Water Analysis in South Africa: Interlaboratory Comparison Studies

Part IV: Mineral Analysis

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Abstract

Part IV of the programme of interlaboratory comparison studies involving South African laboratories engaged in water analysis is concerned with mineral (sodium, potassium, calcium, magnesium, chloride, sulphate, fluoride and total alkalinity) analysis. Evaluation of the results of the study showed that acceptable values were generally obtained for the constituents being determined. Recognized standard methods, or methods based on them, were used for almost all of the analyses. In general, the results from the study compared favourably with those obtained from similar overseas comparison studies.

Introduction

In continuation of the programme of interlaboratory comparison studies involving South African laboratories engaged in water analysis (Smith, 1977; 1978 a,b), Part IV is concerned with mineral (i.e. sodium, potassium, calcium, magnesium, chloride, sulphate, fluoride and total alkalinity) analysis. The results obtained and the analytical methods used by the sixteen laboratories who participated in the study are summarized and evaluated in this paper.

Sample Preparation

Each participating laboratory was supplied with six 250 cm^3 samples, the procedure for the preparation of which was as follows:-

Samples 1 and 2 were prepared by dilution of the calculated volumes of Hopkin and Williams' standard solutions (1 000 mg/dm^3) of sodium, potassium, calcium and magnesium to the required volumes with deionized distilled water, and 250 cm^3 aliquots taken for each laboratory.

For samples 3, 4, 5 and 6, the calculated amounts (based on a 100% purity value) of the following AR (or equivalent) grade chemicals were carefully weighed out and dissolved in known volumes of deionized distilled water: sodium chloride, sodium sulphate, potassium fluoride (samples 3 and 4) and sodium carbonate (samples 5 and 6). After vigorous mixing to ensure complete homogeneity, the solutions were diluted to the required concentrations and 250 cm^3 aliquots taken for each laboratory.

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

(1) Soaking for 24 h in 100 cm^3/dm^3 Contrad cleaning solution, followed by rinsing with deionized distilled water.

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

(3) Rinsing with sample solution.

Samples 1 and 2 were preserved by the addition of 10 cm^3 of AR grade nitric acid per dm^3 of sample. No preservative was added to samples 3, 4, 5 and 6.

The "true" values given in Tables 1 and 2 and shown on

Figures 1 to 8 are based on the theoretical values calculated from the amounts of the reference chemicals added.

Analysis Requested

Samples 1 and 2:	Sodium Potassium Calcium Magnesium
Samples 3 and 4:	Chloride Sulphate Fluoride
Samples 5 and 6:	Total Alkalinity

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 also requested that the total alkalinity of samples 5 and 6 be determined immediately after opening the sample bottles, and that references to standard methods, or copies of the methods used to carry out the various analyses, should be submitted with the results. 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 these results, are given in Tables 1 and 2.

TABLE 1
SUMMARY OF RESULTS FROM ANALYSIS OF SAMPLES 1 AND 2

Constituent	Units	Sample no.	Laboratory number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	True value (mg/dm^3)	Mean value (mg/dm^3)	Mean error (mg/dm^3)	Relative mean error (%)	Standard deviation (mg/dm^3)	Coefficient of variation (%)
Sodium	mg/dm^3 Na	1	61	59	58,1	68,2	60,0	61,1	54,7	59,0	54	54	59,3	57,5	66,0	60,5	61,5	63	60,0	59,8	0,2	0,3	3,9	6,5
		2	49	46	46,9	60,8*	47,0	47,9	43,8	48,0	45	39,5	47,8	46,5	53,0	48,5	48,5	55	48,0	47,5	0,5	1,0	3,6	7,5
Calcium	mg/dm^3 Ca	1	28	29,4	31,2	32,8	31,0	29,5	31,4	30,0	35	34,7	38	29,2	26,8	28,3	30,8	40*	30,0	31,1	1,1	3,7	3,0	9,6
		2	22	24,6	21,9	26,2	26,0	25,0	23,1	25,6	24	28,6	24	24,0	21,0	23,5	25,4	32*	25,0	24,4	0,6	2,4	1,8	7,5
Magnesium	mg/dm^3 Mg	1	30	25,0	25,4	27,9	24,8	26,0	24,4	25,8	21	20,0	21	23,1	22,4	25,0	23,7	29,2	25,0	24,7	0,3	1,2	2,8	11,5
		2	25*	18,1	17,9	20,9	18,2	19,4	16,0	18,8	14	13,5	20	17,0	13,2	18,0	18,0	19,4	18,0	17,8	0,2	1,1	2,0	11,4
Potassium	mg/dm^3 K	1	20	14,8	18,9	14,9	17,2	17,2	15	15,0	20	19,2	16,1	13,9	17,2	16,6	16,0	14	16,0	16,6	0,6	3,8	2,0	12,2
		2	15	11,8	11,6	11,7	12,3	12,0	11	12,0	14	14,6	12,1	10,8	12,8	12,5	12,4	10	12,0	12,3	0,3	2,5	1,3	10,8

