

**DEVELOPMENT AND ACREDITATION OF
PROFICIENCY TESTING SCHEMES BASED ON
FLOW AND "IN SITU" PARAMETERS IN
DIFFERENT MATRICES**

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Istanbul (Turkey), October 2011

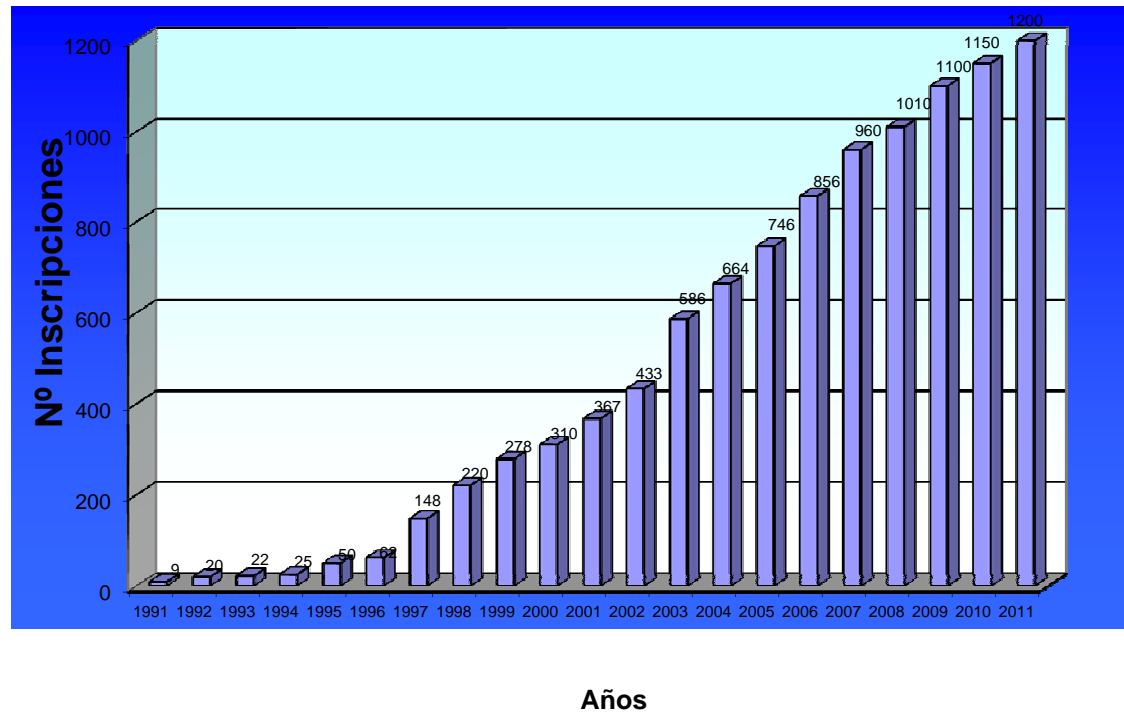



ielab is a company that provides services for the quality control in laboratories such:

- proficiency testing schemes
- certified reference materials

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1. More than 1200 participants from 33 countries
2. Certified according to ISO 9001:2008
3. Accredited by ENAC (Spanish accreditation body) according to ISO 1
4. 24 schemes



- Drinking waters A
 - Drinking waters B
 - Drinking waters C
 - Microbiology in drinking waters
 - Directive 2000/60/EC (list of priority substances)
 - Raw waters
 - DRO+GRO+Hydrocarbons
 - Microbiology in continental waters
 - Waste waters
 - Regenerated waters
 - Solids in waste waters
- 
- Microbiology in waste waters
 - Sea waters
 - Atmospheric pollution
 - Organic compounds in solids
 - Sludges
 - Microbiology in sludges
 - Residues
 - Soils
 - Legionella – culture
 - Legionella PCR
 - Biota
 - PCBs in dielectric oils
 - ***In situ* analysis**

Requirements for laboratories and inspection bodies

- Technical capabilities
 - Reproducibility of samples
- * Internal Quality Control (17025 & 17020)
 - * Intercomparations (PTS)



In situ PTS

DEVELOPMENT OF PTS

- Different locations
- Different parameters (flow, pH, T^a , conductivity & dissolved oxygen)
- Different matrices (waste water, sea water & raw water)



DEVELOPMENT OF PTS



Alicante & Cadiz:
three matrices
Madrid: two matrices

1. Previous visit

- Look for the place before (conditions, way of arriving, enough space, ...)
- OK/NOT OK for the PTS
- Primary study of homogeneity and stability

