

# Water Analysis in South Africa: Interlaboratory Comparison Studies. Part I: Introductory Study

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## Abstract

Interlaboratory comparison studies are regularly carried out in many overseas countries, but until now no programme of studies has been established involving South African laboratories engaged in water analysis.

This paper describes the introduction of such a programme, the first part of which involved the analysis of five synthetic water samples by fifteen laboratories.

The advantages of interlaboratory comparison studies, as well as the factors involved in their successful organisation, are discussed, and a summary and statistical evaluation of the results obtained in this initial study are presented.

## Introduction

Interlaboratory comparison studies can be of considerable benefit to the laboratories taking part. The information gained from such studies can enable individual laboratories to assess the reliability of their existing analytical methods and initiate improvements where unsatisfactory results are obtained. They also provide a mechanism for evaluating the reliability of specific analytical procedures and assessing the interlaboratory variability of results. These studies also supplement and encourage the use of quality control procedures within each laboratory.

For an interlaboratory comparison study to produce meaningful results, a number of factors have to be taken into account. The objective of the study and the benefits which can be derived from it need to be clearly stated and understood. Clear and concise instructions must be issued by the originator of the study. Careful selection, preparation, and packaging of the samples are essential. The complete co-operation of the participating laboratories must be enlisted in carrying out the instructions supplied by the originator of the study.

Various organisations in several countries overseas have regularly carried out comparison studies involving laboratories engaged in the analysis of water and wastewater, e.g.:

Studies by the Analytical Reference Service of the United States Department of Health, Education, and Welfare (United States, 1956, et seq.); Interlaboratory quality control studies for the Inland Water Directorate of the Canada Centre for Inland Waters (Traversey and Wales, 1970; Wales and Traversey, 1972; Wales and McGirr, 1973; McGirr and Wales, 1973); The Chemaqua Programme of the Chemistry Division of the New Zealand Department of Scientific and Industrial Research (Kingford *et al.*, 1973); The intercalibration programme conducted by the Research Laboratory of the National Swedish Environment Protection Board (Ekedahl and Rondell, 1973; Rondell, 1973; Ekedahl *et al.*, 1975).

However, no successful programme of interlaboratory comparison studies has yet been established involving South African laboratories engaged in water analysis. In an attempt to introduce such a programme, eight laboratories were invited to participate in an initial study (Study I). However, several other laboratories subsequently expressed interest in taking part in the exercise, and an additional study, (identical to the first except for alterations to the concentrations of constituents) was therefore carried out involving another seven laboratories (Study II). The results obtained from both studies are summarised and evaluated in this paper.

## Sample Preparation

Five samples were supplied to each participating laboratory. The samples were contained in polythene bottles, which, prior to addition of the sample, were treated as follows:

- (1) Soaking for 24 hours in 10 per cent Decon cleaning solution, followed by rinsing with deionized water.
- (2) Soaking for 24 hours in 10 per cent nitric acid solution, followed by rinsing with deionized water.
- (3) Rinsing with sample solution.

Samples 1 and 3 were prepared by dissolving the required AR grade chemicals in known volumes of deionized water, from which aliquots were taken for each laboratory. This allowed theoretical values to be calculated for each determinant (except for pH, electrical conductivity, and total alkalinity).

Samples 2 and 4 were prepared by dilution of samples 1 and 3 respectively.

Samples 1 to 4 were preserved by the addition of 1 ml of a 1 per cent solution of mercuric chloride per litre of sample.

Sample 5 was prepared by dilution of known amounts of Hopkin and Williams' standard solutions of metals to a known volume with deionized water, thus again allowing the theoretical values to be calculated. The sample was preserved by the addition of 10 ml of AR grade nitric acid per litre of sample.

## Analyses Requested

- (1) Samples 1 and 2: Chemical oxygen demand  
Total organic carbon
- (2) Samples 3 and 4: Kjeldahl, ammonia, and nitrate nitrogen  
Total and orthophosphate  
Chloride, sulphate, fluoride  
Silicon (Study 1 only)  
Total alkalinity; pH; electrical conductivity
- (3) Sample 5: Sodium, potassium, calcium, magnesium, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, strontium, zinc, arsenic, mercury.

Each laboratory was supplied with a table giving the concentration ranges of each constituent, and given complete freedom of choice as to the analytical procedures to be employed. A period of one month was allowed for analysis of the samples and submission of the results.

In order to preserve anonymity, and to avoid any element of competition, each laboratory was assigned a number, known only to that laboratory and the originator of the study.