*Outlier

TABLE 2
SUMMARY OF RESULTS FROM ANALYSIS OF SAMPLES 3, 4, 5 AND 6

Constituent	Units	Sample no.	Laboratory number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	True value (mg/dm^3)	Mean value (mg/dm^3)	Mean error (mg/dm^3)	Relative mean error (%)	Standard deviation (mg/dm^3)	Coefficient of variation (%)
Chloride	mg/dm^3 Cl	3	62	63	60,0	62,9	68,7	63	61	68,0	58	60	67	63,0	53	61,7	65,7	–	61,7	62,5	0,8	1,3	4,0	6,4
		4	50	53	53,3	53,3	54,5	56	51	57,0	51	50	59	54,0	35*	51,3	56,1	–	51,8	53,5	1,7	3,3	2,8	5,2
Sulphate	mg/dm^3 SO_4	3	62	59	58,7	55,0	46,0	60	60	54,0	59	69,5	58	53,9	56	–	55,5	–	60,0	57,6	2,4	4,0	5,2	9,0
		4	53	48	49,2	44,0	41,0	52	51	47,0	50	52,8	48	46,5	48	–	48,5	–	50,4	48,5	2,1	4,2	3,3	6,8
Fluoride	mg/dm^3 F	3	0,97	–	0,32	1,13	0,82	1,10	0,8	0,96	0,90	0,94	1,00	–	1,06	0,96	0,93	–	1,00	0,95	0,05	5,0	0,10	10,9
		4	0,80	–	0,67	0,95	0,68	0,95	0,7	0,80	0,78	0,80	0,95	–	0,93	0,82	0,72	–	0,84	0,81	0,03	3,6	0,10	12,9
Total alkalinity	mg/dm^3 $CaCO_3$	5	25	31,3	35,1	30,9	30,0	29	25	36,0	33	35	35	30,0	38	29,8	34,2	32	30,0	31,8	1,8	6,0	3,7	11,7
		6	16	25,0	29,5	24,1	24,5	19	20	29,7	26	25	27	30,0	32	23,6	28,3	25	24,0	25,3	1,3	5,4	4,3	17,0

*Outlier

TABLE 3
ASSESSMENT OF RESULTS

Lab. No.	Sodium			Calcium			Magnesium			Potassium			Chloride			Sulphate			Fluoride			Total alkalinity			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
1	2	—	—	—	2	—	—	1	1	—	1	1	1	1	—	1	1	—	2	—	—	—	—	2	6	6	4
2	2	—	—	2	—	—	2	—	—	2	—	—	2	—	—	2	—	—	—	—	—	2	—	—	14	—	—
3	2	—	—	1	1	—	2	—	—	1	1	—	2	—	—	2	—	—	—	2	—	2	—	—	12	4	—
4	—	—	2	2	—	—	—	2	—	2	—	—	2	—	—	1	1	—	—	2	—	2	—	—	9	5	2
5	2	—	—	2	—	—	2	—	—	2	—	—	1	1	—	—	—	2	—	2	—	2	—	—	11	3	2
6	2	—	—	2	—	—	2	—	—	2	—	—	2	—	—	1	1	—	—	2	—	1	1	—	12	4	—
7	—	2	—	2	—	—	2	—	—	2	—	—	2	—	—	1	1	—	—	2	—	—	2	—	9	7	—
8	2	—	—	2	—	—	2	—	—	2	—	—	—	2	—	2	—	—	2	—	—	—	2	—	12	4	—
9	1	1	—	1	1	—	—	2	—	—	2	—	1	1	—	2	—	—	2	—	—	2	—	—	9	7	—
10	—	1	1	—	1	1	—	1	1	—	2	—	1	1	—	—	1	1	2	—	—	2	—	—	5	7	4
11	2	—	—	1	—	1	—	2	—	2	—	—	—	2	—	2	—	—	1	1	—	2	—	—	10	5	1
12	2	—	—	2	—	—	2	—	—	—	2	—	2	—	—	2	—	—	—	—	—	1	1	—	11	3	—
13	—	2	—	—	2	—	2	—	—	2	—	—	—	—	2	2	—	—	—	2	—	—	2	—	6	8	2
14	2	—	—	2	—	—	2	—	—	2	—	—	2	—	—	—	—	—	2	—	—	2	—	—	14	—	—
15	2	—	—	2	—	—	2	—	—	2	—	—	2	—	—	2	—	—	2	—	—	2	—	—	16	—	—
16	1	—	1	—	—	2	1	1	—	—	2	—	—	—	—	—	—	—	—	—	—	2	—	—	4	3	3
Totals	22	6	4	21	7	4	21	9	2	21	10	1	20	8	2	20	5	3	13	13	—	22	8	2	160	66	18

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

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 limits of ± 2 standard deviations are unacceptable.