2. Participants

- Minimum of 10 and maximum of 20

3. Instructions

- Place, matrices, equipment, transport to location

4. Previous meeting

- Explain all details according to the test
- Solve doubts of participants

5. Transfer to locations

- Our measurements to check the conditions
- Verify OK/NOT OK
- Measurements from the participants (their own equipments)

- Eurachem-Citac 2007 Guide (measurement uncertainty arising from sampling)
- IUPAC Technical Report (The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories)
- **ILAC-G13:08** "Guidelines for the Requirements for the Competence of Providers of PTS"

HOMOGENEITY AND STABILITY (by IUPAC)

- 10 samples in 2 locations
- Method with a repetibility less than $0.5 \sigma_p$
- Analysis of two replicates in each one of the 10 samples
- Calculus of the variability between samples (S_{am})
- Calculus of the critic value:

$$c = F_1 \sigma_{all}^2 + F_2 S_{an}^2$$

$$\sigma_{all}^2 = (0.3 \sigma_p)^2$$

Homogeneous if $S_{am} < C$

Results of homogeneity and stability (1)

HOMOGENEITY "IN SITU" 2011 (WASTE WATER)							
TIME	PLACE	REPLICATE	pH	CONDUCTIVITY	OXYGEN	TEMPERATURE	FLOW
1	1	1	7.32	2550	1.91	24.64	75.6
2	1	1	7.29	2560	1.82	24.66	76.8
3	1	1	7.29	2560	1.82	24.65	74.1
4	1	1	7.32	2560	1.89	24.64	74.5
5	1	1	7.33	2560	1.90	24.70	76.8
6	1	1	7.32	2550	1.87	24.71	77.6
7	1	1	7.32	2550	1.91	24.70	74.9
8	1	1	7.33	2550	1.92	24.78	72.6
9	1	1	7.31	2540	1.87	24.63	77.2
10	1	1	7.31	2540	1.81	24.60	77.9
1	2	1	7.27	2530	1.85	24.60	73.6
2	2	1	7.35	2540	1.88	24.65	76.1
3	2	1	7.39	2530	1.86	24.66	72.9
4	2	1	7.28	2540	1.95	24.72	73.5
5	2	1	7.36	2540	1.94	24.75	72.1
6	2	1	7.23	2550	1.91	24.61	77.3
7	2	1	7.23	2550	1.82	24.86	73.9
8	2	1	7.30	2530	1.95	24.60	74.6
9	2	1	7.24	2540	1.88	24.71	72.2
10	2	1	7.37	2540	1.87	24.86	75.5
1	1	2	7.31	2540	1.90	24.66	77.9
2	1	2	7.31	2540	1.81	24.65	77.2
3	1	2	7.33	2550	1.82	24.64	72.6
4	1	2	7.32	2550	1.87	24.65	74.9
5	1	2	7.32	2550	1.87	24.70	77.6
6	1	2	7.33	2560	1.88	24.71	76.8
7	1	2	7.32	2560	1.89	24.71	74.5
8	1	2	7.29	2560	1.91	24.66	74.1
9	1	2	7.25	2560	1.85	24.69	76.8
10	1	2	7.32	2560	1.89	24.62	75.6
1	2	2	7.36	2520	1.71	24.70	75.5
2	2	2	7.29	2540	1.85	24.63	72.2
3	2	2	7.24	2540	1.88	24.71	74.6
4	2	2	7.30	2530	1.85	24.69	73.9
5	2	2	7.23	2550	1.79	24.72	77.3
6	2	2	7.23	2550	1.90	24.70	72.1
7	2	2	7.26	2540	1.94	24.69	73.5
8	2	2	7.28	2540	1.85	24.73	73.0
9	2	2	7.39	2540	1.88	24.71	76.2
10	2	2	7.27	2520	1.92	24.62	73.6
MEAN			7.30	2545	1.87	24.68	75.0
UNITS			UpH	µS/cm	mg/L	°C	m3/h
n			40	40	40	40	40
S _{sum} ²			0	0	0	0	0.619
CRITIC VALUE			0.009	18651	0.015	0.046	42.447
S _{sum} ² < CRITIC ??			ACCEPTABLE	ACCEPTABLE	ACCEPTABLE	ACCEPTABLE	ACCEPTABLE

Results of homogeneity and stability (2)

