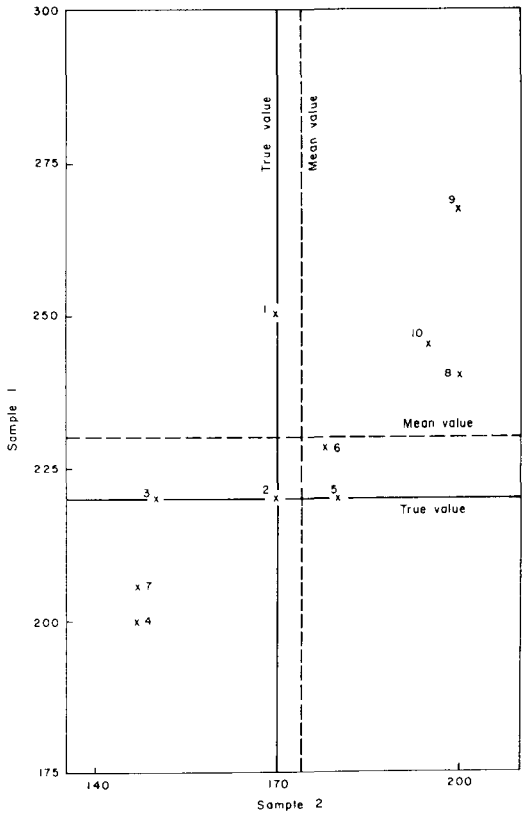

Figure 3
Cobalt (μg/dm³ Co)

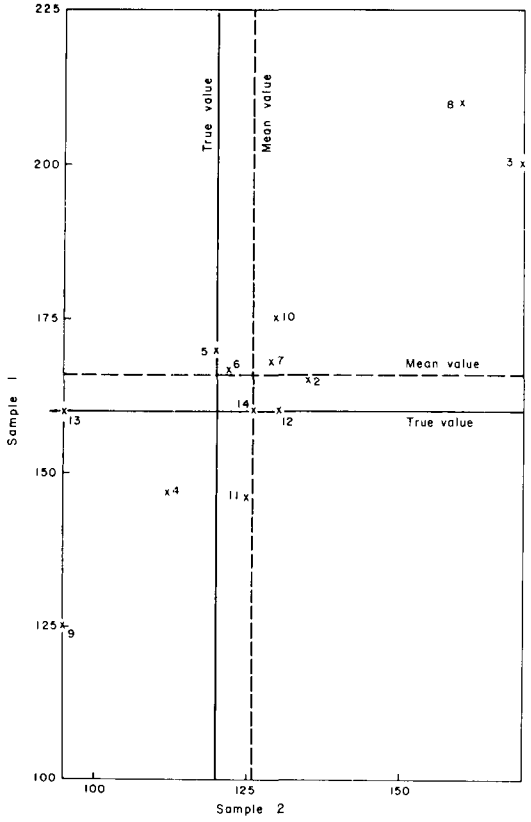

Figure 4
Copper (μg/dm³ Cu)

