

# Water Analysis in South Africa: Inter-laboratory Comparison Studies.

## Part VII: Conclusions

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### Abstract

Part VII of the programme of interlaboratory comparison studies involving sixteen South African water analysis laboratories presents a comparative general assessment of the results obtained from the previous studies and discusses the recommendations and conclusions arising from these studies. The need for a recognised updated set of standard methods of water and wastewater analysis for use by laboratories in this country is highlighted. These comparison studies will be continued on a regular basis and have been extended to include over thirty additional laboratories in South Africa, Zimbabwe-Rhodesia and South West Africa.

### Introduction

From 1976 until 1978 a series of interlaboratory comparison studies was carried out involving the analysis of synthetic water samples of known composition by various South African water analysis laboratories (Smith, 1977, 1978a, b; 1979a, b; 1980). A total of 46 determinands were investigated over the course of the 6 studies, in which between 14 and 18 laboratories participated (Table 1).

This paper gives a general assessment of the results obtained and summarizes and discusses the conclusions and recommendations arising from the various studies.

### General Assessment of Results

For parts II to VI inclusive, the results obtained for the analysis of each determinand by each laboratory were statistically assessed (where possible) according to the method of Greenberg,

Moskowitz, Tamplin and Thomas (1969), *viz*:

- (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.

Table 2 (columns 1, 2, 3 respectively) shows the total number of results from each laboratory falling into each of the above categories.

A further comparative assessment was carried out by means of a procedure used by the Oklahoma Water Resources Board in their laboratory certification programme (Madden, 1978). Each laboratory was allocated 5 points for every result obtained within  $\pm 1$  standard deviation of the mean, 2 points for every result obtained between  $\pm 1$  and  $\pm 2$  standard deviations, and zero points for every result falling outside  $\pm 2$  standard deviations. The total number of points gained is shown in column 4 of Table 2. This number was divided by the total number of analyses carried out (column 5) to give a quotient (column 6). The maximum quotient possible is 5.

In the Oklahoma laboratory certification programme, if all the determinands available are analysed by a laboratory and that laboratory obtains a quotient of greater than 2,5, it is certified 'A' for unrestricted analysis. If a laboratory analyses all the available determinands and obtains a quotient of between 2,0 and 2,5, it is certified 'R' for restricted analysis. If not all the determinands available are analysed, and the laboratory obtains a quotient of greater than 2,0, it is also certified 'R' for restricted analysis. If a laboratory obtains a quotient of less than 2,0, it is

**TABLE 1**  
**PROGRAMME OF ANALYSIS OF SYNTHETIC WATER SAMPLES**

Part No.	Title	Determinands	No. of labs. participating
I	Introductory study	COD, TOC, Kjeldahl, ammonia, nitrate and nitrite nitrogen, total and orthophosphate, chloride, sulphate, fluoride, silicon, total alkalinity, pH, specific conductance, sodium, potassium, calcium, magnesium, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, strontium, zinc, arsenic, mercury.	15
II	COD, pH, and specific conductance determinations	COD, pH, specific conductance	16
III	Nutrient analysis	Kjeldahl, ammonia, nitrate and nitrite nitrogen, total and orthophosphate	16
IV	Mineral analysis	Sodium, potassium, calcium, magnesium, chloride, sulphate, fluoride, total alkalinity.	16
V	Trace metal analysis	(1) Mercury, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel. (2) Zinc, aluminium, arsenic, selenium, beryllium, lithium, strontium, vanadium, barium, silver.	14
VI	Boron, silicon, MBAS, cyanide, phenol, sulphide, BOD, colour and turbidity analyses	Boron, silicon, MBAS, cyanide, phenol, sulphide, BOD, colour, turbidity.	14