Use to calculate the σ_p

WASTE WATER ASSIGNED DEVIATION (TANK)				
PARAMETER	MEDIA	ASSIGNED DEVIATION	UNITS	METHOD
pH	7.30	0.20	UpH	EPA 9040B
CONDUCTIVITY	2545	331	$\mu\text{S/cm}$	ASTM D1125A
DISSOLVED OXYGEN	1.87	0.272	mg/L	HORWITZ MODIFIED BY THOMPSON
TEMPERATURE	24.7	0.50	$^{\circ}\text{C}$	USGS (COLLECTION OF WATER-QUALITY)
FLOW	75	15	m ³ /h	ISO 748:2007

RAW WATER ASSIGNED DEVIATION (RAW WATER CHANNEL)				
PARAMETER	MEDIA	ASSIGNED DEVIATION	UNITS	METHOD
pH	8.24	0.20	UpH	EPA 9040B
CONDUCTIVITY	832	108	$\mu\text{S/cm}$	ASTM D1125A
DISSOLVED OXYGEN	10.01	1.132	mg/L	HORWITZ MODIFIED BY THOMPSON
TEMPERATURE	20.9	0.50	$^{\circ}\text{C}$	USGS (COLLECTION OF WATER-QUALITY)

SEA WATER ASSIGNED DEVIATION (BEACH)				
PARAMETER	MEDIA	ASSIGNED DEVIATION	UNITS	METHOD
pH	8.34	0.20	UpH	EPA 9040B
CONDUCTIVITY	50960	6625	$\mu\text{S/cm}$	ASTM D1125A
DISSOLVED OXYGEN	8.69	1.004	mg/L	HORWITZ MODIFIED BY THOMPSON
TEMPERATURE	24.3	0.50	$^{\circ}\text{C}$	USGS (COLLECTION OF WATER-QUALITY)

HOMOGENEITY (by EURACHEM)

- 4 samples at random (time and space)
- Method with a repetibility less than $0.5 \sigma_p$
- Calculus of the total variance (S_{total})

$$S_{\text{TOTAL}} = \sqrt{s_{\text{time}}^2 + s_{\text{space}}^2 + s_{\text{analysis}}^2}$$

Homogeneous if $S_{\text{total}} < 0.3 p$

Results of homogeneity - Eurachem

TIEMPO	LUGAR 1 REP 1	LUGAR 1 REP 2	LUGAR 2 REP 1	LUGAR 2 REP 2	Tiempo 3 analisis 1	Tiempo 3 analisis 2							
1	24.64	24.66	24.60	24.70									
2	24.66	24.65	24.65	24.63									
3	24.65	24.64	24.66	24.71									
4	24.64	24.65	24.72	24.69									
5	24.70	24.70	24.75	24.72									
6	24.71	24.71	24.61	24.70									
7	24.70	24.71	24.86	24.69									
8	24.78	24.66	24.60	24.73									
9	24.63	24.69	24.71	24.71									
10	24.60	24.62	24.86	24.62									
Nº Lugares	2												
Frecuencias tiempo	10												
Nº Análisis	2												
	media Tiempo 1	media Tiempo 2	media Tiempo 3	desviación analisis entre tiempo1	desviación analisis entre tiempo 2	desviación analisis entre tiempo 3	desviacion de las medias	medias	desviación medias al cuadrado	Desviaciones al cuadrado			
1	24.65	24.65	#iDIV/0!	0.0141	0.0707	#iDIV/0!	0.0000	24.65	0.0000	0.0002	0.0050	#iDIV/0!	
2	24.66	24.64	#iDIV/0!	0.0071	0.0141	#iDIV/0!	0.0106	24.65	0.0001	0.0001	0.0002	#iDIV/0!	
3	24.65	24.69	#iDIV/0!	0.0071	0.0354	#iDIV/0!	0.0283	24.67	0.0008	0.0000	0.0013	#iDIV/0!	
4	24.65	24.71	#iDIV/0!	0.0071	0.0212	#iDIV/0!	0.0424	24.68	0.0018	0.0000	0.0004	#iDIV/0!	
5	24.70	24.74	#iDIV/0!	0.0000	0.0212	#iDIV/0!	0.0247	24.72	0.0006	0.0000	0.0005	#iDIV/0!	
6	24.71	24.66	#iDIV/0!	0.0000	0.0636	#iDIV/0!	0.0389	24.68	0.0015	0.0000	0.0040	#iDIV/0!	
7	24.71	24.78	#iDIV/0!	0.0071	0.1202	#iDIV/0!	0.0495	24.74	0.0025	0.0001	0.0144	#iDIV/0!	
8	24.72	24.67	#iDIV/0!	0.0849	0.0919	#iDIV/0!	0.0389	24.69	0.0015	0.0072	0.0084	#iDIV/0!	
9	24.66	24.71	#iDIV/0!	0.0424	0.0000	#iDIV/0!	0.0354	24.69	0.0013	0.0018	0.0000	#iDIV/0!	
10	24.61	24.74	#iDIV/0!	0.0141	0.1697	#iDIV/0!	0.0919	24.68	0.0085	0.0002	0.0288	#iDIV/0!	
									0.0185	0.0096	0.0631	#iDIV/0!	0.0727
								SC muestras	0.33300			SC analisis	0.0727
								S medias	0.02855				
								S Tiempo	0.01630				
Media cuadratica Analisis:	0.00363												
Media cuadratica Tiempo:	0.01630												
Media cuadratica Lugar	0.01850												
Desviacion analisis	0.06029												
Desviación Lugar	0.01049												
Desviación Tiempo	0.07958												
Desviacion total:	0.10039												

