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# Performance of a Water Analysis Kit



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Information contained herein is available to all persons  
without regard to race, color, sex, or national origin.

# Performance of a Water Analysis Kit

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## INTRODUCTION

**W**ATER ANALYSIS KITS are comparatively inexpensive, easy to use, compact, portable, and suitable for field use. They are often used by field biologists and engineers who are responsible for water quality management. Water analysis kits are manufactured by several companies and have been widely used for many years. Recently, the reliability of several of the more popular kits was determined (2, 3, 4, 5). Results indicated that the precision and accuracy of these water analysis kits were adequate for general surveys of water quality, fisheries management decisions, research requiring approximate water quality data, and similar endeavors. One of the most popular kits in the 1970's was the Hach DR-EL/2 Direct Reading Engineer's Laboratory kit (Hach Chemical Company, Loveland, Colorado). Recently, this kit was modified and the present study was conducted to determine the reliability of the modified kit. Hach biochemical oxygen demand (BOD) and chemical oxygen demand (COD) equipment were also tested.

## MATERIALS AND METHODS

New equipment was used in the evaluations: Hach DR-EL/5 Direct Reading Environmental Laboratory Kit, Hach manometric BOD Apparatus, and Hach COD Reactor. Hach methods are based on acceptable methods of water analysis, usually those described by the American Public Health Association et al. (1) and the Environmental Protection Agency (7). The DR-EL/5 kit can be used to make a number of different water quality tests, 16 of which were evaluated in the present study.

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All reagents and most apparatus needed for the tests are included in the kit. Many reagents are in dry form, premeasured, and packaged in small plastic containers called "powder pillows." The kit contains a spectrophotometer with interchangeable, precalibrated meter scales which permit direct readings of concentrations of various substances. Sample volumes for titrations are usually 100 milliliter, and titrations are conducted with a hand-held digital titrator. A digital pH meter and a conductivity meter are included in the kit. The spectrophotometer and conductivity meter operate either on line voltage, as in the present study, or on a battery. All analyses with the kit and with the COD and BOD equipment employed fresh reagents and followed manufacturer's instructions.

The Hach kit and equipment were compared to standard analytical methods as described by the American Public Health Association et al. (1). The following instruments were used for standard methods: Bausch and Lomb Spectronic 70 spectrophotometer, Coleman Model 9 nephlo-colorimeter, Corning Model 7 pH meter, and Yellow Springs Model 33 S-C-T conductivity meter.

Samples were obtained from ponds, streams, and wells in east-central Alabama, and represented a wide range of water quality. Nevertheless, it was sometimes necessary to add small quantities of substances to be measured to aliquots of samples to produce desired concentrations.

For each water quality variable, three or more samples of water (low, intermediate, and high concentrations) were analyzed by the standard method and the Hach method. Seven replicate determinations were made on each sample by each analytical system. The standard deviation (SD) was taken as a measure of precision of each method. An F-test was used to determine if variances ( $s^2$ ) for the standard method and the Hach method were homogeneous. Differences between means obtained by standard and Hach methods were tested for statistical significance by *t*-tests.

Spike-recovery (6) was used to estimate accuracy. Two or three samples which had been analyzed for a particular variable by each method were spiked with an amount equal to about 20 percent of the initial concentration of the variable. The spiked samples were analyzed in triplicate by both methods

of analysis. The percentage recovery (an estimate of accuracy) was computed as:

$$\text{Recovery (percent)} = \frac{\text{Measured concentration}}{\text{Initial concentration} + \text{spike}} \times 100.$$

It was impossible to conduct spike recovery tests of carbon dioxide, dissolved oxygen, pH, or BOD, and because of expense, only a few spike-recovery tests were conducted for COD.

