

Water Analysis in South Africa: Interlaboratory Comparison Studies. Part VI: Boron, Silicon, MBAS, Cyanide, Phenol, Sulphide, BOD, Colour and Turbidity Analyses

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Abstract

Part VI of the programme of interlaboratory comparison studies involving South African laboratories engaged in water analysis is concerned with boron, silicon, methylene blue active substances (MBAS), cyanide, phenol, sulphide, biochemical oxygen demand (BOD), colour, and turbidity analyses. Evaluation of the results of the study showed that acceptable values were generally obtained for the nine determinands, that recognised standard methods, or methods based on them, were used for almost all of the analyses, and that the results compared favourably with those obtained from similar overseas comparison studies.

It is recommended that only linear alkylate sulphonate (LAS) be used as the reference standard for MBAS determinations and that turbidity values be reported only in Nephelometric Turbidity Units (NTU).

Introduction

In continuation of the programme of interlaboratory comparison studies involving South African laboratories engaged in water analysis (Smith, 1977; 1978a,b; 1979a,b), Part VI is concerned with boron, silicon, methylene blue active substances (MBAS), cyanide, phenol, sulphide, biochemical oxygen demand (BOD), colour and turbidity analyses. The results obtained and the analytical methods used by the fourteen laboratories who participated in the study are summarized and evaluated in this paper. This is the final study of the present programme involving the analysis of synthetic water samples.

Sample Preparation

Details of the preparation and preservation of the samples are given in Table 1.

The samples were contained in 250 cm³ 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/dm³ nitric acid solution, followed by rinsing with deionized distilled water.
- (3) Rinsing with sample solution.

Each laboratory was supplied with those 250 cm³ samples which they were capable of analysing.

Analysis requested

Details of the analyses requested are shown in Table 1, along with the concentration ranges of each determinand. Complete freedom of choice was allowed with regard to the analytical procedures to be employed. It was also requested that —

- (1) each laboratory carrying out the BOD determination

**TABLE 1
SAMPLE PREPARATION AND ANALYSIS DETAILS**

Sample no.	Analysis required	Concentration range	Prepared from	Preservative
1	Boron	0,1 – 2 mg/dm ³	Merck standard metal solution	None
	Silicon	1 – 10 mg/dm ³	BDH standard metal solution	
	MBAS	1 – 10 mg/dm ³	EPA standard reference material (LAS)	
2	Cyanide	0,1 – 2 mg/dm ³	AR grade potassium cyanide	NaOH → pH > 12
3	Phenol	0,1 – 2 mg/dm ³	AR grade phenol	H ₃ PO ₄ → pH < 4 1 g CuSO ₄ ·5H ₂ O/dm ³ sample
4	Sulphide	1 – 10 mg/dm ³	AR grade sodium sulphide	40 drops 1 mol/dm ³ Zn(C ₂ H ₃ O ₂) ₂ ·2H ₂ O per dm ³ sample
5	BOD	10 – 1000 mg/dm ³	AR grade potassium hydrogen phthalate	None
6	Colour	1 – 100 colour units	Reagent grade potassium chloro-platinate + AR grade cobalt chloride	None
7	Turbidity	1 – 100 NTU	AR grade hexamine + AR grade hydrazine sulphate	None
8	Turbidity	1 – 100 NTU	Kaolin (light)	None

**TABLE 2
SUMMARY OF RESULTS**

Determinand	Units	Sample no.	Laboratory Number															True value	Mean value	Mean error	Relative mean error (%)	Standard deviation	Coefficient of variation (%)
			1	2	3	4	5	6	7	8	9	11	12	13	14	15							
Boron	mg/dm ³	1	0,61	—	0,62	—	0,70	0,71	—	0,61	0,72	0,70	—	—	—	—	0,62	0,67	0,05	7,6	0,06	7,5	
Silicon	mg/dm ³	1	—	—	7,64	7,05	7,48	7,00	—	6,10	7,30	6,80	—	5,74	6,79	5,97	7,20	6,79	0,41	5,7	0,65	9,6	
MBAS	mg/dm ³	1	—	—	—	—	4,10*	1,63	1,60	—	2,90*	3,10*	—	—	—	—	—	—	—	—	—	—	—
Cyanide	mg/dm ³	2	—	—	—	—	0,21	0,39	—	—	0,37	0,38	—	—	—	—	—	—	—	—	—	—	—
Phenol	mg/dm ³	3	—	—	—	—	—	0,08	—	—	0,23	0,16	—	—	—	—	—	—	—	—	—	—	—
Sulphide	mg/dm ³	4	—	—	—	—	—	—	—	—	1,1	1,0	—	—	—	1,29	—	—	—	—	—	—	—
BOD	mg/dm ³	5	—	—	—	—	—	—	—	245	—	—	210	—	233	240	321	240	250	10	4,1	42	16,8
Colour	Colour units	6	—	60	—	—	40	50	30	—	45	30	30	41	40	35	45	40	5	11,1	10	24,2	—
Turbidity	NTU	7	—	30	—	—	28	29	23*	26	27	29**	28	31	30	31	32	29	3	9,4	2	6,1	—
	NTU	8	—	12	—	—	16	15	12*	13	18	13**	16	16	15	17	—	15	—	—	—	2	12,2

