Water Analysis in South Africa: Interlaboratory Comparison Studies. Part II: COD, pH, and Electrical Conductivity Analyses

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

Abstract

Part II of the programme of interlaboratory comparison studies involving South African laboratories engaged in water analysis is concerned with chemical oxygen demand (COD), pH, and electrical conductivity analyses. An evaluation of the results of the study shows that acceptable values were generally obtained for the three parameters being determined. Recognized standard methods, or methods based on them, were employed by all the laboratories for COD analysis.

Introduction

A programme of interlaboratory comparison studies, involving South African laboratories engaged in water analysis, was recently established (Smith 1977). Part II of this programme is concerned with chemical oxygen demand (COD), pH, and electrical conductivity determinations. The results obtained from the eighteen laboratories who participated in the study are summarized and evaluated in this paper.

Sample preparation

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

(i) Soaking for 24 hours in 10 per cent Decon cleaning solution, followed by rinsing with deionized water.

(ii) Soaking for 24 hours in 10 per cent nitric acid solution, followed by rinsing with deionized water.

(iii) Rinsing with sample solution.

Sample 1 was prepared by dissolving the required amount of AR grade potassium hydrogen phthalate in a known volume of deionized water. Sample 2 was prepared by 8,33 per cent dilution of sample 1 with deionized water. Both samples were preserved by the addition of 1 mℓ of a 1 per cent solution of mercuric chloride per litre of sample. Each laboratory was allocated 500 mℓ of each sample.

Analyses Requested

(i) Sample 1: pH
Electrical conductivity
COD

(ii) Sample 2: COD

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 (i) the pH of sample 1 be determined immediately after opening the sample bottle; (ii) eight COD determinations be carried out on each sample, and all the results recorded; (iii) a reference to a standard method or a copy of the method used to determine COD 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.

TABLE 1

SUMMARY OF RESULTS FROM COD DETERMINATIONS (INDIVIDUAL VALUES)

Sample No.	Parameter	Units	Laboratory Number																	
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	Individual results: 1	mg ℓ^{-1}	360	340	–	358	340	330	313	–	349	330	363	350	347	336	339	259	360	346
	2		340	336	–	358	340	330	302	–	353	336	364	348	347	338	340	302	360	347
	3		340	364	–	343	335	325	302	–	351	336	354	352	347	340	340	324	400	345
	4		335	336	–	353	330	335	305	–	353	336	357	355	347	336	338	259	376	347
	5		335	340	–	356	330	330	297	–	351	–	355	351	349	351	343	302	380	346
	6		335	336	–	346	320	330	310	–	351	–	359	344	349	336	340	288	380	342
	7		340	339	–	368	335	335	301	–	355	–	360	343	351	334	340	316	320	347
	8		360	335	–	351	335	320	303	–	349	–	357	343	351	344	337	316	360	343
	Theoretical value	mg ℓ^{-1}	343	343	–	343	343	343	343	–	343	343	343	343	343	343	343	343	343	343
1	Mean value	mg ℓ^{-1}	343	341	–	354	333	329	304	–	351	335	359	348	348	339	340	296	367	345
	Mean error	mg ℓ^{-1}	0	2	–	11	10	14	39	–	8	8	16	5	5	4	3	47	24	2
	Relative mean error	%	0	0,7	–	3,2	2,9	4,0	11,3	–	2,5	2,5	4,6	1,5	1,6	1,1	1,0	13,8	7,0	0,7
	Standard deviation	mg ℓ^{-1}	11	10	–	8	7	5	5	–	2	3	4	5	2	6	2	25	23	2
	Coefficient of variation	%	3,1	2,8	–	2,2	2,0	1,5	1,7	–	0,6	0,9	1,0	1,3	0,5	1,7	0,5	8,5	6,4	0,6
	Individual results: 1	mg ℓ^{-1}	26	28	–	28,4	24,5	26	32	–	29	32	40	28	28	28,5	28,3	25,2	25	33
	2		28	28	–	27,4	24,5	27	33	–	29	30	38	28	28	28,3	29,0	25,2	40	31
	3		26	28	–	28,6	23	26	31	–	27	32	34	28	32	28,2	29,1	25,2	28	31
	4		28	26	–	28,8	25	28	34	–	29	28	34	28	32	28,9	29,8	25,2	30	33
	5		28	29	–	27,6	24	28	29	–	27	28	35	28	32	28,9	29,2	28,8	40	31
	6		28	29	–	28,9	23	28	34	–	27	30	36	28	32	27,8	29,0	32,4	20	30
	7		27	27	–	28,8	25	27	32	–	27	30	35	32	32	29,4	30,1	28,8	25	30
	8		28	28	–	28,4	23	25	32	–	31	30	34	28	32	28,3	30,3	21,6	25	31
2	Theoretical value	mg ℓ^{-1}	28,5	28,5	–	28,5	28,5	28,5	28,5	–	28,5	28,5	28,5	28,5	28,5	28,5	28,5	28,5	28,5	28,5
	Mean value	mg ℓ^{-1}	27,4	27,9	–	28,4	24,0	26,9	32,1	–	28,3	30,0	35,8	28,5	31,0	28,5	29,4	26,6	29,1	31,2
	Mean error	mg ℓ^{-1}	1,1	0,6	–	0,1	4,5	1,6	3,6	–	0,2	1,5	7,3	0	2,5	0	0,9	1,9	0,6	2,7
	Relative mean error	%	4,0	2,2	–	0,5	15,8	5,7	12,7	–	0,9	5,2	25,4	0	8,8	0	3,0	6,8	2,2	9,6
	Standard deviation	mg ℓ^{-1}	0,9	1,0	–	0,6	0,9	1,1	1,6	–	1,5	1,5	2,2	1,4	1,9	0,5	0,7	3,3	7,3	1,2
	Coefficient of variation	%	3,3	3,6	–	2,0	3,7	4,2	5,1	–	5,3	5,0	6,1	5,0	6,0	1,8	2,3	12,4	25,1	3,7
	Method reference number (Table 5)		1	2	–	1	1	1	3	–	3	3	3	4	4	(1)4 (2)3	2	4	1	2

