INSTITUT FRESENIUS

Comparative Investigation of Reagent Systems (Powder Pack / Pillow) for Free and Total Chlorine from Lovibond and Hach*

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* HACH is a registered trademark of the HACH Company, Loveland, Colorado, USA.

INTRODUCTION AND PURPOSE

In solutions which are slightly acidic in nature (with a pH value of 6.2 to 6.5) N.N-diethyl-1.4-phenylendiamine (DPD) is oxidized with free chlorine, with a red coloured product being produced. Combined chlorine also produces this coloured product in the presence of iodide ions, (total chlorine determination).

Chlorine concentration is measured either by visual colour comparison or by photometry (colorimetry).

The purpose of this present investigation was to compare the powder reagents produced by Messrs. HACH with those of Messrs. Tintometer GmbH (the product name being Lovibond®) and to demonstrate that the Lovibond powder packs :

- VARIO CHLORINE FREE - DPD
- VARIO CHLORINE TOTAL - DPD

correspond with HACH "powder pillows" and give the same results when used in association with HACH photometers. The investigation was carried out at the request of Tintometer GmbH.

METHODS, REAGENTS AND EQUIPMENT EMPLOYED

1. Methods

1.1 Measurements according to EN ISO 7393 :

The measurements were carried out in accordance with EN ISO 7393-2 [1]. In deviation from this document, all diluted standards were brought to 100 ml by adding 0.3 ml of a 10% solution of potassium iodide in water[1].

1.2 Measurements obtained with powder reagents :

Measurements were carried out in accordance with the manufacturers' instructions.

1.3 Measurements obtained with potassium permanganate :

Measurements were carried out in accordance with EN ISO 7393-2. The potassium iodate standard was replaced by potassium permanganate standards. Here again, all diluted standards were brought to 100 ml by adding 0.3 ml of a 10% solution of potassium iodide in water[1].

[1]The concentration of potassium iodide was inadequate, particularly for very dilute standard solutions .

2. Reagents

2.1 Potassium iodate standard solution :

This solution was prepared by weighing 1.006 g of potassium iodate (from Merck) into one litre of water.

2.2 Potassium permanganate standard solution :

This solution was produced by diluting a standard solution (Titrisol from Merck).

2.3 DPD was obtained from Aldrich

2.4 All other reagents were obtained from Merck.

2.5 Powder reagents :

2.5.1 Free chlorine

	Batch Nos.
Lovibond	204B
Hach	A2256

2.5.2 Total chlorine

Lovibond	203A
Hach	B2242

2.6 Distilled water was used, without further treatment, to produce the solutions.

3. Equipment

1. Spectrophotometer :

   The Spectrophotometer used was a "PERKIN-ELMER, Lambda 2, UV/VIS", with a wavelength of 510 nm, using 1 cm quartz cuvettes.

2. Hach photometer, "DR/890 Colorimeter", with Hach round cuvettes.

I Calibration with potassium iodate

Calibration checks were carried out with powder reagents from Lovibond and Hach for free and total chlorine. The standards used were potassium iodate solutions according to EN ISO 7393-2: 2000. Measurements were made with a spectrophotometer from Perkin Elmer (1 cm quartz cuvette). For comparison, calibration was also carried out using the method set out in EN ISO 7393-2: 2000.

I.1 Measurement results obtained with Lovibond reagents and their statistical evaluation

Table 1 : Calibration with Lovibond reagents

Photometer used	Spectrophotometer		
Potassium iodate	EN ISO 7393-2	Lovibond, free chlorine	Lovibond, total chlorine
mg/l	Extinction		
0.00	0.000	0.004	0.007
0.025	0.006	0.010	0.012
0.05	0.012	0.016	0.020
0.10	0.025	0.032	0.034
0.15	0.039	0.046	0.051
0.20	0.050	0.061	0.066
0.25	0.063	0.077	0.079
0.30	0.076	0.091	0.095
0.35	0.089	0.105	0.109
0.40	0.101	0.117	0.124
0.45	0.115	0.133	0.137
0.50	0.127	0.151	0.152
0.75	0.187	0.219	0.226
1.00	0.246	0.287	0.301
1.25	0.302	0.367	0.366
1.50	0.359	0.429	0.435
1.75	-	0.497	0.490
2.00	0.452	0.548	0.564