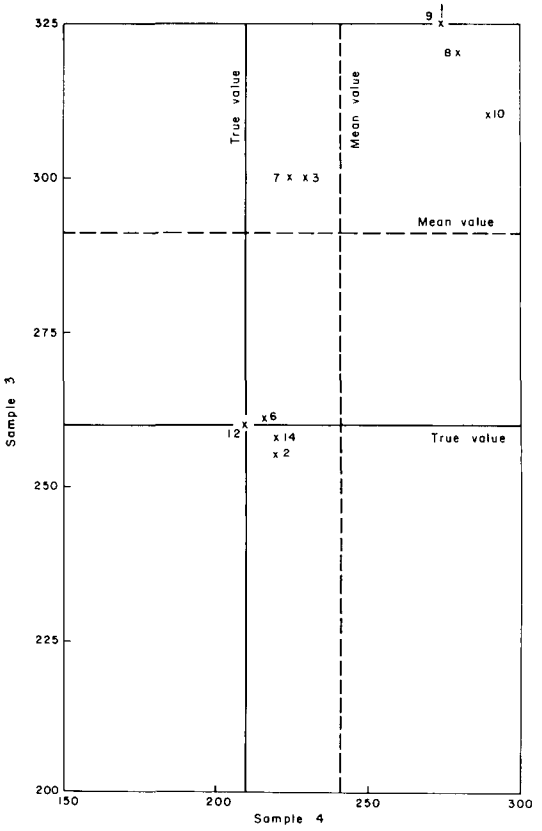

Figure 6
Lead (μg/dm³ Pb)

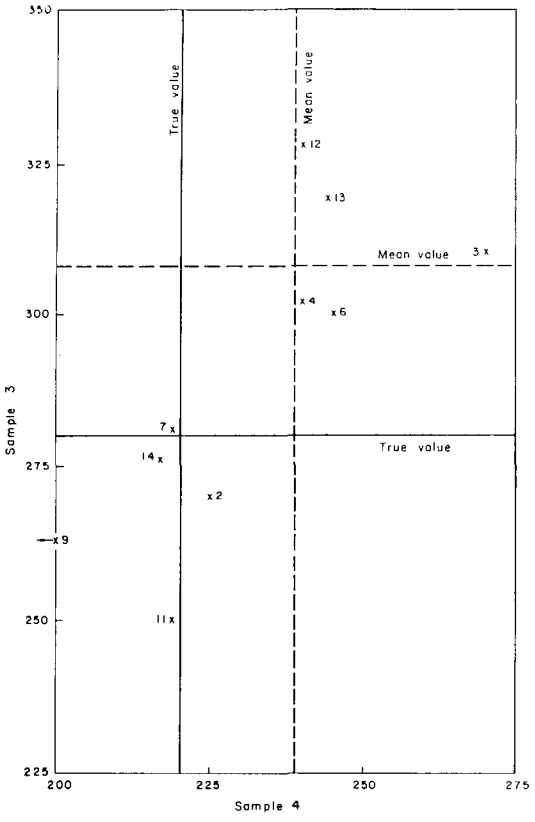

Figure 5
Iron (μg/dm³ Fe)

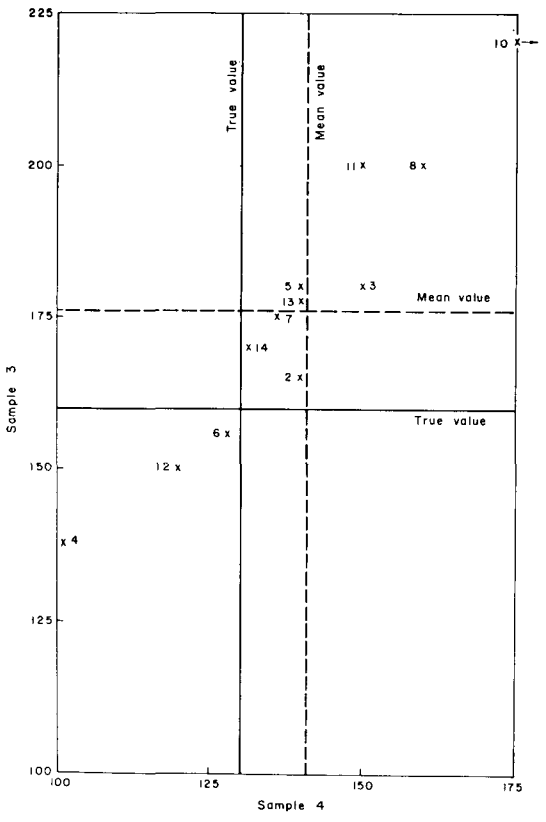

Figure 7
Manganese (μg/dm³ Mn)