* Manoxol OT used as standard.

* JTU

** APHA units (mg/dm³ SiO₂)

Values not used in statistical evaluation.

should supply their own seeded dilution water;

- (2) immediately before carrying out the turbidity determinations, the samples should be vigorously shaken; in addition, the make and model of the instrument used to carry out these determinations should be specified;
- (3) references to standard methods, or copies of the methods used to carry out the various analyses, should be submitted along 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 (where four or more valid results were received) are given in Table 2.

As in previous studies, the results 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, Moskowitz, Tamplin and Thomas (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 which could be statistically analysed, 80 per cent were found to be acceptable and 20 per cent acceptable but questionable. None of these results were unacceptable.

The "true" values given in Table 2 are based on the theoretical values calculated from the amounts of reference chemicals added.

TABLE 3
ASSESSMENT OF RESULTS

Laboratory number	Boron			Silicon			BOD			Colour			Turbidity (7)			Turbidity (8)			Total		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
1	x	-	-																1	-	-
2										x	-	-	x	-	-				1	2	-
3	x	-	-	-	x	-													1	1	-
4				x	-	-													1	-	-
5	x	-	-	-	x	-			x	-	-	x	-	-	x	-	-		4	1	-
6	x	-	-	x	-	-			x	-	-	x	-	-	x	-	-		5	-	-
7							x	-	-	x	-	-	-	-	-	-	-		2	-	-
8	x	-	-	-	x	-							-	x	-	x	-	-	2	2	-
9	x	-	-	x	-	-			x	-	-	x	-	-	-	x	-	-	4	1	-
11	x	-	-	x	-	-	x	-	-	x	-	-	-	-	-	-	-	-	4	-	-
12										x	-	-	x	-	-	x	-	-	3	-	-
13				-	x	-	x	-	-	x	-	-	x	-	-	x	-	-	4	1	-
14				x	-	-	x	-	-	x	-	-	x	-	-	x	-	-	5	-	-
15				-	x	-	-	x	-	-	x	-	-	x	-	-	x	-	3	2	-
Totals	7	-	-	5	5	-	4	1	-	9	1	-	8	1	-	7	2	-	40	10	-

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

For purposes of comparison with similar studies carried out overseas on samples containing approximately similar concentrations of the same determinands. Table 4 shows precision data obtained from comparison studies held in Canada (McGirr, 1974a,b) and the USA (APHA, 1975).

Method Evaluation

(1) Boron

Four of the seven laboratories who carried out this determination used automated techniques based on a method involving the formation of a coloured complex between boron and azomethine-H (Basson *et al.*, 1969). The other three laboratories carried out the determination manually, one using a method based on the reactions involving boron, hydrofluoric acid, and methylene blue, followed by extraction with dichloroethane and measurement at 660 nm, while the other two laboratories used the standard curcumin method, wherein the sample containing boron is acidified and evaporated in the presence of curcumin, resulting in the formation of a red-coloured product, rosocyanine. The rosocyanine is taken up in ethyl alcohol and the intensity of the red colour compared with standards, either visually or photometrically (APHA, 1975; EPA, 1974). Three of the four laboratories who used the automated azomethine-H method obtained results of 0,61, 0,61 and 0,62 mg/dm³ ("true" value: 0,62 mg/dm³). The remaining results were between 0,70 and 0,72 mg/dm³.