## RESULTS AND DISCUSSION

Differences between averages obtained with the standard methods of analyses and the Hach DR-EL/5 kit were usually significant ( $P \leq 0.05$  or  $< 0.01$ ), table 1. Of course, an average obtained by a standard method was considered more reliable than one by the Hach method. Standard methods also provided greater precision (significantly smaller variances;  $P \leq 0.05$ ) than the Hach methods in many cases. A better idea of the reliability of the Hach methods can be achieved by considering the Hach averages as percentages of averages by standard methods. All averages for the Hach method were between 90 and 110 percent of those for the standard method for total alkalinity, calcium hardness, total hardness, nitrite, pH, and orthophosphate. For total acidity, chloride, total chlorine, apparent color, nitrate, dissolved oxygen, specific conductance, and sulfate, all averages for the Hach method were 75 to 125 percent of the standard methods. Greater differences were obtained for carbon dioxide and especially for ammonia. For most variables, spike recoveries were between 90 and 100 percent for both methods. Usually, the standard method had nearer 100 percent spike recovery than the corresponding Hach method, but there were exceptions—notably sulfate.

The essential differences in the new DR-EL/5 kit and the old DR-EL/2 kit are: digital titrator rather than graduated pipets and droppers, pH meter instead of colorimetric procedure for pH, and an improved spectrophotometer. Results of the present study were compared with the earlier evaluation of the DR-EL/2 kit (3). When values for the Hach kit as a percentage of the standard method were considered, the DR-EL/5 was slightly superior to the DR-EL/2 for chloride, calcium hardness, nitrite, and specific conductance; the DR-

TABLE 1. COMPARISONS OF WATER ANALYSES MADE BY STANDARD METHODS AND WITH A HACH DR-EL/5 WATER ANALYSIS KIT. SEVEN REPLICATE DETERMINATIONS ON EACH SAMPLE WERE MADE BY BOTH METHODS FOR CALCULATIONS OF MEAN ( $\bar{x}$ ) AND STANDARD DEVIATION (SD). THE *t*-TEST COMPARISONS WERE USED TO TEST SIGNIFICANCE OF DIFFERENCES BETWEEN MEANS. SPIKE-RECOVERIES WERE MADE IN TRIPPLICATE

Standard method		Hach		<i>t</i>	Hach as pct. of standard method	Spike-recovery, pct.	
$\bar{x}$	SD	$\bar{x}$	SD			Standard method	Hach
<u>Total acidity (mg/liter as CaCO<sub>3</sub>)</u>							
15.6	0.36	18.6	0.83	14.62**	119.2	88.1	88.2
54.8	.61	56.9	2.06 <sup>m</sup>	2.59*	103.8	103.3	99.3
126.7	2.89	143.7	6.34	6.46**	113.4	90.6	107.9
<u>Total alkalinity (mg/liter as CaCO<sub>3</sub>)</u>							
28.2	.13	29.0	.87 <sup>m</sup>	2.12	102.8	99.7	101.8
62.1	.26	63.5	.40	4.56**	102.3	100.2	97.3
106.1	.33	104	2.13 <sup>m</sup>	2.58*	98.0	99.8	103.1
<u>Carbon dioxide (mg/liter)</u>							
7.1	.19	12.6	.56 <sup>m</sup>	24.61**	177.5	—	—
17.3	.24	23.2	.80 <sup>m</sup>	18.69**	134.1	—	—
58.0	1.62	68.3	2.64	8.80**	117.8	—	—
<u>Chloride (mg/liter)</u>							
3.1	.15	3.8	.18	9.03**	122.5	101.3	106.7
18.5	.09	19.9	.33	10.83**	107.6	100.5	101.2
34.1	.15	35.4	.32	9.73**	96.3	100.1	96.9
<u>Total chlorine (mg/liter)</u>							
.22	.014	.21	.010	.24	95.4	88.5	76.7
.68	.016	.65	.010	4.21**	95.6	91.3	91.7
1.74	.033	1.55	.017	13.54**	89.1	93.8	93.5
<u>Calcium hardness (mg/liter as CaCO<sub>3</sub>)</u>							
10.6	.21	10.6	.10	.00	100.0	97.6	98.8
34.7	.26	35.7	.55	4.35**	102.6	100.2	100.8
58.4	.28	60.9	.52	11.20**	104.3	99.8	103.3
<u>Apparent color (color units)</u>							
25	.1	26	3.78 <sup>m</sup>	.70	104.0	84.0	72.7
45	.1	47	5.67 <sup>m</sup>	.93	104.4	80.0	77.3
50	.1	60	8.66 <sup>m</sup>	3.05*	120.0	82.0	67.7
<u>Total hardness (mg/liter as CaCO<sub>3</sub>)</u>							
21.1	.19	20.8	.44	1.66	98.6	101.5	98.4
64.9	.34	65.2	.49	.43	100.5	100.9	101.0
108.7	.93	109	3.20 <sup>m</sup>	.24	100.3	100.4	98.1
<u>Nitrate (mg/liter)</u>							
.24	.011	.20	.029 <sup>m</sup>	2.47*	83.3	101.0	50.5
1.59	.019	1.24	.053 <sup>m</sup>	16.45**	78.0	97.0	88.8
5.28	.048	4.60	.160 <sup>m</sup>	10.77**	87.1	98.9	100.2