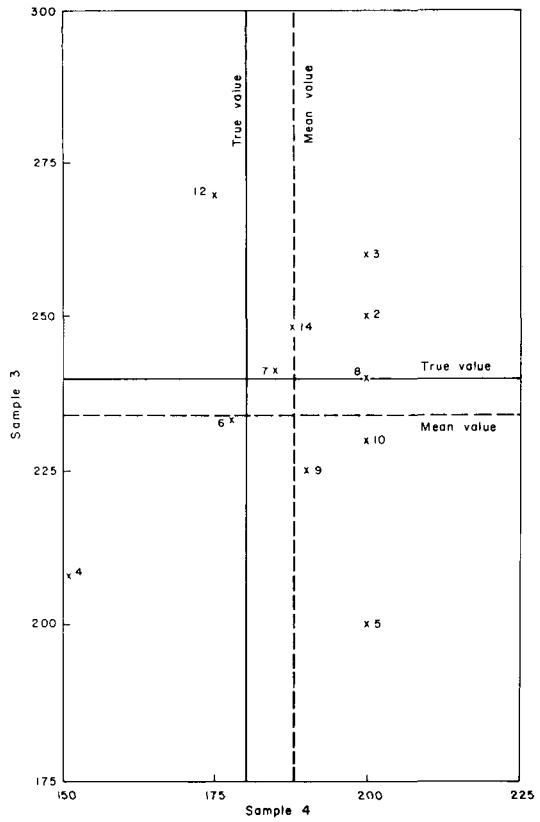

Figure 8
Nickel (µg/dm³ Ni)

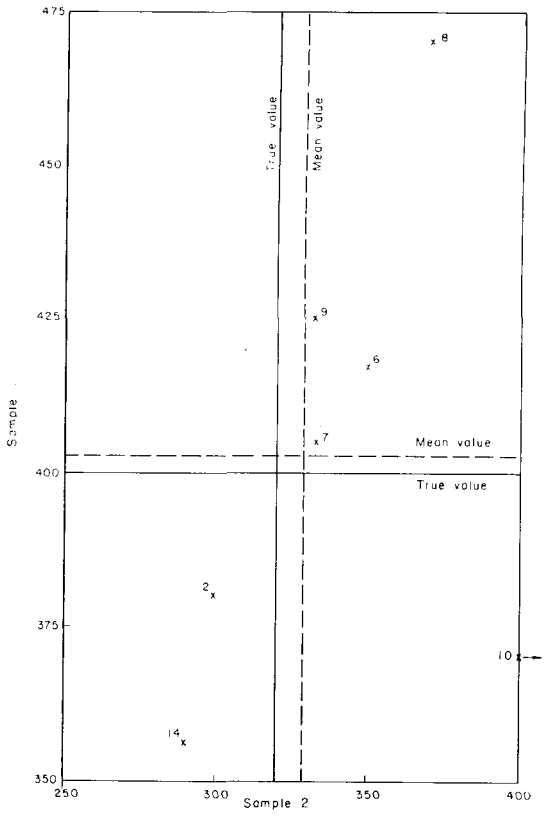

Figure 10
Aluminium (µg/dm³ Al)