Of the results received, 66% were found to be acceptable, 27% were acceptable but questionable, while 7% proved unacceptable.

The results 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).

Figures 1 — 8 represent Youden graphs of the result pairs obtained by each laboratory for the eight constituents studied. In all cases, most of the plotted points fell in the upper right or lower left quadrants of the graphs, indicating a predominance of systematic errors. In general, the graphs showed the results to be less accurate and precise than those obtained from the nutrient analysis comparison study (Smith, 1978b).

Finally, the mean, standard deviation, and coefficient of variation were calculated for the sets of results obtained from each of the methods used in the analysis of the various constituents (where four or more results were available), in order that precision data obtained for different methods of analysis for each constituent could be compared (Table 4). For purposes of comparison with similar studies carried out overseas, the table also includes precision data obtained from comparison studies held in Sweden (Ekedahl *et al.*, 1973), Canada (McGirr and Wales, 1973), and the USA (McFarren *et al.*, 1969; Lishka and McFarren, 1971).

Method Evaluation

Sodium, Potassium, Calcium and Magnesium

Nine of the participants determined sodium by the flame photometric technique (APHA, 1975; ASTM, 1975), while seven used atomic absorption methods (EPA, 1974). In the case of potassium, ten laboratories employed flame photometry and six atomic absorption. The atomic absorption results showed, for both these elements, a slightly better degree of precision than those results obtained by flame emission (Table 4).

For the calcium and magnesium determinations, nine laboratories used atomic absorption methods (APHA, 1975; EPA, 1974), while seven employed EDTA titration methods, the magnesium being calculated from the difference between the total

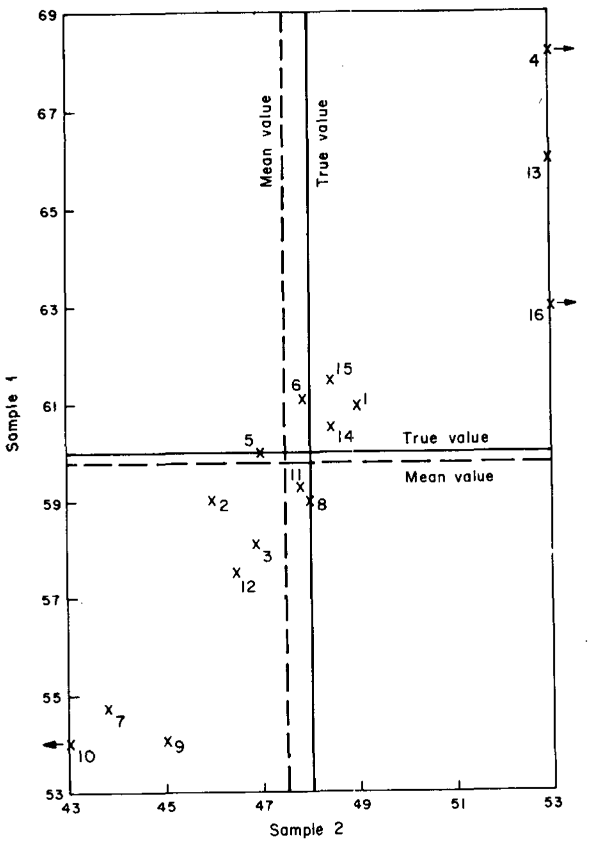

Figure 1
Sodium (mg/dm³ Na)

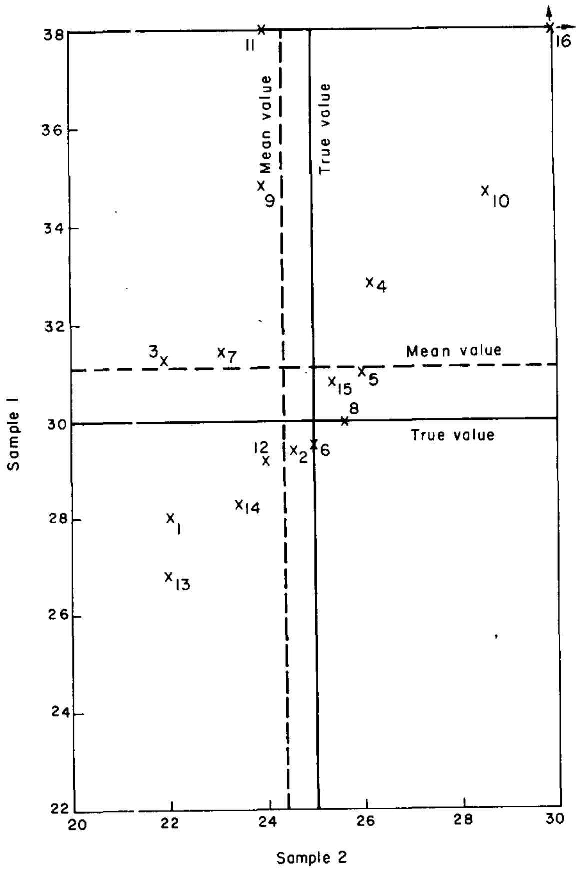

Figure 2
Calcium (mg/dm³ Ca)