Continued

TABLE 1 (Continued). COMPARISONS OF WATER ANALYSES MADE BY STANDARD METHODS AND WITH A HACH DR-EL/5 WATER ANALYSIS KIT. SEVEN REPLICATE DETERMINATIONS ON EACH SAMPLE WERE MADE BY BOTH METHODS FOR CALCULATIONS OF MEAN ( $\bar{x}$ ) AND STANDARD DEVIATION (SD). THE *t*-TEST COMPARISONS WERE USED TO TEST SIGNIFICANCE OF DIFFERENCES BETWEEN MEANS. SPIKE-RECOVERIES WERE MADE IN TRIPLICATE

Standard method		Hach		<i>t</i>	Hach as pct. of standard method	Spike-recovery, pct.	
$\bar{x}$	SD	$\bar{x}$	SD			Standard method	Hach
<u>Nitrite (mg/liter)</u>							
.039	.001	.038	.001	1.89	97.4	103.2	103.3
.015	.001	.103	.001	3.77**	98.1	99.2	99.2
.190	.001	.182	.001	15.09**	95.8	96.7	99.4
<u>Ammonia (mg/liter as N)</u>							
.22	.018	.49	.011	33.86**	222.7	101.4	99.5
.57	.016	1.15	.017	65.73**	201.8	96.9	97.3
1.16	.023	1.82	.051	31.21**	156.9	95.7	98.6
<u>Dissolved oxygen (mg/liter)</u>							
2.80	.069	3.00	.032	6.96**	107.1	—	—
4.93	.053	5.50	.049	20.89**	111.6	—	—
7.78	.067	8.69	.054	27.98**	111.7	—	—
<u>pH</u>							
4.85	.15	4.86	.20	.11	100.2	—	—
7.82	.10	7.47	.13	5.65**	95.5	—	—
9.81	.03	9.59	.07	7.64**	97.8	—	—
<u>Soluble orthophosphate (mg/liter as PO<sub>4</sub>)</u>							
.123	.015	.130	.112	.16	105.7	92.9	107.2
.342	.004	.365	.005	9.50**	106.7	97.1	99.7
.978	.004	.980	.008	.66	100.2	99.9	99.1
<u>Specific conductance (µmho/cm)</u>							
65	.76	75	2.36 <sup>m</sup>	10.67**	115.4	92.3	100.6
404	3.45	453	18.90 <sup>m</sup>	6.75**	112.1	99.1	99.8
1,651	3.78	1,854	15.12 <sup>m</sup>	34.46**	112.3	96.0	103.0
<u>Sulfate (mg/liter)</u>							
11.1	.83	13.9	.85	5.97**	125.2	93.5	101.1
31.6	2.90	36.6	1.93	3.80**	86.3	92.2	94.4
48.4	3.55	57.3	2.00	7.07**	118.0	83.6	96.6

\*,\*\*Significant at  $\alpha = 0.05$  and  $\alpha = 0.01$ , respectively.