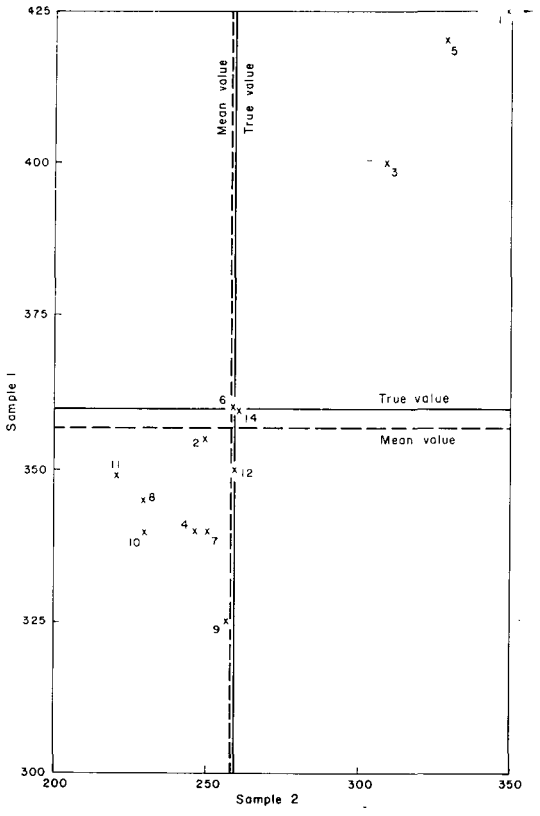

Figure 9
Zinc (µg/dm³ Zn)

For purposes of comparison with similar studies carried out overseas on samples containing approximately similar concentrations of trace metals, Table 4 shows precision data obtained from comparison studies held in Canada (Wales and McGirr, 1973; McGirr and Wales, 1973) and the USA (McFarren *et al.*, 1968; Lishka and McFarren, 1970). Data from the USA studies was obtained from atomic absorption determinations only. Data from the Canadian studies, while mainly obtained from atomic absorption determinations, also includes a few results from colorimetric analyses.

Method Evaluation

Of a total of 282 separate determinations, only 15 were carried out by means of non-atomic absorption techniques. Laboratory no. 3 determined vanadium by an automated technique based on the standard gallic acid method (APHA, 1975), and used the AA instrument in the emission mode to determine lithium and strontium. Laboratory no. 7 also made use of the emission mode, in this case to determine strontium and barium. Laboratory no. 12 determined iron by the colorimetric phenanthroline method (APHA, 1975). Copper was determined by laboratory no. 13 by means of a solvent extraction method involving the formation of the "neo-cuproin" complex and measurement of its absorbance at 475 nm (Vogel, 1961). The same laboratory determined manganese by the persulphate oxidation method and iron by the phenanthroline method (SABS, 1971). Aluminium was determined by laboratory no. 14 using the AA spectrometer in the emission mode. All other determinations were carried out by means of atomic absorption.

TABLE 4
PRECISION DATA FROM SIMILAR OVERSEAS COMPARISON STUDIES

Element	CANADA					USA				
	No. of analyses	True value ($\mu g/dm^3$)	Mean value ($\mu g/dm^3$)	Standard deviation ($\mu g/dm^3$)	Coefficient of variation (%)	No. of analyses	True value ($\mu g/dm^3$)	Mean value ($\mu g/dm^3$)	Standard Deviation ($\mu g/dm^3$)	Coefficient of variation (%)
Cadmium	6	102	102	7	7,2	26	100	107	15	13,8
	8	68	62	14	23,0					
Chromium	7	150	155	11	7,2	30	200	195	50	26,0
Copper	8	150	139	6	4,1	57	250	271	65	24,0
Iron	–	–	–	–	–	43	300	302	50	16,5
Lead	–	–	–	–	–	17	200	189	65	34,7
Manganese	7	75	74	4	5,2	40	250	251	40	16,3
Zinc	7	250	254	10	3,8	48	500	502	40	8,1
Aluminium	–	–	–	–	–	15	300	320	67	22,2
Barium	–	–	–	–	–	11	500	543	54	10,0
Silver	–	–	–	–	–	21	200	238	47	20,0

Table 5 gives details of instrumentation, flame type, any interference suppressant and dilution or concentration procedures used, as well as the mode of preparation of the standard solutions by the various laboratories.

Instrumentation

Varian-Techtron instruments were used by 9 of the 14 participants, but these included 5 different model variations. The remaining 5 laboratories used a total of 4 different instruments from 3 manufacturers.

