A comparative study of the performance of Reagecon COD vials and Hach® COD vials using the Hach® DR/2010 photometer

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Abstract:

This paper describes a comparative study on the performance of the Reagecon and Hach® COD vials when used in conjunction with the Hach® DR/2010 photometer. The results show that the Reagecon vials give comparable results to the Hach® vials in terms of accuracy and repeatability for both COD standards and effluent samples. Therefore the Reagecon COD vials can be used with confidence with the Hach® DR/2010 photometer. As the single range of Hach® COD vials are designed for use on the entire range of Hach® spectrophotometers, the Reagecon COD vials can equally be used on the full range of Hach® spectrophotometers.

1 Introduction

Chemical oxygen demand (COD) is widely used as a measurement of pollutants in wastewater and natural waters. COD is defined as the amount of a specified oxidant that reacts with a sample under controlled conditions[1] and is expressed in mg/l. Because of its unique chemical properties the dichromate ion ($Cr_2O_7^{2-}$) is the specified oxidant in both Standard Methods 5220[1], and USEPA Method 410.4[2]. Both organic and inorganic components of a sample are subject to oxidation, but in most cases the organic components predominate and are of greater interest[1].

Traditionally COD was determined by the open reflux method, as outlined in Standard Method 5220A[1], which is suitable for a wide range of wastes where a large sample size is available. This method has an inherent disadvantage in terms of the amount of hazardous waste generated, and is labour intensive. The colorimetric closed reflux method outlined in Standard Methods 5220D[1] offers a more economical alternative to the open reflux method as the quantity of reagents required, the amount of hazardous waste generated and the labour required are all lower. A variety of kits containing premeasured reagents are readily available for performing the closed reflux method. These kits are composed of prepackaged vials of reagent to which a specified volume of sample is added. The vial is then sealed and digested by heating at 150°C for 2 hours. Once cooled, the COD concentration can be read using a pre-programmed spectrophotometer, which is designed for use with these vials. These reagents offer the user a simple, convenient and safe method of COD analysis. Once the test has been performed the sealed vial should be disposed of safely.

This study investigates the comparability of two commercially available closed reflux method reagents - the Reagecon COD vials and the corresponding Hach® COD vials.

The Reagecon COD vials have been designed and formulated so that they can be used on Hach® photometers. This gives users of Hach® reagents an alternative source of test consumables of comparable quality for their COD analysis.

To establish user confidence when substituting the Reagecon COD vials for the Hach® vials the following factors need to be established:

- Accuracy of response using COD standards
- Repeatability and precision using COD standards
- Performance comparison using effluent samples

Accuracy and repeatability can only be established using COD standards, as the true COD value of the sample must be known. As COD analysis is based on chemical digestion, it is also important to check the reagents using actual effluent samples, as they may not be as readily digested as COD standards.

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2 Experimental

2.1 Reagents & Apparatus

The following commercially available reagents were used to perform the comparison:

A. Reagecon COD reagent vials
- Low range COD vials 0 - 150 mg/l Cat. No. 420720)
- Medium range COD vials 0 - 1500 mg/l (Cat. No. 420721)
- High range COD vials 0 - 15000 mg/l (Cat. No. 420722)

B. Hach® COD vial tests
- Vial test COD 0 - 150 mg/l (Cat. No. 21258)
- Vial test COD 0 - 1500 mg/l (Cat. No. 21259)
- Vial test COD 0 - 15000 mg/l (Cat. No. 24159)

As Hach® supply a variety of different photometers the DR/2010 was chosen for this evaluation as being representative of the range of photometers in which the Hach® COD vials can be tested.

2.2 Procedure

All tests were carried out in accordance with the Hach® DR/2010 Photometer instruction manual[3].

2.3 Test samples

Solutions of potassium hydrogen phthalate in purified water were prepared for use as COD standards to check the accuracy of both reagents.

Analysis of real effluent samples was also performed. These were composed of both municipal and industrial effluents (approximately 50% each), sampled both upstream and downstream of treatment plants. All samples were homogenized prior to testing.

3 Results

In order to compare the two vials a variety of both standards and real samples were analysed, and the results compared using standard statistical methods.

3.1 Accuracy

Accuracy was determined using potassium hydrogen phthalate standards, and was tested at seven points across the full measuring range of both sources of vials (see Table 1).

3.2 Repeatability of results

A single control standard was selected for each measuring range and tested sevenfold to determine the repeatability results for each product (see Table 2)

3.3 Analysis of effluent samples

The measuring range of 0-1500 mg/l COD was selected in order to check the comparability of the two products due to the ready availability of effluent samples in this range. Forty different samples from this measuring range were analysed (see Table 3).