Data Evaluation

Summaries of the results received, together with a statistical analysis of these results, are given in Tables 1 and 2. The theoretical values shown were obtained from an article in "Deeds and Data" (Masselli *et al.,* 1971). The value for the electrical conductivity is not included owing to the effect of the added mercuric chloride, but will obviously be slightly higher than the theoretical value of 16,8 mS/m.

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.

TABLE 2

SUMMARY OF RESULTS FROM pH, ELECTRICAL CONDUCTIVITY, AND COD (MEAN VALUES) DETERMINATIONS

Sample No.	Parameter	Units	Laboratory Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Theoretical value	Mean value	Mean error	Relative mean error %	Standard Deviation	Coefficient of variation %
1	pH	–	4,4	4,2	4,1	4,4	4,4	4,1	3,9	4,2	3,9	4,2	4,2	4,3	3,6*	4,1	4,2	4,2	–	–	4,4	4,2	0,2	4,5	0,2	3,7
1	Electrical Conductivity	mSm⁻¹	14,8	17,4	17,3	17,1	17,8	18,5	17,5	17,4	17,2	17,	19,9	16,8	16,4	17,0	17,5	–	–	–	–	17,3	–	–	1,1	6,2
1	COD (mean values)	mg ℓ⁻¹	343	341	–	354	333	329	304	–	351	335	359	348	348	339	340	296	367	345	343	340	3	0,9	18	5,4
2	COD (mean values)	mg ℓ⁻¹	27,4	27,9	–	28,4	24,0	26,9	32,1	–	28,3	30,0	35,8	28,5	31,0	28,0	29,4	26,6	29,1	31,2	28,5	29,1	0,6	2,1	2,7	9,1

*Outlier

Figures 1 and 2 illustrate graphically the ranges and mean values of each laboratory's COD results. For comparison purposes, precision data obtained from similar comparison studies are given in Table 3. Finally, the results from each laboratory were assessed (Table 4) according to the method of Greenberg *et al.* (1969), who arbitrarily established the following criteria:

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

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

(iii) Results outside the limits of ± 2 standard deviations are unacceptable.