Flame

Laboratory no. 1 elected to carry out the determination of Cd, Cr, Co, Fe, Pb, Mn and Ni by means of the graphite furnace technique on a 10x dilution of the samples. Poor results were obtained for the Cd, Cu, Pb, Mn and Ni determinations. (Zinc was determined by direct flame ionisation).

Excluding of course, the mercury, arsenic, and selenium determinations, which will be discussed later, all other participating laboratories employed direct flame atomisation methods. For the Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Zn and Ag determinations, these laboratories, with three exceptions, used the air-acetylene flame, as stipulated in the latest edition of "Standard Methods" (APHA, 1975). The exceptions were all in the case of the chromium determination, which was carried out by laboratories 4, 7 and 14 using the nitrous oxide-acetylene flame. The use of the nitrous oxide-acetylene flame for chromium determinations has been recommended for the elimination of interferences due to Co, Fe, Ni, Cu, Ba, Al, Mg and Ca (Parker, 1972).

For the determination of Al, Ba, Be and V, the nitrous oxide-acetylene flame was used in all cases, also as recommended in "Standard Methods". In the case of the Li and Sr determinations, the air-acetylene flame was employed by the three laboratories carrying out the lithium determination in the absorption mode, while for the strontium determinations by atomic absorption, two laboratories used the nitrous oxide-acetylene flame, and one the air-acetylene flame. The current edition of "Standard Methods" stipulates the use of the flame photometric method for these two metals, but they have been included with the other metals determined by atomic absorption, using an air-acetylene flame, in a draft copy of the proposed "Determination of Metals" section of the 15th edition of this manual (APHA, 1977).

Interference Suppression

Laboratories 2 and 6 made use of a cesium-lanthanum solution as an interference suppressant for all their direct flame determinations excluding that for silver. Laboratory no. 14 used a potassium solution for all but the lead and cadmium determinations, while laboratory no. 7 used a similar solution for the determination of aluminium and vanadium only. Laboratory no. 8 employed a cesium solution for the determination of alu-