## Data Evaluation

Results received from the laboratories were first reviewed for outliers (wild results). For the purpose of this particular investigation, where relatively few results are involved, only obvious outliers were discarded. However, for more accurate evalua-

tion, suspected outliers may be tested by the method of Dixon and Massey (1969), in which the difference between the suspected outlier and the nearest result is compared to the overall range of results. Reference to appropriate tables of probability values indicates whether the result in question should be rejected or retained. Alternatively, the ASTM (ASTM, 1975) procedure for rejection of outliers may be used. In this method, the difference between the value of the suspected outlier and the arithmetic mean of all the results is compared to the standard deviation. Again, reference to tables of probability values will indicate rejection or retention of the result.

The remaining results, apart from those determinants where less than four significant results were received, were then analysed for mean, standard deviation, coefficient of variation, mean error and relative mean error. Owing to the relatively small number of results, no further statistical evaluation, other than these simple measures of precision and accuracy was attempted. If a larger number of results were available, one could, for example, define the acceptability of any laboratory's results using the method of Greenberg, who arbitrarily established the following criteria (Greenberg *et al.*, 1969):

- (1) Results falling between the mean and  $\pm 1$  standard deviation are acceptable.
- (2) Results falling between  $\pm 1$  and  $\pm 2$  standard deviations are acceptable but questionable.
- (3) Results outside the limits of  $\pm 2$  standard deviations are unacceptable.

Another technique which has been suggested for judging the acceptability of a result is to use the formula:

$$\% \text{ Total error} = \frac{(\bar{x} - T) + 2S}{T} \times 100$$

Where T = true value

$\bar{x}$  = mean estimate of T

S = estimated standard deviation.

Values of less than 25 per cent of the total error are rated excellent. Values less than 50 per cent are rated acceptable. Values exceeding 50 per cent are unacceptable. (McFarren *et al.*, 1970).

Summaries of the results received, together with the statistical evaluation of the data, are shown in Tables 1 to 6.

**TABLE 1**  
**STUDY I: SUMMARY OF RESULTS FROM ANALYSIS OF SAMPLES 1 AND 2**

Sample No.	Determinant	Units	Laboratory No.								Theoretical value	Mean value	Mean error	Relative mean error (%)	Standard deviation	Coefficient of variation (%)
			1	2	3	4	5	6	7	8						
1	COD	mg/l	91	85	—	91	80	85	76	—	86	85	1	1,2	5,8	6,9
	TOC (C)	mg/l	—	—	—	—	—	38	—	—	35	—	—	—	—	—
2	COD	mg/l	8	5	—	8,3	9,5	5	12	—	7,6	8,0	0,4	5,3	2,7	33,8
	TOC (C)	mg/l	—	—	—	—	—	2	—	—	3,1	—	—	—	—	—

TABLE 2

## STUDY II: SUMMARY OF RESULTS FROM ANALYSES OF SAMPLES 1 AND 2

Sample No.	Deter- minant	Units	Laboratory No.							Theore- tical value	Mean value	Mean error	Relative mean error (%)	Standard devia- tion	Coefficient of variation (%)
			9	10	11	12	13	14	15						
1	COD	mg/l	52*	37	45	37	35	72*	34,6	34,3	37,7	3,4	9,9	4,2	11,2
2	COD	mg/l	0	9,3	14,6	13,5	5,8	9	3,6	2,7	—	—	—	—	—

\*Outlier

## Discussion

## Samples 1 and 2 (Tables 1 and 2)

## (1) Chemical oxygen demand

Results for the determinations at the more concentrated level, apart from two obviously 'wild' results in Study II were generally acceptable, but the wide spread of values obtained from the determinations at the lower level illustrates the difficulty of obtaining reliable results around this concentration.

## (2) Total organic carbon

In study II, no laboratory submitted results for this determination, and it is therefore omitted from Table 2. In fact, only one laboratory, out of five known to be equipped to carry out this analysis, submitted results. An investigation into the reasons for this indicated that, in the main, problems were being encountered with the instrument used for this determination.