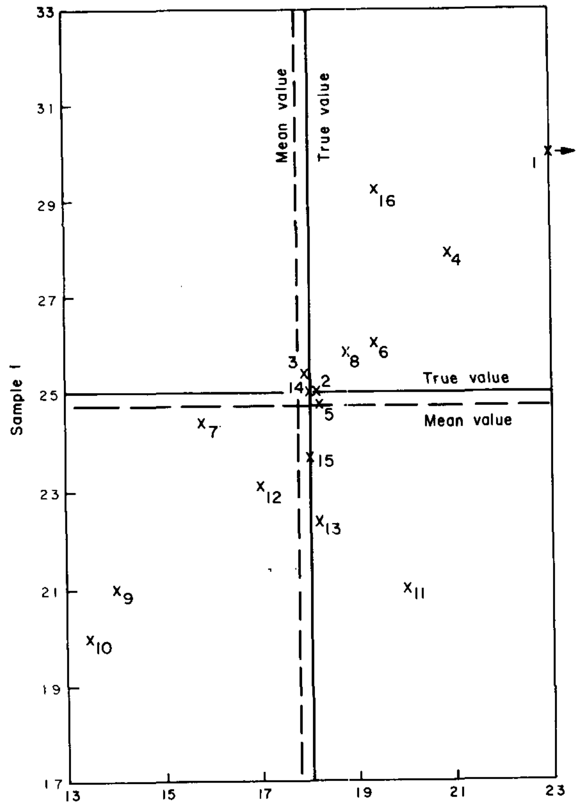

Figure 3
Magnesium (mg/dm³ Mg)

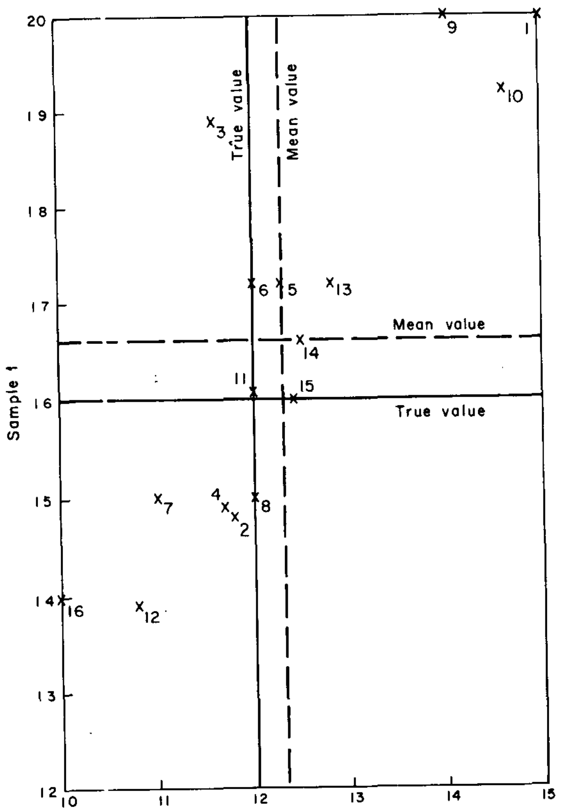

Figure 4
Potassium (mg/dm³ K)

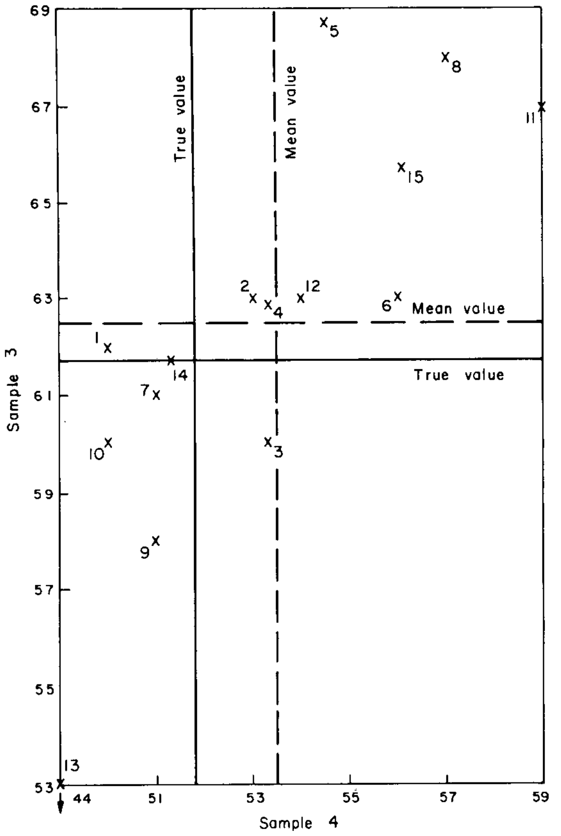

Figure 5
Chloride (mg/dm^3 Cl)