0-150 mg/L	Hach®	Reagecon
0	0	0
25	24	26
50	51	52
75	76	77
100	103	104
125	127	129
150	149	152

0-1500 mg/L	Hach®	Reagecon
0	0	0
250	254	255
500	522	514
750	752	754
1000	1016	1011
1250	1252	1258
1500	1512	1525

0-15000 mg/L	Hach®	Reagecon
0	0	0
2500	2548	2580
5000	5220	5147
7500	7568	7545
10000	10184	10160
12500	12523	12585
15000	15123	15251

Table 1. Accuracy results with COD standards for all 3 test ranges

0-150 mg/l range			0-1500 mg/l range			0-15000 mg/l range		
100 mg/l std	Hach®	Reagecon	1000mg/l std	Hach®	Reagecon	10000mg/l std	Hach®	Reagecon
1	105	103	1	998	1007	1	9840	10150
2	104	103	2	995	1009	2	9640	10150
3	104	104	3	994	1010	3	9870	9960
4	104	102	4	1005	1011	4	9800	10060
5	103	102	5	998	1005	5	9875	9984
6	104	104	6	1002	1007	6	9912	10004
7	103	103	7	1001	1010	7	9884	9982
Average	103.86	103.0	Average	999	1008	Average	9832	10041
Std. Deviation	0.69	0.82	Std. Deviation	3.92	2.15	Std. Deviation	91.6	80.4

Table 2 Repeatability results with COD standards for all 3 ranges

Sample	Hach®	Reagecon	Sample	Hach®	Reagecon
1	175	178	21	1352	1347
2	548	550	22	732	740
3	1254	1255	23	681	679
4	658	660	24	1257	1257
5	1154	1149	25	325	330
6	852	850	26	754	759
7	352	350	27	210	207
8	746	749	28	948	950
9	254	250	29	697	700
10	987	989	30	550	555
11	56	54	31	996	1001
12	1420	1418	32	1402	1398
13	1010	1014	33	518	520
14	653	658	34	395	401
15	265	260	35	1457	1460
16	1258	1260	36	1312	1305
17	436	440	37	1103	1098
18	890	887	38	941	935
19	1454	1449	39	497	501
20	952	965	40	1059	1074

Table 3. Analysis of 40 random effluent samples in 0-1500mg/l range

4 Discussion

4.1 Accuracy

The accuracy of both vials was determined using potassium hydrogen phthalate standards. This allows the determination of a direct relationship between the actual value and the measured value, and shows the performance of the reagent throughout the full measuring range.

A plot of the accuracy results for each of the 3 ranges in Tables 1 can be seen in Figures 1-3. The upper and lower ranges shown are the Hach® specification of ±5% or ±7.5ppm (whichever is the greater value) for their COD vials on the DR/2010 photometer. This means that results obtained with a COD standard can be deemed acceptable if they are within 5% or 7.5ppm of the expected value when tested using Hach® vials on a Hach® spectrophotometer.

For each of the three measuring ranges it can be seen that the values obtained for the Reagecon vials closely match the results for the Hach® products, and are well within the acceptable limits