<sup>m</sup>Variances ( $s^2$ ) were homogeneous and pooled variances used in t-test ( $s_1^2 = s_2^2$ , degrees of freedom ( $d_t$ ) = 12;  $s_1^2 \neq s_2^2$ ,  $d_t = 6$ ).

EL/5 and DR-EL/2 were roughly equal for total alkalinity, total chlorine, apparent color, total hardness, ammonia, nitrite, dissolved oxygen, pH, orthophosphate, and sulfate; the DR-EL/2 was slightly better than the DR-EL/5 for total acidity and carbon dioxide. Spike-recovery tests were not conducted in the evaluation of the DR-EL/2 (3). Although the modifications have not greatly improved the reliability of the DR-EL/5 as compared to the DR-EL/2, the new kit is much easier to use than the old one. The digital titrator permits larger sample volumes (100-milliliter as compared to 10-milliliter) and requires much less skill to use accurately than droppers or pipets. The meter permits easier and more rapid pH measurements than did the colorimetric procedure.

Results of the COD and BOD comparisons indicate that the Hach equipment yields data that compare reasonably well with those obtained by standard methods, table 2. This was especially true for the low range COD. Both the titrametric and colorimetric finishes for the COD by the Hach method compared well with the standard method. All standard COD determinations were with a titrametric finish.

In earlier comparisons of six different water analysis kits (Hach, Bausch and Lomb, Ecologic, CHEMetrics, Hellige, and LaMotte), data obtained with kits usually did not differ by more than 25 percent from those obtained by standard methods of analysis (5). The DR-EL/5 kit evaluated in the present study appears just as reliable as the kits tested in earlier studies.

The precision and accuracy of all water analysis kits and standard methods are equally dependent upon "good technique." Water analysis kit users cannot expect the degree of accuracy and precision reported herein unless tests are conducted carefully and acceptable techniques are used in making all measurements. Reagents in kits deteriorate with age and should be replaced occasionally (about once a year) for best results.

Kits are generally not as reliable as standard methods of analysis. However, they perform well enough to justify their use in many water quality considerations. If accuracy and precision limits for a particular effort are established, data presented in this and earlier papers (2,3,4,5) can be used to determine if water analysis kits and related equipment are suitable analytical systems.



TABLE 2. COMPARISONS OF BIOCHEMICAL OXYGEN DEMAND (BOD) AND CHEMICAL OXYGEN DEMAND (COD) ANALYSES MADE BY STANDARD METHODS AND WITH HACH EQUIPMENT. SEVEN REPLICATE DETERMINATIONS ON EACH SAMPLE WERE MADE BY BOTH METHODS FOR CALCULATION OF MEAN ( $\bar{x}$ ) AND STANDARD DEVIATION (SD). THE *t*-TEST COMPARISONS WERE USED TO TEST SIGNIFICANCE OF DIFFERENCES BETWEEN MEANS. SPIKE-RECOVERIES WERE MADE IN TRIPPLICATE

Standard method		Hach		<i>t</i>	Hach as pct. of standard method	Spike-recovery, pct.	
$\bar{x}$	SD	$\bar{x}$	SD			Standard method	Hach
<u>High range COD, titrametric finish (mg/liter)</u>							
229	1.3	200	15.1 <sup>m</sup>	5.06**	87.3	—	—
634	9.5	683	11.4	8.74**	107.7	—	—
1,084	6.9	1,120	43 <sup>m</sup>	2.19	103.3	—	—
<u>High range COD, colorimetric finish (mg/liter)</u>							
229	1.3	255	9.6 <sup>m</sup>	7.10**	111.4	—	—
634	9.5	691	9.0 <sup>m</sup>	11.52**	109.0	—	—
1,084	6.9	1,143	40 <sup>m</sup>	3.85**	105.4	—	—
<u>Low range COD, titrametric finish (mg/liter)</u>							
15.5	.64	17.6	5.71 <sup>m</sup>	.97	113.5	98.5	111.8
53.4	.98	48.9	7.17 <sup>m</sup>	1.65	91.5	99.8	105.5
127.8	1.46	131.0	8.02 <sup>m</sup>	1.04	102.5	—	—
<u>Low range COD, colorimetric finish (mg/liter)</u>							
15.5	.64	19.1	5.34 <sup>m</sup>	.87	123.2	98.5	132.5
53.4	.98	49.6	6.08 <sup>m</sup>	.70	92.8	99.8	105.1
127.8	1.46	130.6	7.72 <sup>m</sup>	.94	102.2	—	—
<u>BOD (mg/liter)</u>							
11.1	1.40	12.3	2.94	.37	110.8	—	—
16.0	.46	18.9	.63	9.84**	118.1	—	—
33.9	2.07	26.5	1.00	2.46*	78.2	—	—
87.8	2.98	88.0	11.51 <sup>m</sup>	.04	100.2	—	—