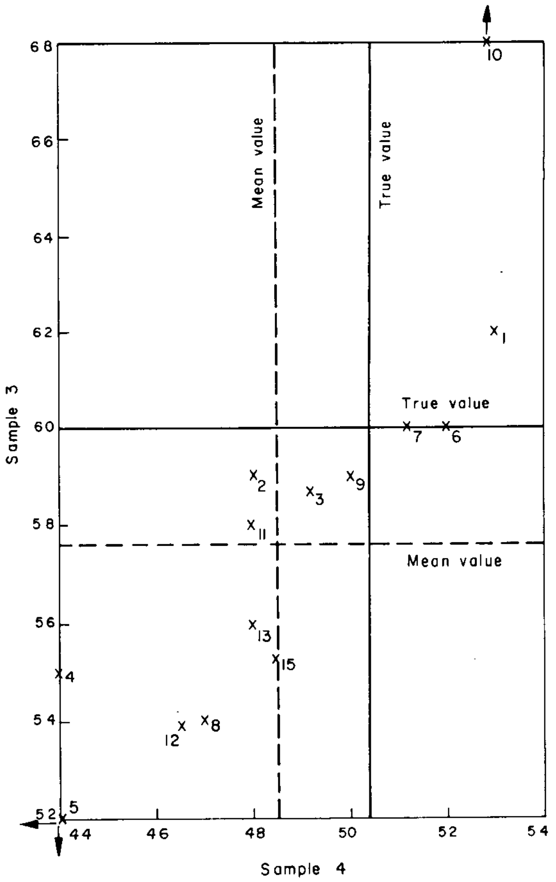

Figure 6
Sulphate (mg/dm^3 SO$_4$)

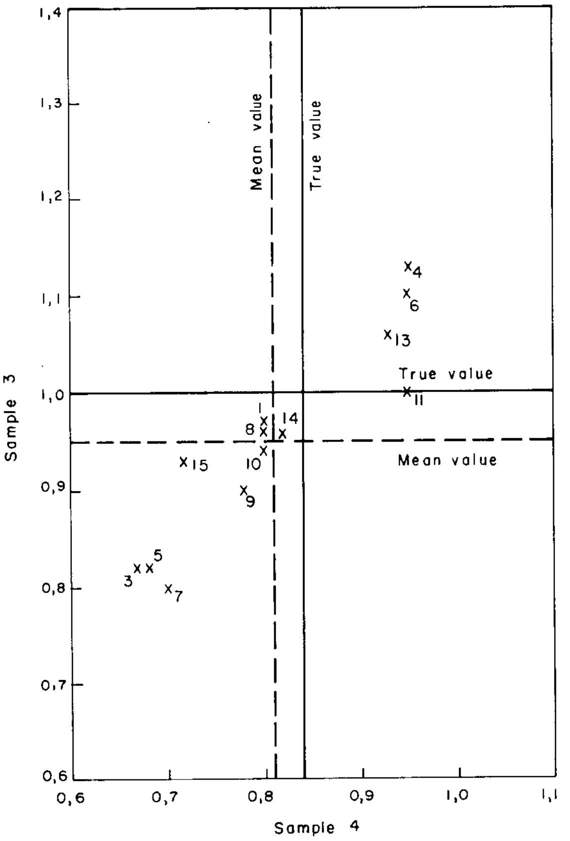

Figure 7
Fluoride (mg/dm^3 F)