**TABLE 2**  
**GENERAL ASSESSMENT OF RESULTS**

Lab. No.	(1) A	(2) B	(3) C	(4) No. of points	(5) No. of analyses	(6) Quotient
1	26	9	16	148	51	2,90
2	46	9	4	248	59	4,20
3	27	13	1	161	41	3,93
4	36	12	3	204	51	4,00
5	34	9	4	188	47	4,00
6	54	8	0	288	62	4,65
7	40	18	0	236	58	4,07
8	33	20	0	205	53	3,87
9	34	19	5	208	58	3,59
10	26	15	7	160	48	3,33
11	33	11	3	187	47	3,98
12	38	8	1	206	47	4,38
13	30	12	3	174	45	3,86
14	48	5	0	250	53	4,72
15	31	2	2	159	35	4,54
16	10	3	6	56	19	2,95
Totals	546 (70,5%)	173 (22,4%)	55 (7,1%)	3076	774	Average = 3,97

A = Results between mean and  $\pm 1$  standard deviation  
 B = Results between  $\pm 1$  and  $\pm 2$  standard deviations  
 C = Results outside  $\pm 2$  standard deviations

not given certification, and is regarded as being unable to submit to the board 'data relating to the discharge of industrial water and to natural water quality'.

Quotients obtained by the laboratories participating in this series of analyses ranged from 2,90 to 4,72 with an average of 3,97, which means that all of the participants would qualify for certification in terms of the Oklahoma laboratory certification programme.

## Discussion, Recommendations and General Conclusions

The information gained from the various studies has enabled a fairly comprehensive picture to be built up of the state of water analysis in this country.

It became evident early in the series that the laboratories involved were employing, for many determinands, a wide variety of both standard and non-standard methods. The preparation of an updated recognised set of standard methods for the analysis of waters and wastewaters, for use by laboratories in this country, is therefore recommended. This should also include recommended SI units and form in which the results obtained from the analyses of the various determinands should be reported.

Specific findings and recommendations made during the studies are summarized as follows:

- (1) The importance of determining pH and alkalinity immediately after opening the sample container was emphasized.
- (2) It was recommended, for purposes of standardization and comparison, that specific conductance determinations be carried out at a temperature of 25 °C, as stipulated in standard texts (APHA, 1975; EPA, 1974). Alternatively, the appropriate temperature correction factor should be applied to the value obtained.
- (3) It was found that a wide variety of digestion procedures were being used in the Kjeldahl nitrogen and total phosphorus determinations. Some of these methods could possibly give varying results when used on natural and wastewater samples containing organic phosphorus and nitrogen compounds.
- (4) A wide variation was also found in the type and quality of interference suppressants being used in flame atomic absorption analysis.
- (5) The potentiometric titration method for total alkalinity was found to give, in general, more accurate results than those obtained from indicator methods (both manual and automated), and was therefore recommended for use where greatest accuracy was required. The mixed indicator procedure has been shown to give the best results from among indicator titration methods (Lishka and McFarren, 1971). It was also recommended that the end-point pH or, where applicable, the particular indicator used, should be reported along with the result of the determination.
- (6) Sodium borohydride should be used in preference to zinc slurry as the hydride generant in the 'hydride generation'

method for arsenic and selenium determinations by atomic absorption.

- (7) Turbidity determinations should be carried out by means of Hach Turbidimeter Model 2100 or 2100A or similar instruments. Results of turbidity determinations should be reported in Nephelometric Turbidity Units (NTU).
- (8) Linear alkylate sulphonate (LAS) was recommended for use as the standard reference material in the determination of methylene blue active substances (MBAS). Manoxol OT should no longer be used for this purpose.

It is hoped that this series of interlaboratory comparison studies has been of assistance to the participating laboratories in assessing the effectiveness of their analytical procedures and the comparative reliability of the results obtained therefrom, and that the foregoing findings and recommendations will make a significant contribution to the achievement of a greater degree of standardization with regard to the adoption of analytical procedures and the form in which the various results are reported.

Similar studies will be conducted at regular intervals in the future and in this regard it was decided to extend the programme of studies to include any laboratory in South Africa, South West Africa and Zimbabwe-Rhodesia engaged in water analysis. Over thirty of the additional laboratories contacted have indicated their interest and will participate in future studies of this kind.

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