TABLE 3

## STUDY I: SUMMARY OF RESULTS FROM ANALYSIS OF SAMPLES 3 AND 4

Sample No.	Determinant	Units	Laboratory No.								Theoretical value	Mean value	Mean error	Relative mean error (%)	Standard deviation	Coefficient of variation (%)
			1	2	3	4	5	6	7	8						
3	Kjeldahl nitrogen (N)	mg/l	5,0	—	—	7,69	—	7,4	—	—	7,0	—	—	—	—	—
	Ammonia nitrogen (N)	mg/l	5,7	3,6	—	4,42	5,5	3,5	3,7	—	4,0	4,1	0,1	2,5	0,8	20,0
	Nitrate nitrogen (N)	mg/l	7,0	7,2	6,95	7,04	10	7,2	6,8	9,0	7,0	7,2	0,2	2,9	1,6	22,1
	Total phosphate (P)	mg/l	6,6	—	—	8,01	—	9,0	—	—	8,0	—	—	—	—	—
	Orthophosphate (P)	mg/l	6,6	6,2	6,12	5,89	7,0	6,2	5,9	5,0	6,0	6,1	0,1	1,7	0,6	9,3
	Silicon (Si)	mg/l	8,4	—	9,8	9,4	3,3*	9,0	—	8,9	10,0	9,1	0,9	9,0	0,5	5,8
	Chloride (Cl)	mg/l	185	190	190	—	200	204	176	197	187	192	5	2,7	9,5	5,0
	Sulphate (SO <sub>4</sub> )	mg/l	63	61	60	—	70	54	82*	52	60	60	0	0	6,5	10,8
	Fluoride (F)	mg/l	2,6	—	2,95	—	12,0*	3,14	3,3	2,6	3,0	2,9	0,1	3,3	0,3	10,3
	Total alkalinity (CaCO <sub>3</sub> )	mg/l	108	62	123	59,7	85	56	55	—	—	—	—	—	—	—
	pH	—	9,9	9,2	9,9	—	9,6	8,7	10,0	—	—	9,6	—	—	0,5	5,2
	Electrical conductivity	mS/m	98,0	98,0	103	—	135*	93,5	100	—	—	99	—	—	3,5	3,5
4	Kjeldahl nitrogen (N)	mg/l	0,4	—	—	0,70	—	2,0	—	—	0,60	—	—	—	—	—
	Ammonia nitrogen (N)	mg/l	0,6	0,52	—	0,41	0,75	0,5	0,80	—	0,34	0,59	0,25	73,5	0,14	23,7
	Nitrate nitrogen (N)	mg/l	1,4	1,3	0,68	0,66	1	0,5	0,45	1,0	0,60	0,87	0,27	45,0	0,34	39,1
	Total phosphate (P)	mg/l	0,6	—	—	0,70	—	1,2	—	—	0,68	—	—	—	—	—
	Orthophosphate (P)	mg/l	0,6	0,7	0,53	0,52	0,48	0,5	0,5	0,45	0,51	0,54	0,03	5,9	0,08	14,8
	Silicon (Si)	mg/l	0,6	—	0,87	0,88	0,55	0,8	—	0,93	0,85	0,77	0,08	9,4	0,16	20,5
	Chloride (Cl)	mg/l	20	16	17	—	19	39*	18	20	18	18,3	0,3	1,7	1,6	8,9
	Sulphate (SO <sub>4</sub> )	mg/l	15*	5	5,5	—	7	4	—	5	5	5,3	0,3	6,0	1,1	20,7
	Fluoride (F)	mg/l	0,21	—	0,26	—	0,245	0,23	0,13*	0,26	0,26	0,24	0,02	7,7	0,02	8,3
	Total alkalinity (CaCO <sub>3</sub> )	mg/l	10	4	11,5	4,2	45	4	—	—	—	—	—	—	—	—
	pH	—	6,5	6,4	6,7	—	6,8	6,8	6,6	—	—	6,6	—	—	0,2	2,5
	Electrical conductivity	mS/m	10,2	11	10,4	—	39*	13,6	9	—	—	10,8	—	—	1,7	15,7