Results of homogeneity - Eurachem

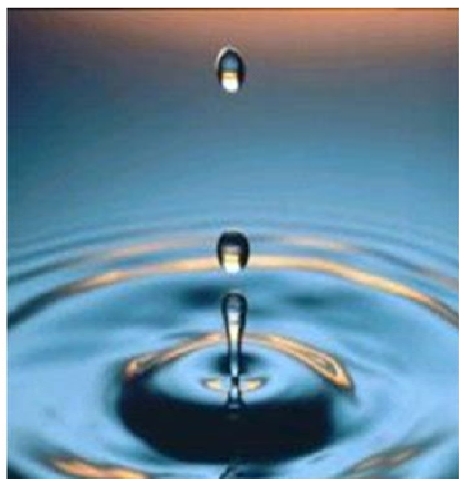
WASTE WATER				
PARAMETER	TOTAL S	ASSIGNED S	0.3*ASSIGNED S	COMPLIANCE
pH	0.057	0.20	0.060	OK
CONDUCTIVITY	18.097	331	99	OK
OXYGEN	0.081	0.272	0.082	OK
TEMPERATURE	0.100	0.50	0.150	OK
FLOW	3.348	15.21	4.563	OK

RAW WATER				
PARAMETER	TOTAL S	ASSIGNED S	0.3*ASSIGNED S	COMPLIANCE
pH	0.039	0.20	0.060	OK
CONDUCTIVITY	2.850	108	32.400	OK
OXYGEN	0.300	1.130	0.339	OK
TEMPERATURE	0.115	0.50	0.150	OK

SEA WATER				
PARAMETER	TOTAL S	ASSIGNED S	0.3*ASSIGNED S	COMPLIANCE
pH	0.051	0.20	0.060	OK
CONDUCTIVITY	96.820	6625	1987.500	OK
OXYGEN	0.297	1.004	0.301	OK
TEMPERATURE	0.140	0.50	0.150	OK

- Results must be collected at the end of the day after the PTS
- It would be accepted between one and three replicates (we will calculate the mean value)
- Outliers must be eliminated
- Calculus of the robust mean and robust standard deviation
- Calculus of the uncertainty $\left(\frac{\sigma_p}{\sqrt{n}} \right)$

- Target of the study
- Parameters of the PTS
- Main characteristics of the different locations
- Development of the PTS
- Information about homogeneity and stability (reference documents and values)
- Statistical treatment of the results



INFORME SOBRE EL EJERCICIO DE INTERCOMPARACION "IN SITU"