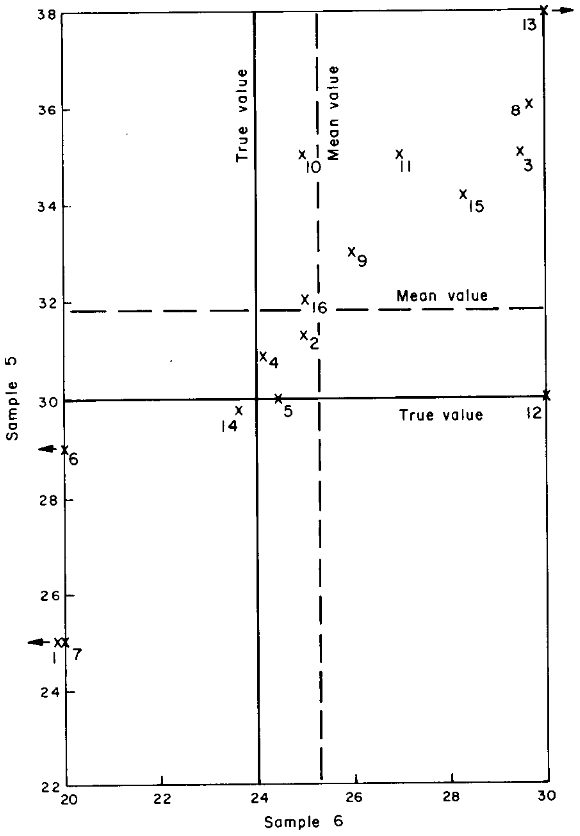

Figure 8
Total alkalinity (mg/dm^3 CaCO$_3$)

TABLE 4
PRECISION DATA FROM THIS STUDY AND SIMILAR OVERSEAS STUDIES

Constituent	Comparison Study	Statistical Data				
		No. of Analyses	True Value (mg/dm^3)	Mean Value (mg/dm^3)	Standard Deviation (mg/dm^3)	Coefficient of Variation (%)
Sodium	Sweden (1973)	25	—	15,0	2,1	12,2
(1) Flame	Canada (1973)	13	53,0	51,5	4,5	8,9
Emission	South Africa - Sample 1	9	60,0	59,7	4,0	6,6
	Sample 2	9	48,0	48,0	4,5	9,3
(2) Atomic	Sweden (1973)	5	—	15,9	2,5	15,9
Absorption	Canada (1973)	5	53,0	50,9	3,9	7,6
	South Africa - Sample 1	7	60,0	59,9	4,1	6,9
	Sample 2	6	48,0	46,7	1,6	6,0
Potassium	Sweden (1973)	25	—	7,0	0,4	5,6
(1) Flame	Canada (1973)	13	19,1	19,0	1,5	8,0
emission	South Africa - Sample 1	10	16,0	16,9	2,3	13,5
	Sample 2	10	12,0	12,5	1,6	13,1
(2) Atomic	Sweden (1973)	5	—	7,0	0,8	11,1
absorption	Canada (1973)	5	19,1	19,1	0,7	3,7
	South Africa - Sample 1	6	16,0	16,2	1,6	10,1
	Sample 2	6	12,0	11,9	0,2	1,7
Calcium	Sweden (1973)	23	—	26,0	1,4	5,4
(1) EDTA	Canada (1973)	8	39,0	38,8	2,0	5,3
Titration	South Africa - Sample 1	6	30,0	32,4	4,2	12,9
	Sample 2	6	25,0	24,7	2,2	9,0
(2) Atomic	Sweden (1973)	15	—	26,6	2,2	8,3
absorption	Canada (1973)	7	39,0	34,9	4,2	12,0
	South Africa - Sample 1	9	30,0	30,2	1,6	5,2
	Sample 2	9	25,0	24,2	1,6	6,8
Magnesium	Sweden (1973)	22	—	6,6	1,2	18,5
(1) EDTA	South Africa - Sample 1	7	25,0	22,9	3,1	13,3
Titration	Sample 2	7	18,0	17,2	2,5	14,7
(2) Atomic	Sweden (1973)	14	—	6,0	0,4	6,1
absorption	Canada (1973)	10	8,0	8,1	0,5	6,4
	South Africa - Sample 1	9	25,0	26,1	1,8	6,9
	Sample 2	8	18,0	18,4	1,4	7,6
Chloride	Canada (1973)	11	69,1	66,2	3,6	5,4
(1) Thiocyanate	South Africa - Sample 3	7	61,7	63,7	3,4	5,3
method (automated)	Sample 4	7	51,8	53,5	2,5	4,7
(2) Argentometric	Sweden (1973)	43	—	20,6	1,8	8,6
Titration	Canada (1973)	4	69,1	69,0	8,2	12,0
	South Africa - Sample 3	8	61,7	61,4	4,5	7,3
	Sample 4	7	51,8	53,5	3,2	5,9
Sulphate	Sweden (1973)	4	—	38,9	9,6	24,7
(1) Turbidimetric	Canada (1973)	5	55,0	55,4	6,0	11,0
method	South Africa - Sample 3	5	60,0	59,4	5,9	9,9
(manual)	Sample 4	5	50,4	48,7	3,2	6,6
(2) Turbidimetric	South Africa - Sample 3	4	60,0	57,9	2,7	4,6
method (automated)	Sample 4	4	50,4	48,8	1,7	3,5
Fluoride	USA (1969)	111	0,85	0,84	0,03	3,6
Electrode method	South Africa - Sample 3	9	1,00	0,99	0,10	10,2
	Sample 4	9	0,84	0,83	0,09	10,9
Total Alkalinity	Canada (1973)	11	11,4	10,0	1,1	11,0
	USA (1971)	72	47,3	50,1	2,5	5,0
(1) Potentiometric	South Africa - Sample 5	4	30,0	30,5	0,7	2,3
titration	Sample 6	4	24,0	24,3	0,6	4,0
(2) Indicator titration	Sweden (1973) — mixed indicator	50	—	53,7	2,4	4,6
	USA (1971) — mixed indicator	37	47,3	50,9	3,2	6,2
	USA (1971) — methyl-orange	41	47,3	55,7	8,4	15,1
	South Africa - Sample 5	8	30,0	34,2	2,4	7,2
	(various indicators) Sample 6	8	24,0	27,9	2,5	9,2
(3) Bromocresol	South Africa Sample 5	4	30,0	28,5	4,8	16,7
Green method (automated)	Sample 6	4	24,0	21,2	5,8	27,6