\*Outlier

**TABLE 4**  
**STUDY II: SUMMARY OF RESULTS FROM ANALYSIS OF SAMPLES 3 AND 4**

Sample No.	Determinant	Units	Laboratory No.							Theoretical value	Mean value	Mean error	Relative mean error (%)	Standard deviation	Coefficient of variation (%)
			9	10	11	12	13	14	15						
3	Kjeldahl nitrogen (N)	mg/l	—	5,6	—	6,28	—	—	—	7,0	—	—	—	—	—
	Ammonia nitrogen (N)	mg/l	4,4	3,9	2,3	6,06	7,0	4,8	—	4,0	4,7	0,7	17,5	1,7	34,8
	Nitrate nitrogen (N)	mg/l	10,0	6,1	6,7	6,35	6,18	5,6	7,27	7,0	6,9	0,1	1,4	1,5	21,3
	Total phosphate (P)	mg/l	6,0	—	—	6,1	—	6,6	—	6,0	—	—	—	—	—
	Orthophosphate (P)	mg/l	5,8	—	6,6	—	5,96	6,1	5,96	6,0	6,1	0,1	1,6	0,3	5,1
	Chloride (Cl)	mg/l	74	75	78	76	76	74	75,0	74	75	1	1,4	1,4	1,9
	Sulphate (SO <sub>4</sub> )	mg/l	55	85,4*	60	54,7	—	—	65,5	60	59	1	1,7	5,1	8,7
	Fluoride (F)	mg/l	2,6	2,95	2,5	—	—	2,9	—	3,0	2,7	0,3	10,0	0,2	8,1
	Total alkalinity (CaCO <sub>3</sub> )	mg/l	0	0	2,0	0	—	0	—	—	—	—	—	—	—
	pH		5,4	5,78	6,0	4,45	6,0	4,2	—	—	5,3	—	—	0,8	15,0
4	Electrical conductivity	mS/m	47	488	498	470	—	45,2	—	—	—	—	—	—	—
	Kjeldahl nitrogen (N)	mg/l	—	—	—	1,3	—	—	—	0,52	—	—	—	—	—
	Ammonia nitrogen (N)	mg/l	0,46	—	0,37	1,0	0,68	1,3	—	0,30	0,84	0,54	180,0	0,40	47,9
	Nitrate nitrogen (N)	mg/l	1,0	0,7	—	0,56	0,92	1,3	0,68	0,52	0,86	0,34	65,0	0,27	31,4
	Total phosphate (P)	mg/l	0,46	—	—	0,78	—	0,60	—	0,45	—	—	—	—	—
	Orthophosphate (P)	mg/l	0,42	—	0,50	—	0,48	0,63	0,43	0,45	0,49	0,04	8,9	0,08	17,0
	Chloride (Cl)	mg/l	10	9	11,2	8,0	8,0	8	10,3	8,0	9,2	1,2	15,0	1,3	14,2
	Sulphate (SO <sub>4</sub> )	mg/l	3	3,8	3,0	—	—	—	4,5	4,5	3,6	0,9	20,0	0,7	20,2
	Fluoride (F)	mg/l	0,21	0,24	0,3	—	—	0,23	—	0,23	0,25	0,02	8,7	0,03	15,8
	Total alkalinity (CaCO <sub>3</sub> )	mg/l	0	0	2,2	1	0	0	—	—	—	—	—	—	—
	pH		4,8	5,36	6,08	4,90	4,6	4,3	—	—	5,0	—	—	0,6	12,6
	Electrical conductivity	mS/m	4,5	44	60,1	60	—	4,5	—	—	—	—	—	—	—

\*Outlier

### Samples 3 and 4 (Tables 3 and 4)

#### (1) Kjeldahl, ammonia and nitrate nitrogen

Results for these three determinations were rather widespread. Coefficients of variation ranging from 20,9 per cent to 47,9 per cent were obtained for the ammonia nitrogen and nitrate nitrogen determinations.

#### (2) Total and orthophosphate

Results for these determinations were much better than those obtained for the other nutrients, and could be considered acceptable, bearing in mind the levels of concentration being measured.

#### (3) Chloride, sulphate, fluoride, silicon

Apart from a few wild values, the results of these analyses could again be regarded as acceptable.

#### (4) Total alkalinity, pH, electrical conductivity

Results for total alkalinity determinations in study I were so widespread that it was difficult to carry out a reliable statistical evaluation on them. Also, pH and electrical conductivity values from study II showed considerably more variation than those obtained in study I.

### Sample 5 (Tables 5 and 6)

The majority of the analyses were carried out by means of atomic absorption, and the results obtained are indicative of the reliability of this technique. In study I, out of six obviously wild results, four were from one laboratory, and two of these were obtained by techniques other than atomic absorption. In study II, only two wild results were obtained.

Some laboratories used flame photometry for the determination of sodium and potassium, and a few determined calcium and magnesium by EDTA titration methods. The results obtained by these laboratories were in good agreement with those obtained by laboratories using atomic absorption for the determination of these elements.

### Conclusions

In general, most of the results obtained can be regarded as acceptable, taking into consideration the levels of concentration used in the study. In particular, the reliability of the atomic absorption technique for the analysis of metals in water has been shown. A study of the results should enable each participating laboratory to investigate and improve or replace those methods where unreliable results were obtained by that laboratory.