Quadratic Regression			
n (c)	-0.020	-0.014	-0.014
m (b)	0.268	0.305	0.306
b (a)	-0.002	0.001	0.004
Sy	0.001	0.004	0.003
Sxo	0.006	0.012	0.010
Vxo (%)	1.1	2.0	1.6

Linear Regression			
Intercept	0.006	0.006	0.010
Slope	0.232	0.279	0.280
Sy	0.007	0.006	0.005
Sxo	0.029	0.021	0.019
Vxo (%)	5.3	3.3	3.0

Significant best fit	quadratic	quadratic	quadratic

Limits of detection & quantitation (calculated from concentrations of up to 0.4 mg/l)			
Detection	0.007	0.01	0.01
Quantitation	0.023	0.04	0.04
VB (lower limit)	0.02	0.03	0.03
VB (upper limit)	0.04	0.08	0.07

I.2 Measurement results obtained with Hach reagents and their statistical evaluation

Table 2 : Calibration with Hach reagents

Photometer used	Spectrophotometer	
Potassium iodate	Hach, free chlorine	Hach, total chlorine
mg/l	Extinction	
0.00	0.001	0.003
0.025	0.006	0.010
0.05	0.014	0.016
0.10	0.029	0.032
0.15	0.044	0.049
0.20	0.059	0.064
0.25	0.074	0.079
0.30	0.090	0.094
0.35	0.105	0.109
0.40	0.119	0.124
0.45	0.131	0.140
0.50	0.147	0.153
0.75	0.219	0.231
1.00	0.292	0.300
1.25	0.360	0.372
1.50	0.424	0.440
1.75	0.496	0.508
2.00	0.554	0.578

Quadratic Regression		
n (c)	-0.013	-0.011
m (b)	0.304	0.310
b (a)	-0.0010	0.0021
Sy	0.002	0.001
Sxo	0.006	0.004
Vxo (%)	1.0	0.7

Linear Regression		
Intercept	0.004	0.007
Slope	0.281	0.289
Sy	0.004	0.0039
Sxo	0.016	0.014
Vxo (%)	2.6	2.2

significant best fit	quadratic	quadratic

Limits of detection & quantitation (calculated from concentrations of up to 0.4 mg/l)		
Detection	0.01	0.01
Quantitation	0.03	0.03
VB (lower limit)	0.02	0.02
VB (upper limit)	0.05	0.05

Evaluation

1. Regression :

During all calibrations, the quadratic regression provided the significant best fit.

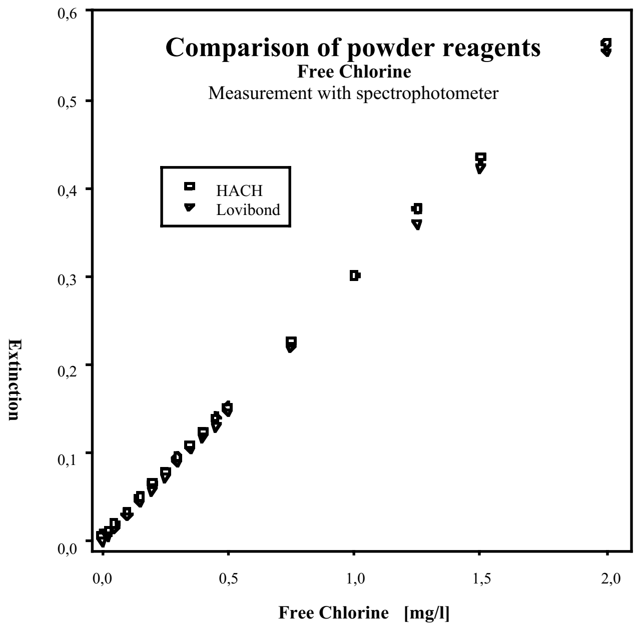
The spread of figures around the calculated curves (quadratic regression) is described by the standard deviations V_{X0} associated with the procedure [3]. These are low and lie between 0.7% and 2.0%.