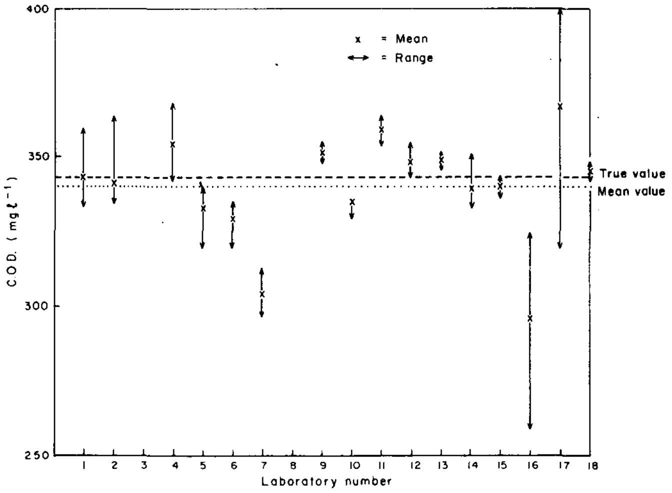

Figure 1

Ranges and mean values of individual COD results (Sample 1)

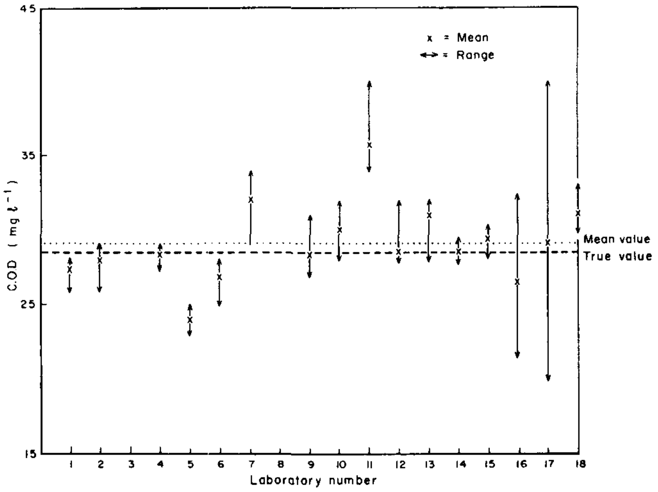

Figure 2

Ranges and mean values of individual COD results (Sample 2)

TABLE 3

PRECISION DATA OBTAINED FROM SIMILAR COMPARISON STUDIES

Reference	Precision		
	pH	Electrical Conductivity	COD
EPA (1974): Methods for chemical analysis of waters and wastewaters.	44 analysts in 20 laboratories analysed 6 synthetic water samples with pH values between 3,5 and 8,0. Standard deviations varied from 0,10 to 0,20 pH units.	41 analysts in 17 laboratories analysed 2 synthetic water samples with conductivity values of 10,0 and 10,6 mS/m respectively. The standard deviations were 0,76 and 0,81 mS/m respectively.	86 analysts in 58 laboratories analysed 2 distilled water solutions containing oxidizable organic matter equivalent to 270 and 12,3 mg ℓ^{-1} COD respectively. The standard deviations were 17,76 and 4,15 mg ℓ^{-1} COD respectively.
APHA-AWWA-WPCF (1975): Standard methods for the examination of water and wastewater, 14th edition.	A synthetic sample consisting of a Clark and Lubs buffer solution of pH 7,3 was analysed electrometrically by 30 laboratories with a standard deviation of 0,13 pH unit.	A synthetic sample with conductivity value of 14,7 mS/m was analysed by 117 laboratories, with a coefficient of variation of 8,6%.	A synthetic sample containing potassium acid phthalate equivalent to 200 mg ℓ^{-1} COD was tested by 74 laboratories. The standard deviation was 13 mg ℓ^{-1} COD and the coefficient of variation was 6,5%.
Inland waters directorate, Canada (1974): Interlaboratory quality control study no. 6	A buffered synthetic water sample of pH 8,4 was analysed by 18 laboratories. The standard deviation was 0,13 pH unit.	A synthetic water sample with a conductivity value of 14,7 mS/m was analysed by 18 laboratories, with a standard deviation of 1,5 mS/m and a coefficient of variation of 9,6%.	

Discussion

pH

With one exception, the results obtained were within a range of 0,5 pH unit. The laboratory submitting the outlying result also reported, however, that the pH had not been determined until 24 hours after the sample container had been first opened, a factor which possibly contributed to the low result. It is recommended that pH should be measured immediately after first opening the sample container. (Total alkalinity and calcium determinations, if required on the same sample, should also be carried out as soon as possible after first opening the sample container, in order to avoid possible concentration changes owing to loss or gain of carbon dioxide, etc.)