TABLE 5
DETAILS OF INSTRUMENTS AND ANALYTICAL TECHNIQUES USED BY INDIVIDUAL LABORATORIES

Lab. No.	AA Instrument	Metals determined	Flame	Interference suppressant	Dilution/ concentration	Preparation of standard solutions
1	Jarrell-Ash 810	Cd,Cr,Co,Cu,Fe,Pb, Mn,Ni,Zn	Zn: Air-acetylene Others: Graphite furnace (Perkin-Elmer HGA 2200)	None	Zn: None Others: 10x dilution with water	AR grade chemicals
2	Varian Techtron 1000	Cd,Cr,Co,Cu,Fe, Pb,Ma,Ni,Zn,Al, Hg,Be,Li,Sr,Ba,Ag	Hg: Vapour generation Al,Ba,Be: N_2O-acetylene Others: Air-acetylene	Ag,Hg: None Others: 2g/dm³La; 0,5g/dm³Cs	None	Standard solutions of metals
3	Jarrel-Ash 810	Cd,Cr,Co,Cu,Fe, Pb,Mn,Ni,Zn,Li, Sr,V,Ag.	V: non AA technique Others: Air-acetylene (Li,Sr: Emission mode)	None	None	Standard solutions of metals
4	Varian Techtron AA6	Cd,Cr,Co,Cu,Fe, Mn,Ni,Zn,Hg	Hg: Vapour generation. Cr: N_2O-acetylene Others: Air-acetylene	None	None	Standard solutions of metals
5	Perkin Elmer 306	Cd,Cr,Co,Cu,Mn, Ni,Zn,Hg,Se	Hg: Vapour generation. Se: Heated graphite analyzer Others: Air-acetylene	None	None	AR grade chemicals
6	Varian Techtron AA5	Cd,Cr,Co,Cu,Fe, Pb,Mn,Ni,Zn,Al, Hg,As,Se,Be,Sr, Ba,Ag	Hg: Vapour generation. As,Se: Hydride generation Al,Ba,Be,Sr: N_2O-acetylene Others: Air-acetylene	Hg,As,Se,Ag: None Others: 2g/dm³ La; 0,5g/dm³ Cs	Al: 6x concentration (by evaporation) Others: None	Standard solutions of metals
7	Pye Unicam SP 192	Cd,Cr,Co,Cu,Fe, Pb,Mn,Ni,Zn,Al, Li,Sr,V,Ba,Ag	Al,Ba,Cr,Sr,V: N_2O- (Sr,Ba: Emission mode) Others: Air-acetylene	Al,V: 1g/dm³ K Others: None	Al: 10x concentration (by evaporation) V: 8x concentration (by evaporation) Others: None	V, Al: Pure metals Ba,Li,Sr: AR grade chemicals Others: Standard solutions of metals
8	Varian Techtron AA6	Cd,Cr,Co,Cu,Fe, Pb,Mn,Ni,Zn,Al, Be,Li,Sr,Ba	Al,Ba,Be,Sr: N_2O-acetylene Others: Air-acetylene	Al, Ba, Li: 1,7 g/dm³ Cs. Sr: 1,8g/dm³ Cs; 3,3g/dm³ La Others: None	None	Standard solutions of metals
9	Varian Techtron AA5	Cd,Cr,Co,Cu,Fe, Pb,Mn,Ni,Zn,Al, As,Se,Ag	As,Se: Hydride generation. Al: N_2O-acetylene Others: Air-acetylene	None	Pb,Al: concentrated by chelation and solvent extraction Others: None	Cd,Zn: Pure metals Others: AR grade chemicals
10	Perkin Elmer 370A	Cd,Cr,Co,Cu,Fe, Pb,Mn,Ni,Zn,Al	Al: N_2O-acetylene Others: Air-acetylene	None	None	Standard solutions of metals
11	Varian Techtron 1000	Cd,Cr,Cu,Fe, Mn,Zn,Ag	All: Air-acetylene	None	Cd,Cu,Cr,Fe,Mn; 2xconcentration (By evaporation) Others: None	Standard solutions of metals
12	Varian Techtron AA4	Cd,Cr,Cu,Fe,Pb, Mn,Ni,Zn	Fe: Non AA technique Others: Air-acetylene	None	Cu,Cr,Pb,Mn,Ni,Zn: 10x concentration (by evaporation) Fe,Cd: None	AR grade chemicals
13	Varian Techtron 1200	Hg,Cu,Fe,Mn	Cu,Fe,Mn: Non AA techniques Hg: vapour generation	None	None	Pure metals
14	Varion Techtron AA5	Cd,Cr,Cu,Fe,Pb, Mn,Ni,Zn,Al	Al,Cr: N_2O-acetylene (Al: Emission mode). Others: Air-acetylene	Cr,Cu,Fe,Mn,Ni,Al,Zn: 1g/dm³ K Pb,Cd: None	None	Standard solutions of metals

minium, barium, and lithium, and a cesium-lanthanum solution for strontium only. In all other cases, no interference suppressant was used.

The current edition of "Standard Methods" makes no recommendations regarding the use of interference suppressants in analysis for the following metals: Ag, Al, Be, Cd, Co, Cr, Cu, Ni, Pb, V, and Zn. It does, however, recommend the addition of 2 g/dm³ Na for barium determinations, in order to suppress ionization in the nitrous oxide-acetylene flame, and the addition of 0,05 g/dm³ Ca for manganese determinations (in order to eliminate interference from silica) and for iron determinations (no reason is given for the addition in this case).

The EPA manual (EPA, 1974) makes no stipulations with regard to interference suppressants for the determination of Ag, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. In the case of barium, it is recommended that 1 g/dm³K be added for ionisa-

tion suppression, while, unlike "Standard Methods", the addition of 1 g/dm^{3}K is also recommended for ionisation suppression in aluminium determinations, and for elimination of interference from high aluminium concentrations in vanadium determinations.