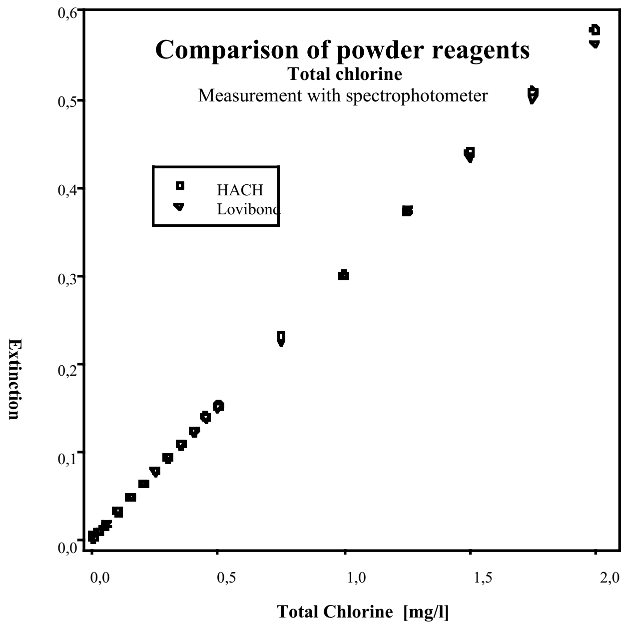
2. Limits of detection and quantitation :

The limits of detection and quantitation were calculated in accordance with DIN 32645: 1994 [2]. Only measured values as far as 0.40 mg/l were taken for calculation purposes, in order to ensure linearity and variance homogeneity. The quantitation limit (LOQ) is between 0.023 mg/l and 0.04 mg/l. No significant differences were observed between the data provided in EN ISO 7393 and figures obtained for the two powder reagents, since confidence intervals is overlap.

I.3 Graphical presentation of results : comparison of Lovibond and Hach reagents

The following graphs show the results of measurements obtained by spectrophotometer for free chlorine and for total chlorine.





II Precision Measurements

Table 3 : Mean value t test (powder reagents for free chlorine)
Measurement using a spectrophotometer

Reagent	EN ISO 7393-2	Lovibond	Hach	Lovibond	Hach	Lovibond	Hach	EN ISO 7393-2	Lovibond	Hach
Concentr.	0.25 mg/l			1.00 mg/l		2.00 mg/l		1.50 mg/l		
	0.063	0.071	0.072	0.288	0.294	0.560	0.565	0.354	0.439	0.435
	0.064	0.071	0.075	0.288	0.291	0.561	0.560	0.358	0.437	0.432
	0.064	0.074	0.074	0.288	0.296	0.565	0.571	0.357	0.435	0.432
	0.064	0.073	0.074					0.357	0.434	0.432
	0.064	0.073	0.074					0.355	0.433	0.429
	0.063	0.073	0.075					0.354	0.436	0.432
	0.064	0.071	0.074					0.354	0.432	0.429
	0.063	0.071	0.073					0.353	0.432	0.429
	0.064	0.071	0.073					0.356	0.433	0.432
	0.063	0.071	0.073					0.358	0.433	0.435
Mean	**0.064**	**0.072**	**0.074**	**0.288**	**0.294**	**0.562**	**0.565**	**0.356**	**0.434**	**0.432**
Std. dev.	**0.0005**	**0.0012**	**0.0009**	**0.0000**	**0.0025**	**0.0026**	**0.0055**	**0.0018**	**0.0023**	**0.0023**
CV. %	0.81	1.67	1.29	0.00	0.86	0.47	0.97	0.52	0.53	0.52
Variance* 10^{-7}	0.3	1,4	0.9	0	6,3	7,0	30	3,4	5,4	5,1
Number	10	10	10	3	3	3	3	10	10	10