(2) Silicon

Four laboratories determined this constituent by automated techniques, while six used manual methods of analysis. All par-

ticipants used either the standard molybdosilicate or heteropoly blue methods (APHA, 1975), or some modification of these methods. The molybdosilicate method involves the reaction between ammonium molybdate and silica in the sample at pH 1,2 (oxalic acid is added to eliminate phosphate interference) to form greenish yellow molybdosilicic acid, the intensity of which is measured either photometrically or by visual comparison with standards. In the heteropoly blue method, molybdosilicic acid formed as in the molybdosilicate method is reduced by means of amino naphthol sulphonic acid to heteropoly blue. This blue colour is more intense than the yellow colour of the molybdosilicic acid and provides increased sensitivity. Modifications used included the use of tartaric acid in place of oxalic acid for removal of phosphate interference and the use of ascorbic acid for reduction of the molybdosilicic acid to heteropoly blue. Results obtained ranged from 5,74 to 7,64 mg/dm³ ("true" value: 7,20 mg/dm³).

(3) Methylene blue active substances (MBAS)

Seven laboratories carried out this determination, five manually and two by automated techniques. All participants used either the standard methylene blue method (APHA, 1975) or some modification thereof, in which methylene blue in aqueous solution reacts with anionic type surface active materials to form a blue-coloured salt, which is extracted with chloroform. The intensity of colour produced is proportional to the concentration of MBAS. However, only three laboratories used linear alkylate sulphonate (LAS) as the standard reference material, as recommended by "Standard Methods" (APHA, 1975), obtaining results of 1,60, 1,63 and 2,23 mg/dm³ (average: 1,82 mg/dm³; "true" value: 1,92 mg/dm³). The other four laboratories used Manoxol OT as the standard reference material, obtaining results of 2,90, 4,07 and 4,10 mg/dm³ (average 3,54 mg/dm³).

TABLE 4
PRECISION DATA FROM SIMILAR OVERSEAS COMPARISON STUDIES

Determinand	No. of results	True value	Mean value	Standard deviation	Coefficient of variation (%)	Reference
Boron (mg/dm ³)	30	0,24	—	—	22,8	APHA (1975) Curcumin Method (p. 287)
Silicon (mg/dm ³)	19	5,0	—	—	14,3	APHA (1975) Molybdosilicate method (p. 487)
	11	5,0	—	—	27,2	APHA (1975) Heteropoly blue method (p. 490)
BOD (mg/dm ³)	73	194	175	26	15	APHA (1975) (p. 543)
Colour (colour units)	13	45	42	8,1	20	McGirr (1974a) (Visual comparison)
Turbidity (JTU)	9	—	40	6,3	15	McGirr (1974b) Hach 2100 Turbidimeter
	7	—	40	5,0	12	McGirr (1974b) Hach 2100A Turbidimeter

The use of LAS as standard reference material for this determination has been specified in "Standard Methods" since the detergent industry changed over in 1965 from the use of alkyl benzene sulphonate (ABS) to the more biodegradable LAS.

For purposes of standardisation and comparison therefore, it is strongly recommended that all laboratories should use LAS as the standard reference material for the determination of MBAS. This material is obtainable from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268.

(4) Cyanide

Of the four laboratories carrying out this determination, one used an automated technique based on the conversion of cyanide by bromine water to cyanogen bromide, and the reaction of the cyanogen bromide with benzidine in dilute pyridene solution to give an intense orange to red colour which is proportional to the amount of cyanogen bromide present (Aldridge, 1944). The other three laboratories carried out the determination manually, using different procedures. One used the standard colorimetric method (APHA, 1975; EPA, 1974), in which cyanide, after a preliminary distillation step, is converted to cyanogen chloride by reaction with chloramine-T, which then forms, on the addition of a pyridine-barbituric acid reagent, a red-blue dye, the intensity of which is read at 578 nm. The second laboratory used the standard ion-selective electrode method, in which the cyanide in the distillate from the preliminary distillation step is determined potentiometrically by the 'known addition' technique, (APHA, 1975). The remaining laboratory made use of the standard titrimetric method, involving the titration of the cyanide in the distillate from the preliminary distillation step with standard silver nitrate solution, using paradimethylamino benzalrhodanine as indicator (APHA, 1975). Significantly high results of between 0,37 and 0,39 mg/dm³ were obtained by three laboratories. The other laboratory obtained a result of 0,21 mg/dm³, using the standard colorimetric method ("true" value: 0,24 mg/dm³).

(5) Phenol

Only three laboratories attempted the determination of this constituent. Of these, one used an automated technique based on the standard direct photometric method (APHA, 1975; EPA, 1974), in which steam-distillable phenols react with 4-aminoantipyrene at a pH of 10,0 ± 0,2 in the presence of potassium ferricyanide to form a coloured dye, the absorbance of which is measured in aqueous solution at 510 nm. A low result (0,08 mg/dm³) was obtained by this laboratory ("true" value: 0,22 mg/dm³).