Dilution/concentration procedures

As previously stated, laboratory no. 1 carried out a ten times dilution procedure for the analysis of Cd, Cr, Co, Cu, Fe, Pb, Mn and Ni, by the graphite furnace technique. Laboratory no. 9 determined Al and Pb on samples concentrated by chelation and solvent extraction techniques. Concentration by evaporation was carried out by laboratories 6 (Al), 7 (Al, V), 11 (Cd, Cu, Cr, Fe, Mn) and 12 (Cu, Cr, Pb, Mn, Ni, Zn). All other determinations were carried out on the samples as received. With the possible exceptions of aluminium and vanadium, the metal concentrations chosen for the study were such that they could be expected to be determined without recourse to concentration procedures. Such procedures are, however, completely acceptable, and particularly where the metal concentration is close to the detection limit, are advisable for improved precision and accuracy.

Preparation of Standard Solutions

Eight laboratories prepared their standard solutions by dilution of standard metal solutions, while five used AR grade chemicals and/or pure metals. One laboratory employed both methods of preparation. As well as being less time consuming, preparation of standard solutions from guaranteed standard metal solutions avoids possible errors from the weighing out and dissolution of standard materials.

Determination of Mercury

All five laboratories carrying out the mercury determination made use of methods based on the cold vapour technique of Hatch and Ott (1968), in which mercury in the sample is reduced to the elemental state and aerated from solution in a closed system. The mercury vapour passes through a cell positioned in the light path of an AA spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner. Detection limits of as low as 0,2 μg Hg/dm^3 can be achieved by this technique. "Standard Methods" and the EPA manual both recommend this method.

Determination of Arsenic and Selenium

Only two laboratories carried out the arsenic determination and three the selenium determination. Laboratory no. 6 used methods based on the hydride generation technique using sodium borohydride as the hydride generant (Duncan and Parker, 1972) and a nitrogen-hydrogen flame.

Laboratory no. 9 used basically the same process but passed the liberated hydrides through a silica tube mounted in the flame in order to increase sensitivity (Thompson and Thomerson, 1974) and used an air-acetylene flame. Laboratory no. 5 determined selenium only, in this case by means of the graphite furnace technique. The current edition of "Standard Methods" and the EPA manual also recommend the hydride generation technique, but with zinc slurry as the hydride generant, and an argon-hydrogen flame. However, these are superceded by sodium borohydride and a nitrogen-hydrogen flame in a draft copy of the proposed "Determination of Metals" section of the 15th edition of "Standard Methods" (APHA, 1977).

Sodium borohydride is preferred as the hydride generant for the following reasons:

(1) As it is added in the form of a solution, it is easier to add reproducible quantities to each sample than in the case of zinc, which is added in the form of a slurry.

(2) It gives a faster reaction than zinc.

(3) It generally produces lower arsenic blanks than the zinc.

(4) It is capable of generating the hydrides of more elements than the zinc generation method, e.g. Sb, Te, Bi, and Sn hydrides.

Conclusions

With the exception of a few wild results, most of which emanated from one laboratory, the results can generally be considered satisfactory, bearing in mind the levels of concentration of the metals being determined.

Results of the lead, and rather surprisingly, the iron determinations were the least accurate and precise.

Just under 95% of all the determinations were carried out by means of atomic absorption techniques.

Variations were found in the type and quantity of interference suppressants being employed in the direct flame atomic absorption analysis.

Concentration procedures are recommended for the determination of metals whose concentrations are near the detection limit.

The standard "cold vapour" technique was used by all laboratories carrying out the mercury determinations.

Sodium borohydride is preferred to zinc as the hydride generant in the "hydride generation" method for the determination of arsenic and selenium in water.

The results obtained from this study should assist each participating laboratory in assessing the effectiveness of their analytical procedures and the comparative reliability of the results obtained therefrom.

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