\*\*\*Significant at  $\alpha = 0.05$  and  $\alpha = 0.01$ , respectively.

<sup>m</sup>Variances ( $s^2$ ) were homogeneous and pooled variances used in t-test ( $s_1^2 = s_2^2$ , degree of freedom ( $d_f$ ) = 12;  $s_1^2 \neq s_2^2$ ,  $d_f = 6$ ).

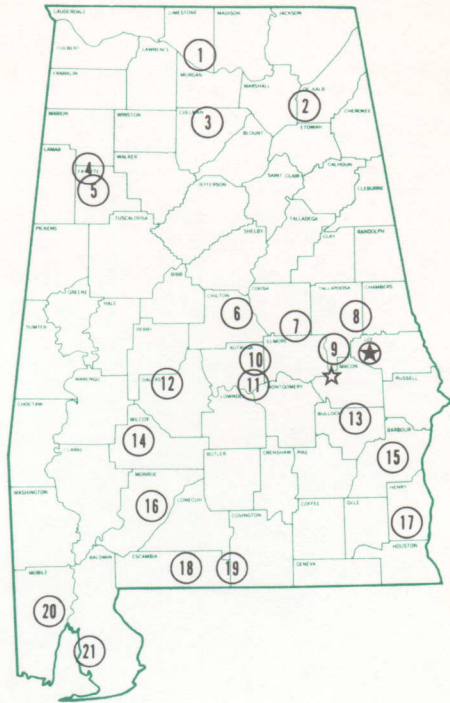
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## Alabama's Agricultural Experiment Station System AUBURN UNIVERSITY

With an agricultural research unit in every major soil area, Auburn University serves the needs of field crop, livestock, forestry, and horticultural producers in each region in Alabama. Every citizen of the State has a stake in this research program, since any advantage from new and more economical ways of producing and handling farm products directly benefits the consuming public.



### Research Unit Identification

- ★ Main Agricultural Experiment Station, Auburn.
- ☆ E. V. Smith Research Center, Shorter.

1. Tennessee Valley Substation, Belle Mina.
2. Sand Mountain Substation, Crossville.
3. North Alabama Horticulture Substation, Cullman.
4. Upper Coastal Plain Substation, Winfield.
5. Forestry Unit, Fayette County.
6. Chilton Area Horticulture Substation, Clanton.
7. Forestry Unit, Coosa County.
8. Piedmont Substation, Camp Hill.
9. Plant Breeding Unit, Tallassee.
10. Forestry Unit, Autauga County.
11. Prattville Experiment Field, Prattville.
12. Black Belt Substation, Marion Junction.
13. The Turnipseed-Ikenberry Place, Union Springs.
14. Lower Coastal Plain Substation, Camden.
15. Forestry Unit, Barbour County.
16. Monroeville Experiment Field, Monroeville.
17. Wiregrass Substation, Headland.
18. Brewton Experiment Field, Brewton.
19. Solon Dixon Forestry Education Center,  
Covington and Escambia counties.
20. Ornamental Horticulture Field Station, Spring Hill.
21. Gulf Coast Substation, Fairhope.