Electrical conductivity

Only 2 out of the 15 results submitted could be regarded as unacceptable. It was apparent from an examination of the results first received that not all the determinations had been carried out at the standard temperature of 25°C. (EPA, ASTM and APHA-AWWA-WPCF standard methods all stipulate that conductivity be measured at this temperature). Each laboratory was therefore requested to either confirm that the test had been carried out at 25°C or to submit a corrected value. In response to the request, 5 laboratories confirmed that they had carried out the test at 25°C. Of the remaining 10 laboratories which had not done so, 8 submitted corrected values, 1 had not noted the temperature at which the test had been carried out, and 1 again submitted an uncorrected value, but gave the temperature at which the measurement had been

TABLE 4

ASSESSMENT OF RESULTS

Lab. No.	pH			Electrical Conductivity			COD (sample 1)			COD (sample 2)		
	A	B	C	A	B	C	A	B	C	A	B	C
1	X					X	X			X		
2	X			X			X			X		
3	X			X								
4	X			X			X			X		
5	X			X			X				X	
6	X				X		X			X		
7		X		X				X			X	
8	X			X								
9		X		X			X			X		
10	X			X			X			X		
11	X					X		X				X
12	X			X			X			X		
13			X	X			X			X		
14	X			X			X			X		
15	X			X			X			X		
16	X								X	X		
17								X		X		
18							X			X		

A: Results between mean and ± 1 standard deviation
B: Results between ± 1 and ± 2 standard deviations
C: Results outside ± 2 standard deviations

TABLE 5

METHODS USED FOR COD DETERMINATIONS

Method No.	Method Reference
1	NIWR Analytical guide, Part II, p. 35-37: Oxygen Demand (Chemical) – Automated Method.
2	NIWR Analytical guide, Part II, p. 149-152: Oxygen Demand (Chemical) – Manual Method.
3	Standard methods for the examination of water and wastewater, 14th Edition, p. 550-554 – Oxygen Demand (Chemical)
4	Government gazette no. 2512, 29 August, 1969, p. 8-9: Determination of Chemical Oxygen Demand.

made. It was therefore necessary to correct this last value before carrying out the statistical analysis.

COD

From the assessment of the results (Table 4), 2 out of 32 could be considered unacceptable and 5 acceptable but questionable. The possible presence of significant determinate errors is indicated in the results from laboratories 7, 11, 16, 17 (sample 1), and 5 and 11 (sample 2), while results from laboratories 16 and 17 (both samples) show a high degree of indeterminate error. (Table 1). Precision values obtained from a statistical analysis of the mean values (Table 2) compare reasonably well with other published data (Table 3).

Manual methods of analysis were used by 11 laboratories, and automated methods by 5 laboratories. F and t-tests indicated no significant differences in the precision or accuracy between manual and automated methods. All 11 laboratories who carried out the determination manually employed the standard dichromate reflux method (methods 2, 3 and 4 of Table 5 are almost identical), with, in two cases, minor modifications. An interesting modification, from an economic point of view, was mentioned by one laboratory who used only 7,5 g silver sulphate per 4 kg bottle of sulphuric acid, as recommended by Moore (1976), instead of the currently specified amount of 22 g per 4 kg bottle (APHA, 1975). The 5 laboratories who did the analysis by automated techniques all used the NIWR automated method (NIWR 1973), which is an adaption of a Technicon method (Technicon, 1969). This procedure is also based on the standard dichromate reflux method, but mercuric nitrate is used instead of mercuric sulphate to complex any chloride present, and the hexavalent chromium depletion is, of course, measured colorimetrically and not titrimetrically.

Conclusions

On the whole, pH, electrical conductivity and COD results showed a marked improvement over those obtained in the introductory study.

The importance of determining the pH value immediately after opening the sample container is emphasised.

For purposes of standardization and comparison, it is recommended that the electrical conductivity should either be determined at a temperature of 25°C, or the appropriate temperature correction factor should be applied to the value obtained. At the very least, the temperature at which the test was carried out should be reported.

All the laboratories who determined COD manually used recognized standard methods, while those who did the test by automated techniques employed a procedure based on a standard method, the results from which did not differ significantly from those results obtained by standard manual methods.

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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South African Bureau of Standards (Water Division), Pretoria.
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