**TABLE 5**  
**STUDY I: SUMMARY OF RESULTS FROM ANALYSIS OF SAMPLE 5**

Determinants	Units	Laboratory No.								Theoretical value	Mean value	Mean error	Relative mean error (%)	Standard deviation	Coefficient of variation (%)
		1	2	3	4	5	6	7	8						
Sodium (Na)	mg/l	49	44	43,5	44,1	44	43	38	45	43	43,8	0,8	1,9	3,0	6,8
Potassium (K)	mg/l	11	11	11,5	10,8	11,5	11,2	12	11	11	11,3	0,3	2,7	0,4	3,5
Calcium (Ca)	mg/l	28	23,6	25,0	26,2	30,8	23	28	29	24	26,7	2,7	11,3	2,7	10,2
Magnesium (Mg)	mg/l	18	20	20,5	20,4	21,8	19	18	20	20	19,7	0,3	1,5	1,3	6,6
Cadmium (Cd)	µg/l	180	830*	—	270	290	250	—	300	260	278	18	6,9	22	8,0
Chromium (Cr)	µg/l	500	610	—	640	550	615	490	550	600	565	35	5,8	58	10,3
Cobalt (Co)	µg/l	500	400	—	420	500	390	340	400	390	421	31	7,9	59	14,0
Copper (Cu)	µg/l	520	515	—	500	500	530	480	550	520	514	6	1,2	23	4,5
Iron (Fe)	µg/l	80*	920	—	930	1 200	1 040	980	1 000	920	1 012	92	10,0	102	10,1
Manganese (Mn)	µg/l	500	480	—	480	510	495	500	525	480	499	19	4,0	16	3,2
Lead (Pb)	µg/l	710	765	—	780	1 000	785	760	900	760	814	54	7,1	100	12,3
Nickel (Ni)	µg/l	430	330	—	—	400	325	410	350	340	374	34	10,0	45	12,0
Strontium (Sr)	µg/l	60*	455	—	480	—	495	—	570	430	500	70	16,3	50	10,0
Zinc (Zn)	µg/l	620	610	—	620	710	580	590	600	600	604	4	0,7	58	9,6
Arsenic (As)	µg/l	19*	8	—	—	<30	9	—	—	8,0	—	—	—	—	—
Mercury (Hg)	µg/l	0*	11	—	10,7	2*	9	—	—	8,0	—	—	—	—	—

\*Outlier

**TABLE 6**  
**STUDY II: SUMMARY OF RESULTS FROM ANALYSIS OF SAMPLE 5**

Determinant	Units	Laboratory No.							Theore- tical value	Mean value	Mean error	Re- lative mean error (%)	Stand- ard deviation	Coeffi- cient of vari- ation (%)
		9	10	11	12	13	14	15						
Sodium (Na)	mg/l	38	32,7	37,1	35	45	35	36	37	37	0	0	3,9	10,6
Potassium (K)	mg/l	10	12	9,5	12	9,1	10,9	10,3	9	10,5	1,5	16,7	1,1	10,9
Calcium (Ca)	mg/l	20	20,8	—	21	—	19,5	21,7	21	21	0	0	0,9	4,2
Magnesium (Mg)	mg/l	—	17,5	—	18	—	16,9	16,8	17	17	0	0	0,6	3,2
Cadmium (Cd)	µg/l	180	—	200	—	200	189	—	180	192	12	6,7	9,7	5,0
Chromium (Cr)	µg/l	660	—	800	—	870	770	—	740	775	35	4,8	87	11,2
Cobalt (Co)	µg/l	300	—	300	—	—	—	—	320	—	—	—	—	—
Copper (Cu)	µg/l	950	—	1 000	880	1 040	980	—	1 000	970	30	3,0	60	6,2
Iron (Fe)	µg/l	830	—	900	930	900	820	—	840	876	36	4,3	48	5,5
Lead (Pb)	µg/l	660	—	700	630	1 560*	630	—	630	655	25	4,0	33	5,1
Manganese (Mn)	µg/l	400	—	500	—	470	450	—	440	455	15	3,4	42	9,2
Nickel (Ni)	µg/l	400	—	500	800*	470	430	—	420	450	30	7,1	44	9,8
Strontium (Sr)	µg/l	—	—	—	—	—	—	—	500	—	—	—	—	—
Zinc (Zn)	µg/l	660	—	700	680	740	700	—	680	696	16	2,3	30	4,3
Arsenic (As)	µg/l	40	—	—	—	—	—	—	14	—	—	—	—	—
Mercury (Hg)	µg/l	14	—	—	—	—	—	—	14	—	—	—	—	—

\*Outlier