Variance F Test										
F(EN-Lov.)	5.37							1.59		
assessment	Significant difference							No sign. difference		
F(EN-Hach)			3.37							1.48
assessment	No sig.		difference					No sig.		difference
F(Lov.-Hach)		1.59							1.08	
assessment		No sign. difference							No sign. difference	
F(99%;*f*1,*f*2)	5.35							5.35		

Mean value t Test										
PG		3.73		3.90		0.95			2.53	
T (99%)		2.88		4.60		4.60			2.88	
assessment		Significant difference		No sign. difference		No sign. difference			No sign. difference	

Assessment of the Variance F Test

The results of the precision measurements were used to check whether there was any comparison between the distribution, or "scatter" of measured values for extinction via the F test. In each case, the values obtained using the method described in EN ISO 7393 were compared with the values obtained by Lovibond and Hach methods. The F test was not carried out for concentrations of 1 mg/l and 2 mg/l, because the number of measurements (three in each case) was too small and the test would therefore be too insensitive.

The variation coefficients for all three procedures were extremely low, between 0.81% and 1.67% for the 0.25 mg/l standard, or between 0.52% and 0.53% for the 1.50 mg/l standard. No statistically significant differences between the different methods were noted for any of the comparisons for the 1.50 mg/l standard, or for two of the three comparisons for the 0.25 mg/l standard. Only for one of the comparisons using 0.25 mg/l was there a significant difference in distribution or "scatter" between EN ISO 7393 and Lovibond methods. However, the difference was extremely small (F = 5.37; test figure = 5.35). The variation coefficient (CV) using the EN ISO 7393 method was 0.81%. The figure for the Hach method was 1.29%, with 1.67% for the Lovibond method. These slight differences are of no practical significance[1].

Assessment of the mean value t test :

The results of extinction measurements according to EN ISO 7393 cannot be compared with those from Lovibond or Hach, because other concentration conditions apply which must result in different extinctions.
A statistically significant difference was noted between the mean extinction figures for Lovibond and Hach for the samples having a concentration of 0.25 mg/l of free chlorine. However, the difference is very small (Lovibond = 0.072; Hach = 0.074) and therefore of no practical significance. No statistically significant differences were noted at any of the other concentrations.

[1] This becomes also apparent if the level of measurement accuracy is calculated from the measured distribution : EN ISO 7393 (0.25 ± 0.004); Hach (0.25 ± 0.006) and Lovibond (0.25 ± 0.008) mg/l (VB 95% or k = 2).

III Calibration with potassium permanganate

III.1 Comparison of calibrations with potassium iodate and potassium permanganate in line with EN ISO 7393-2: 2000

Measurements with potassium iodate were carried out in accordance with EN ISO 7393-2: 2000. Thereafter, appropriate standards were used with potassium permanganate. The results are shown in Table 4 :

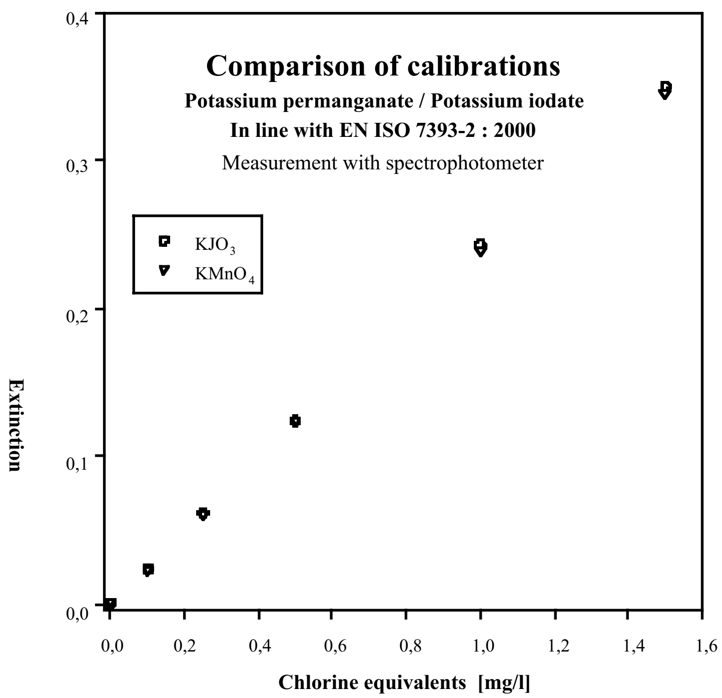
Table 4 : Results of measurements with potassium iodate and potassium permanganate in line with EN ISO 7393-2: 2000