hardness and calcium titrations (APHA, 1975; EPA, 1974). In both cases the atomic absorption results proved to be slightly more precise than those obtained by the titration method. (Table 4)

As regards instrumentation, seven of the laboratories who carried out the sodium and potassium determinations by flame emission used among them three different types of flame photometers, while two laboratories used their atomic absorption spectrophotometers in the emission mode. Seven different models of atomic absorption spectrophotometer, from three manufacturers, were used by the nine laboratories carrying out the determinations by atomic absorption methods. Four of these laboratories had automated their procedures. The majority of the determinations were carried out using an air-acetylene flame, with the nitrous oxide-acetylene flame being used for calcium and magnesium determinations in two cases only, and the air-propane flame being used by one laboratory for the determination of sodium.

Considerable variation was found in the type and quantity of interference suppressants used in the atomic absorption determinations. In a few cases no suppressants were added, while in others varying concentrations of lanthanum and cesium together, or potassium, lanthanum, or cesium alone, were used. It is perhaps here that standardization procedures could most effectively be introduced.

"Standard Methods" (American Public Health Association, 1975) recommends that, for calcium and magnesium determinations, where chemical interferences can occur in the air-acetylene flame, 100 cm^3 aliquots of both standards and samples should be mixed with 25 cm^3 of a solution containing 50 g/dm^3 lanthanum as La_2O_3 (APHA, 1975). The EPA manual of methods for the chemical analysis of water and wastes makes a similar recommendation for calcium and magnesium determinations, but, in addition, stipulates the addition of 1 g/dm^3 potassium to samples and standards for the determination of sodium, in order to control ionization effects, while, for potassium determinations, matching of the sodium content of the potassium standards with that of the samples is recommended, in order to eliminate the enhancement effect of sodium (EPA, 1974.) The manufacturer of most of the atomic absorption instruments used by the participating laboratories makes the following recommendations (Parker, 1972):

(1) In order to suppress the partial ionization of sodium in the air-acetylene flame, a potassium nitrate or chloride solution should be added to all solutions, to give a final concentration of 2 g/dm^3 potassium. Ionization is negligible in the air-propane flame.

(2) Potassium is also partially ionized in the air-acetylene flame, and cesium nitrate or chloride solution should be added to all solutions to give a final concentration of 1 g/dm^3. Ionization is negligible in the air-propane flame.

(3) In the case of calcium, chemical interferences occur in the air-acetylene flame, and a releasing agent such as strontium (5 g/dm^3) or lanthanum (10 g/dm^3) should be added to sample and standard solutions in order to control the majority of these effects. In the nitrous oxide-acetylene flame, ionization of calcium itself can occur, which can be overcome by the addition of a more readily ionizable element, such as potassium (2 – 5 g/dm^3).

(4) In the determination of magnesium, chemical interferences in the air-acetylene flame can be overcome by the addition of a known excess of releasing agent such as strontium (1 – 5 g/dm^3) or lanthanum (10 g/dm^3) to sample and standard solutions. In the nitrous oxide-acetylene flame, a general absorbance enhancement, due to ionization suppression by the alkali metals, can occur. This can be overcome by the addition of a strontium solution.

Chloride

Seven laboratories determined chloride by the automated ferricyanide method (APHA, 1975; EPA, 1974), in which thiocyanate ion, liberated from mercuric thiocyanate by the formation of soluble mercuric chloride, forms, in the presence of ferric ion, a highly coloured ferric thiocyanate, which is proportional to the chloride concentration. The remaining nine laboratories carried out the determination manually, six of whom used the argentometric method (APHA, 1975; ASTM, 1975), and two the Mohr method. These two methods are basically similar, both involving direct titration with silver nitrate, using potassium chromate as indicator. One laboratory used Volhard's method, in which the sample is treated with excess silver nitrate and the residual silver nitrate titrated with standard thiocyanate solution, using ferric alum as indicator (NIWR, 1973).