Better results (0,23 and 0,16 mg/dm³) were obtained by the other two laboratories, who both used the standard chloroform extraction method (APHA, 1975), in which the antipyrene dye, obtained as previously described, is extracted from aqueous solution with chloroform, and its absorbance measured at 460 nm.

(6) Sulphide

Of the three laboratories who determined this constituent, two used the standard methylene blue method, involving the reaction between para-aminodimethylaniline, ferric chloride, and sulphide ion, resulting in the formation of methylene blue, the intensity of which is measured photometrically at 625 nm or by

visual comparison (APHA, 1975). The other laboratory used the standard titrimetric (iodine) method, involving the titration of sulphide in acid solution with standard iodine solution, using starch solution as indicator (APHA, 1975; EPA, 1974).

Owing to the hygroscopic and unstable nature of the material used to prepare the sample for sulphide determination, it is highly possible that the "true value" given is somewhat high and that it probably lies closer to the values actually obtained.

Also, the necessity of preserving the sample by the addition of zinc acetate, as recommended in "Standard Methods" (APHA, 1975), results in the precipitation of some of the sulphide. Determination of sulphide by means of ion-selective electrode or polarographic techniques, as attempted by one laboratory, is therefore not feasible.

(7) Biochemical oxygen demand (BOD)

Of the five laboratories carrying out the determination of this parameter, four measured the dissolved oxygen by means of the standard iodometric method (azide modification), and one used the standard membrane electrode method (APHA, 1975). The results obtained ranged from 210 to 321 mg/dm³ ("true" value: 240 mg/dm³).

(8) Colour

Ten laboratories carried out the determination of this parameter. Of these, three used the standard visual comparison method (APHA, 1975; EPA, 1974), in which the colour of the sample is compared with platinum-cobalt standards. One laboratory used an automated procedure involving the photometric comparison of the sample with platinum-cobalt standards at a pH of 7,6 at 400–440 nm. The other six laboratories carried out the determination by means of colour-disc techniques, using either the Lovibond comparator with Hazen comparator discs (four laboratories) or the Hellige Aqua Tester with 'colour of water' discs (two laboratories). Results obtained by these laboratories were not significantly different from those obtained by the laboratories using the standard visual comparison method.

"Standard Methods" (APHA, 1975) allows for the use of these colour discs as standards for laboratory work provided they have been individually calibrated against platinum – cobalt standards.

(9) Turbidity

Seven of the eleven laboratories carrying out this determination did so by means of the Hach Turbidimeter Model 2100 A. One laboratory used the Hach Turbidimeter Model 2100, while another used an EEL Nephelometer. Results from these nine participants were reported in Nephelometric Turbidity Units (NTU) and showed good agreement. Results from the remaining two laboratories, which were not included in the statistical evaluation, were obtained on a Hellige Turbidimeter and a HF Instruments Turbidimeter, Model DRT100, and were reported in American Public Health Association (APHA) units (mg/dm³ SiO₂) and Jackson Turbidity Units (JTU) respectively.

The Hach Turbidimeters, Model 2100 and 2100A, are specifically recommended by both the EPA (EPA, 1974) and the Canada Centre for Inland Waters (McGirr, 1974b) as instruments for the determination of turbidity in water. It is, therefore, recommended that for purposes of standardisation and comparison, laboratories who are not yet in possession of such

instruments should seriously consider the purchase of one or other of these turbidimeters, or alternatively, the purchase of an instrument meeting the design criteria of the Hach instruments, and capable of giving comparable results.

Also, turbidity values have been previously, and in some cases still are, reported in terms of Formazin Turbidity Units (FTU) or Jackson Turbidity Units (JTU).

Again for purposes of standardisation and comparison, as well as to eliminate any confusion, it is recommended that Nephelometric Turbidity Units (NTU) should be used exclusively. NTU's are considered to be comparable to FTU's and JTU's (EPA, 1974).

Conclusions

In general, satisfactory results were obtained. Recognised standard methods, or slight modifications of these methods, were used for most of the analyses.

Insufficient results were obtained for the cyanide, phenol, sulphide and BOD results to allow any definite conclusions to be drawn with regard to the relative reliability of the methods used for their analysis.

For purposes of standardisation and comparison it is recommended that LAS should be used by all laboratories as the standard reference material for the determination of MBAS.

The Hach Turbidimeter Model 2100 or 2100A is recommended for use in the determination of turbidity. Turbidity results should be reported in Nephelometric Turbidity Units (NTU).

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