FECHA: 27 DE OCTUBRE DE 2010

LUGAR: CADIZ

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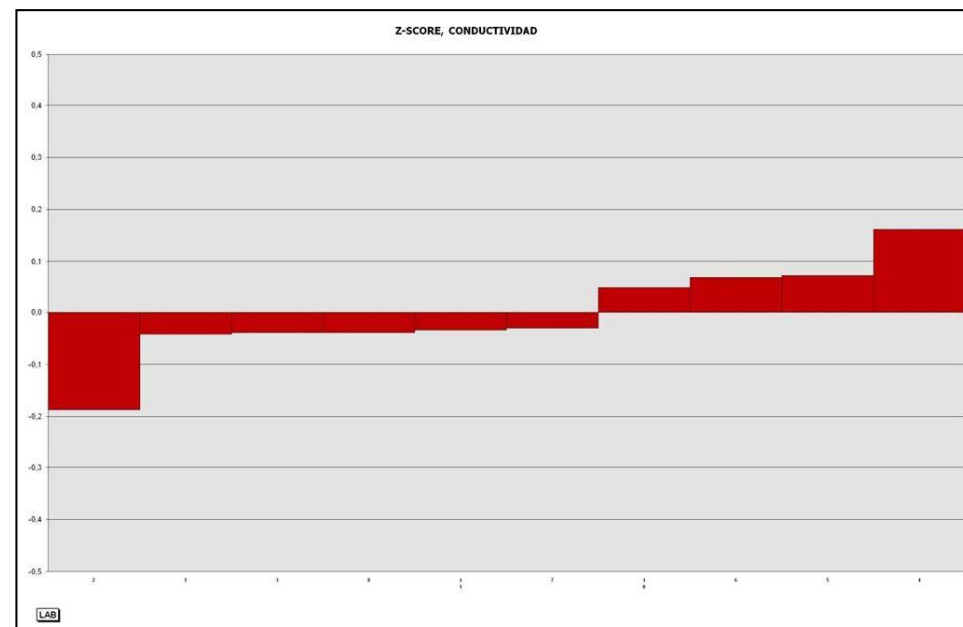
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LAB	X ₁	X ₂	X ₃	MEDIA	SD	INTERVALO		Z-SCORE
1	3018	3017	3012	3016	3,21	3019	3012	-0,04
2	2970	2970	2940	2960	17,32	2977	2943	-0,19
3	3020	3010	3020	3017	5,77	3022	3011	-0,04
4	3093,9	3093,9	3093,9	3094	0,00	3094	3094	0,16
5	3051	3062	3064	3059	7,00	3066	3052	0,07
6	3058	3058	3057	3058	0,58	3058	3057	0,07
7	3020	3020	3020	3020	0,00	3020	3020	-0,03
8	3020	3020	3010	3017	5,77	3022	3011	-0,04
9	755	754	753	754	1,00	755	753	-5,93
10	3050	3050	3050	3050	0,00	3050	3050	0,05
11	3030	3004	3022	3019	13,32	3032	3005	-0,03