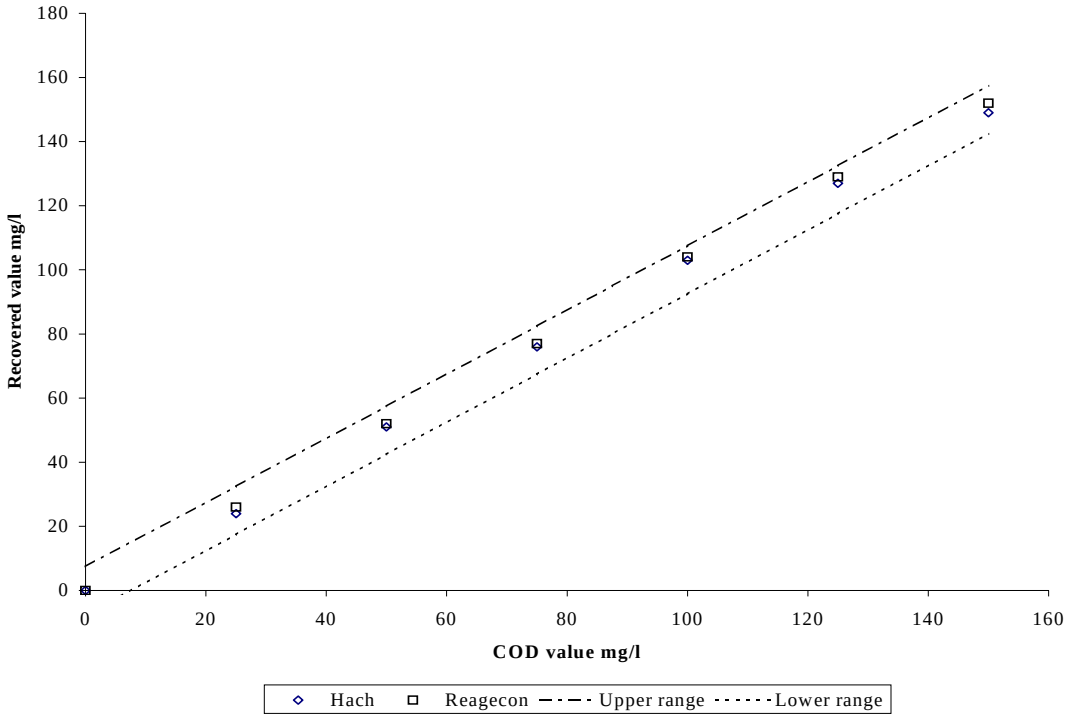

Figure 1. Accuracy testing of 0-150 mg/l COD range

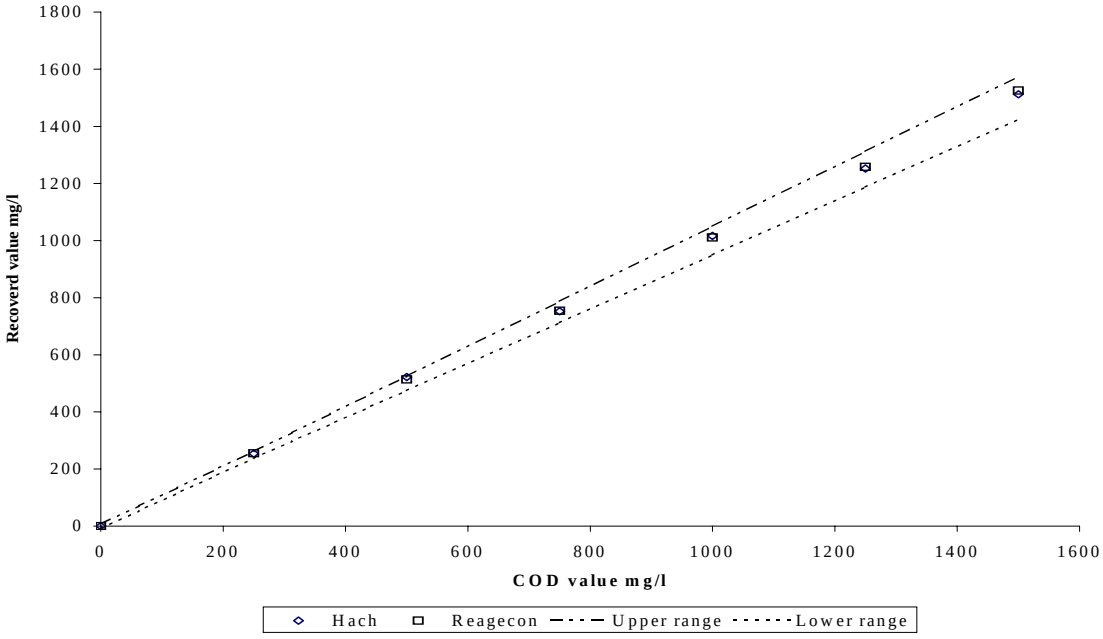

Figure 2. Accuracy results of 0-1500 mg/l COD range

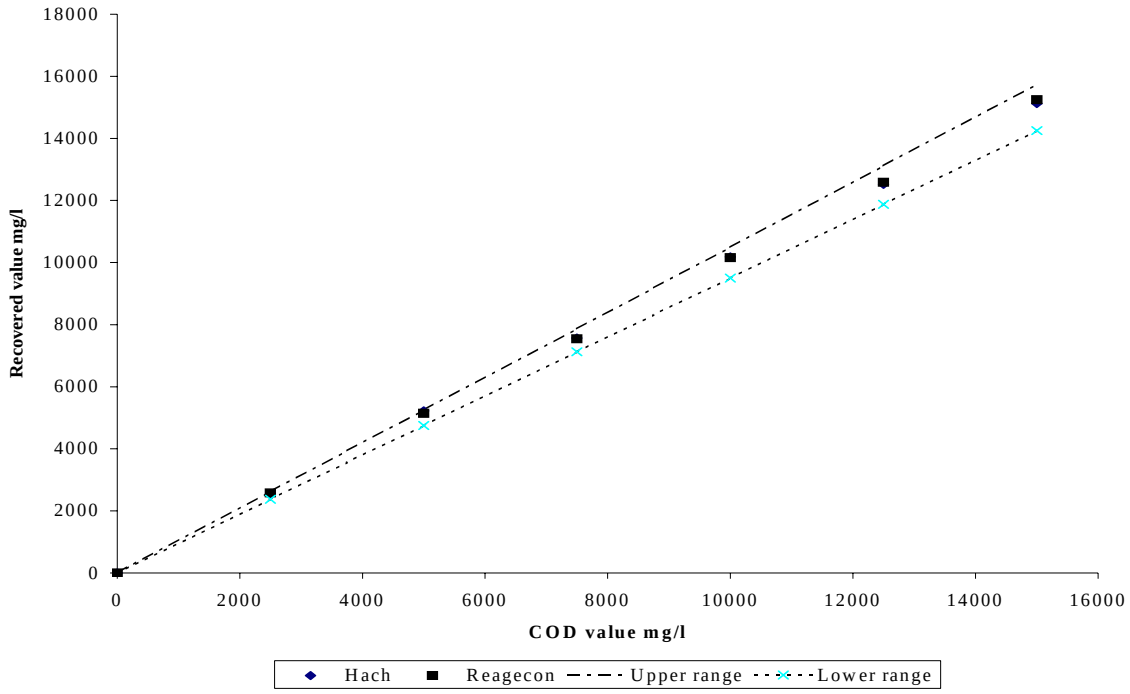

Figure 3. Accuracy results of 0-15000 mg/l COD range

claimed by Hach® for their vials when tested on the DR/2010 photometer. These graphs clearly demonstrate that the Reagecon vials have comparable accuracy to Hach® throughout the full measuring range of each COD vial range. This means that users can be confident in the accuracy of results obtained using the Reagecon vials irrespective of where these results may lie within the respective measuring range.

4.2 Repeatability

The repeatability of the Reagecon vials was determined as outlined in the Hach® DR/2010 manual for the Hach® COD vials[3]. The results in Table 2 were analysed and compared against the quoted Hach® values (see Table 4).

It can be seen that the standard deviation results for the Reagecon COD vials are well within the values quoted by Hach® for their vials[3]. In the case of the 0-1500 mg/l and 0-15000 mg/l COD ranges the Reagecon vials actually show better repeatability than the equivalent Hach® vials in this experiment.

Statistical analysis by the Means Paired Student's t-test was also performed to verify that there is no significant difference between the results obtained. This statistical method is employed when evaluating data where the sample population is small. The results obtained confirmed that there is no significant difference between the results obtained using both sets of vials.

Thus, users of Hach® COD vials with Hach® photometers can use Reagecon COD vials with confidence as the above results clearly demonstrate that there is no significant difference between the Reagecon and Hach® vials in terms of repeatability of measurement.

	Standard Deviation values (mg/l)		
COD vial range mg/l	Reagecon values	Hach® values	Hach® specification[3]
0-150	0.82	0.69	± 2.7
0-1500	2.15	3.92	± 18
0-15000	80.4l	91.6	± 100

Table 4 Repeatability values for COD vial tests.

4.3 Analysis of Effluent samples

To fully compare both reagents it is necessary to determine their performance with effluent samples to accurately reflect the real environmental effects of the sample.
Unlike COD standards, effluent samples may prove more difficult to digest under the stated test conditions. For this reason 40 random samples were tested after being homogenized in a blender.

A graphical representation of the results in Table 7 for effluent samples in the 0-1500 mg/l range can be seen in Figure 4,