There were no significant differences in the precision or accuracy between the automated ferricyanide and manual argentometric methods.

Sulphate

Of the seven laboratories who determined sulphate by automated techniques, four used the turbidimetric method (NIWR, 1973), in which sulphate ion is precipitated in a hydrochloric acid medium with barium chloride to form a barium sulphate suspension, the absorbance of which is measured photometrically. The other three laboratories used the methyl thymol blue method (APHA, 1975), in which the barium sulphate, formed by reaction of the sulphate ion with barium chloride at low pH, reacts at a high pH with methylthymol blue to produce a blue coloured chelate. The amount of gray, uncomplexed methylthymol blue indicates the concentration of sulphate ion.

Seven laboratories employed manual methods of analysis of which five used the turbidimetric method (APHA, 1975; ASTM, 1975), the principle of which is similar to the automated method above. The remaining two laboratories used a gravimetric method (APHA, 1975; ASTM, 1975; EPA, 1974), in which sulphate is precipitated in a hydrochloric acid medium with barium chloride. After a period of digestion, the precipitate is filtered, washed with water until free of chlorides, ignited or dried, and weighed as $Ba\ SO_4$.

Again, the differences in precision and accuracy between the manual and automated methods were not significant.

Fluoride

Twelve laboratories carried out this determination by manual methods. Of these, nine used the electrode method (APHA, 1975; ASTM, 1975; EPA, 1974), in which the fluoride is determined potentiometrically using an ion-selective fluoride electrode in conjunction with a standard single-junction, sleeve-type, reference electrode and a pH meter having a direct millivolt scale or a selective ion meter having a direct concentration scale for fluoride. The obvious advantage of this method lies in the fact that a time-consuming distillation process is not required. Two laboratories used the SPADNS procedure, in which, following distillation to remove interferences, the sample is treated with SPADNS reagent. The loss of colour resulting from the reaction of fluoride with the zirconyl-SPADNS dye is a function of the fluoride concentration (APHA, 1975; ASTM, 1975; EPA, 1974). One laboratory used the alizarin visual method (APHA, 1975), in which the colour produced by reaction of fluoride with zirconyl-alizarin reagent is compared visually with a series of standards in Nessler tubes. Only one laboratory employed an automated technique, incorporating the SPADNS method.

Total Alkalinity

All four participants who determined the total alkalinity by automated techniques used the bromocresol green method (NIWR, 1973). Of the twelve laboratories who carried out the determination manually, four used the potentiometric titration method (APHA, 1975; ASTM, 1975; EPA, 1974), while the remainder used the colour change titration method, but with various indicators, *viz*: methyl orange, methyl red, methyl purple, or bromocresol green — methyl red mixed indicator (APHA, 1975; ASTM, 1975).

Reference to Figure 8 and Table 4 shows that the results from the four laboratories (nos. 2, 4, 5 and 14) using the potentiometric titration method were the most accurate and precise of all the results received. In contrast, results from the laboratories using the automated bromocresol green method (nos. 1, 3, 6, 7) exhibited very poor accuracy, along with a considerable degree of systematic error.

Results from the remaining eight laboratories, who used some form of the colour change titration method were widely spread, and almost all showed a high positive bias.

The USA (1971) comparison survey (Lishka and McFarren, 1971) found that the use of methyl orange indicator for end-point detection produced greater errors than the mixed indicator or potentiometric methods, results from the potentiometric titration method being the best. (Table 4.)

For the greatest accuracy therefore, the potentiometric method should be employed. Furthermore, as is stipulated in the ASTM and APHA standard methods, the pH to which the sample was titrated should be reported along with the result. The ASTM method further stipulates that, where the colour titration method is used, the indicator selected should also be reported.

Conclusions

Although only about 7% of the results submitted could be regarded as unacceptable according to Greenberg's assessment method, they showed, in general, poorer accuracy and precision than was obtained for the nutrient analysis results from the previous study.

Standard methods, or methods based on them, were employed for almost all of the analyses.

In the case of the four cations, the results obtained by atomic absorption methods exhibited a slightly better degree of precision than those obtained by flame emission (sodium and potassium) or EDTA titration methods (calcium and magnesium). A wide variation was found in the type and quantity of interference suppressants being employed in the atomic absorption analyses.

Comparisons between automated and manual methods of analysis for chloride and sulphate showed no significant differences in precision or accuracy.

Fluoride results showed good accuracy and precision. Analysis of fluoride by ion-selective electrode proved to be the most popular technique.

In the determination of total alkalinity, the potentiometric titration method gave more accurate results than the other methods used, and should be used where greatest accuracy is required. For purposes of standardization and comparison, the end-point pH, or alternatively the particular indicator used, should be reported along with the result of the determination.

In general, the results from this study compared favourably with those obtained in similar overseas comparison studies.

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