N
10

Valor consenso	3032
Desvest. asignada	384
Desvest. robusta	31
incertidumbre	10

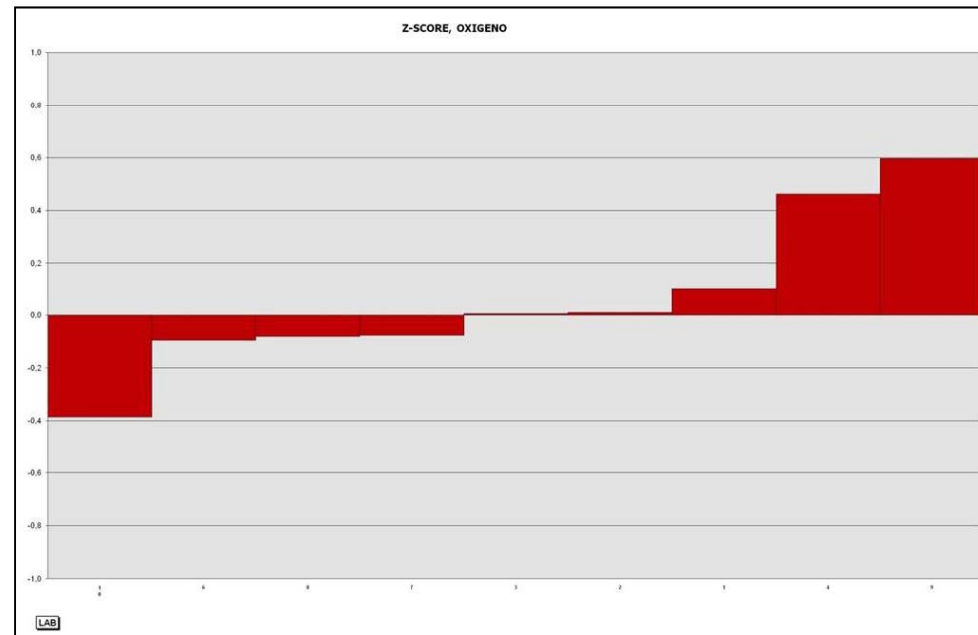
conductivity in
waste water



LAB	X ₁	X ₂	X ₃	MEDIA	SD	INTERVALO		Z-SCORE
1	7,9	8,0	8,0	7,97	0,06	8,02	7,91	0,10
2	7,87	7,93	7,85	7,88	0,04	7,92	7,84	0,01
3	7,87	7,92	7,85	7,88	0,04	7,92	7,84	0,01
4	8,32	8,31	8,27	8,30	0,03	8,33	8,27	0,46
5	-	-	-					
6	7,78	7,80	7,78	7,79	0,01	7,80	7,78	-0,10
7	7,88	7,71	7,82	7,80	0,09	7,89	7,72	-0,08
8	7,78	7,82	7,80	7,80	0,02	7,82	7,78	-0,08
9	8,43	8,41	8,43	8,42	0,01	8,43	8,41	0,60
10	7,53	7,53	7,50	7,52	0,02	7,54	7,50	-0,39
11	-	-	-					

N
8

Valor consenso	7,87
Desvest. asignada	0,92
Desvest. robusta	0,14
incertidumbre	0,05



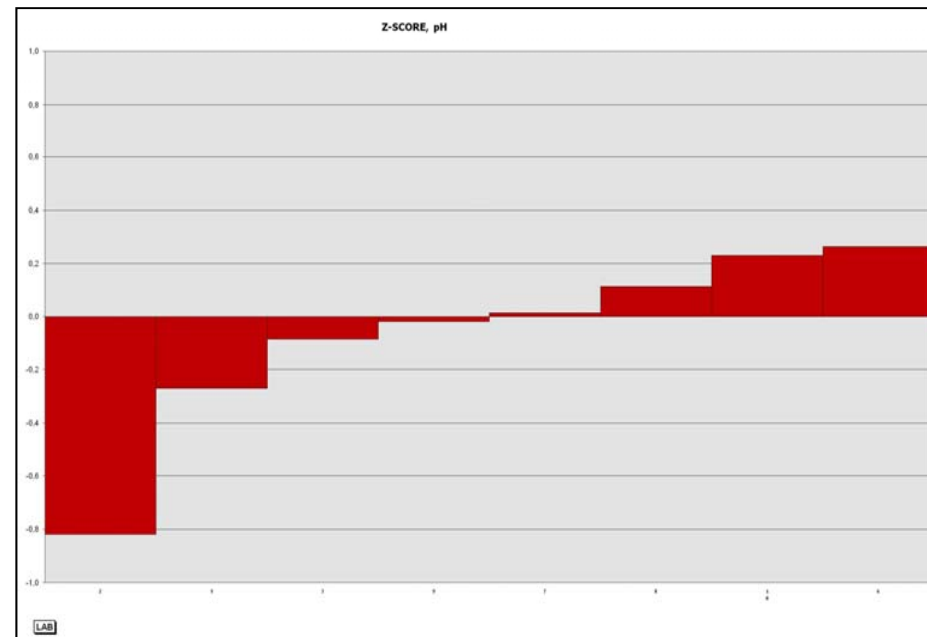
dissolved oxygen in raw water

FINAL REPORT

LAB	X ₁	X ₂	X ₃	MEDIA	SD	INTERVALO		Z-SCORE
1	8,3	8,3	8,3	8,30	0,00	8,30	8,30	-0,27
2	8,18	8,21	8,18	8,19	0,02	8,21	8,17	-0,82
3	8,35	8,33	8,33	8,34	0,01	8,35	8,33	-0,09
4	-	-	-					
5	-	-	-					
6	8,40	8,41	8,41	8,41	0,01	8,41	8,40	0,26
7	8,36	8,36	8,35	8,36	0,01	8,36	8,35	0,01
8	8,38	8,40	8,35	8,38	0,03	8,40	8,35	0,11
9	8,35	8,35	8,35	8,35	0,00	8,35	8,35	-0,02
10	8,39	8,39	8,42	8,40	0,02	8,42	8,38	0,23
11	-	-	-					

N
8

Valor consenso	8,35
Desvest. asignada	0,20
Desvest. robusta	0,05
incertidumbre	0,02



pH in sea water

- PTS: 6 in two years (3 in 2010 and 3 in 2011)
- Participants: nearly 35 per year
- During two years, we have done 3 in 2010 and 3 in 2011 (two of them will be this month)
- Since 2010, this PTS has been accredited by ENAC



**THANK YOU VERY MUCH
FOR YOUR ATTENTION**