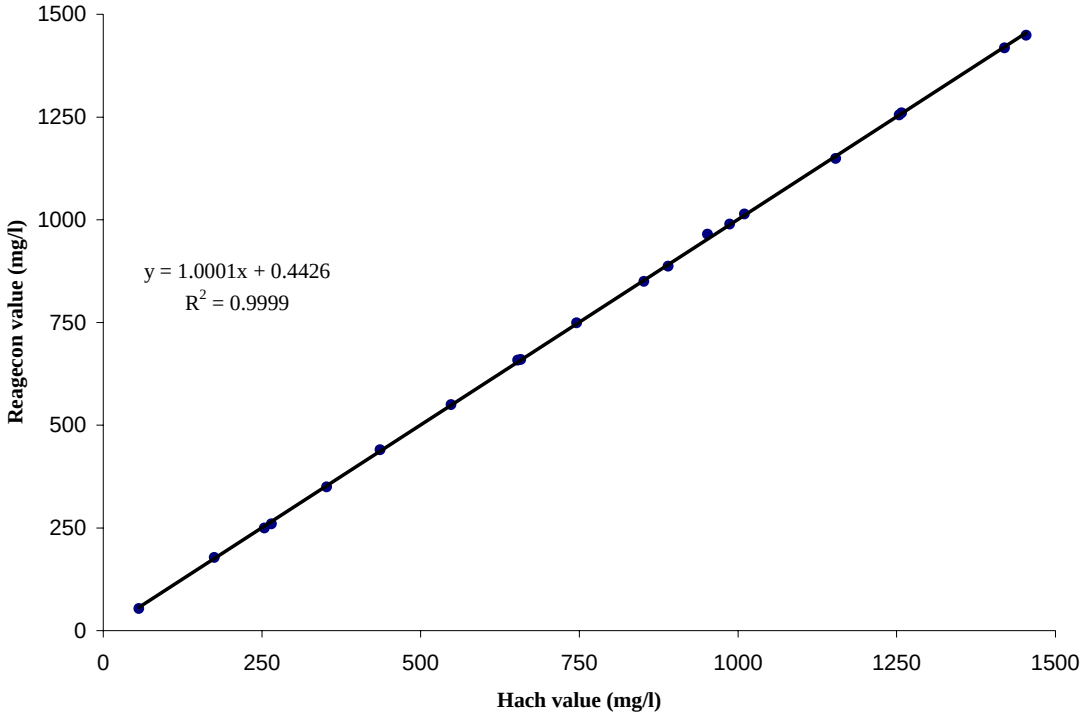

Figure 4. Comparison of effluent samples in 0-1500 mg/l COD range

Regression is a common statistical tool that is used to evaluate the relationship between two or more sets of variables. A plot of the regression line gives an indication of the linear relationship between data sets. In addition, a statistical function called the R^2 value is often quoted as it reflects the extent of the linear relationship between two data sets (a perfect fit being an R^2 value of 1.0). From Figure 4 it can be seen that there is good linearity between the results from both methods throughout the full measuring range. The regression R^2 value of 0.9999 proves this to be the case.

Several effluent samples in the ranges of 0-150 mg/l and 0-15000 mg/l were also tested. Unfortunately the numbers of samples in these ranges was not sufficient to perform an extensive comparison between the results. However, the comparison performed did show that there was no noticeable difference between the results obtained with both brands of COD vials.

From these results it can thus be concluded that the Reagecon COD vials perform in an equivalent manner to the Hach® vials when tested with effluent samples.

Conclusion

As COD is an important environmental parameter the users of COD vials must have the utmost confidence in results obtained using them. The effects of an inaccurate result could be very serious in terms of both environmental impact and breaches of discharge licenses. Thus the user should be cautious and not substitute one brand of reagent for another without having confidence that the new product is equivalent to their existing brand.

This paper clearly shows that the Reagecon range of COD vials are comparable to the Hach® COD vials when compared on the following parameters:

- Accuracy- the Reagecon COD vials have been show n to have comparable accuracy to the Hach® COD vials when tested with COD standards.
- Repeatability - the Reagecon COD vials clearly show repeatability of measurement which is comparable to that quoted by Hach® for their COD vials when tested on the DR/2010 photometer.
- Analysis of effluent samples- the results for the Reagecon COD vials demonstrate a linear relationship to those obtained using the Hach® COD vials

Based on these facts the end-user can confidently substitute the Reagecon COD vials for Hach® COD vials as they have been shown to be comparable for both standards and effluent samples.

6 References

1. American Standards for Testing And Materials. 1995. Standard Test Methods for Chemical Oxygen Demand (dichromate Oxygen Demand) of Water D1252-95, American Soc. Testing & Materials, Philadelphia, Pa.

2. U.S. EPA National Exposure Research Laboratory. 1978. Method 410.4 Chemical Oxygen Demand (Colorimetric, Automated; Manual). Methods for the Chemical Analysis of Water and Wastes (MCAWW) (EPA/600/4-79/020). U.S. EPA National Exposure Research Laboratory (NERL), Cincinnati, Ohio

3. Hach® DR/2010 Instruction Manual. 2000. 7th edition, rev. 2.

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