Standard	KIO_3	$KMnO_4$
mg/l	Extinction	
0,00	0,001	0,001
0,10	0,024	0,024
0,25	0,062	0,061
0,50	0,124	0,124
1,00	0,243	0,240
1,50	0,350	0,346

Assessment :

The regression calculation results in an intercept of 0.0003 and a slope of 0.988. If the measured extinctions were fully in line, the figures would be 0 and 1. The calibrations with potassium iodate and with potassium permanganate are thus similar for all practical purposes.

Results in graphical form



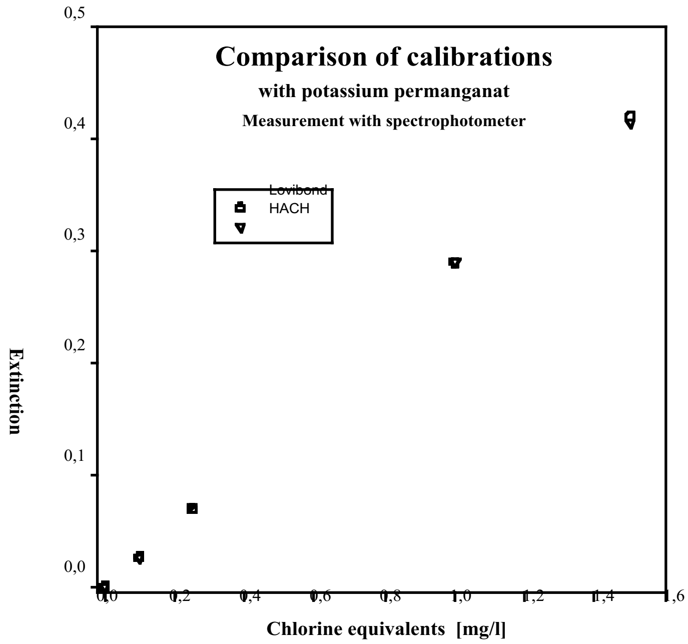
III.2 Comparison of calibrations with potassium permanganate, using reagents for free chlorine from Lovibond and from Hach.

Extinctions for free chlorine were determined, using potassium permanganate standards.

Table 5 : Calibration with potassium permanganate

Standard	Free Chlorine	
$KMnO_4$	Lovibond	Hach
mg/l	Extinction	
0.00	0.001	0.001
0.10	0.027	0.026
0.25	0.070	0.073
1.00	0.290	0.290
1.50	0.420	0.415

Results in graph form :



Assessment :

The regression calculation results in an intercept of 0.0011 and a slope of 0.990. If the measured extinctions were fully in line, the figures would be 0 and 1. For all practical purposes, therefore, the calibrations with potassium permanganate are similar for both powder reagents.

Bibliography :

[1] EN ISO 7393-2 : 2000 : "Determination of Free Chlorine and Total Chlorine"; 2000-04
[2] DIN 32 645 : "Demonstration, Logging & Determination Limits"; May 1986
[3] E DIN 38402-71 : "Equivalence of two Analysis Procedures, based on a Comparison of Analysis results and their Statistical Evaluation; Procedure for Quantitative Characteristics with a Continuous Value Spectrum (A 71)"; 2001-10

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Appendix

Measurements with a Hach photometer, to check the inter-changeability of Lovibond and Hach reagents

Assessment :

In practice, both powder reagents tested produced comparable results when used with the Hach photometer. With totally compliant results, the measurement points would lie exactly on the dashed line.

Results in graphical form :