Comparison of Modified USGS Ammonia Method to modified EPA 350.1

Parallel study of tartrate/citrate buffered segmented flow versus EDTA buffered flow injection

	New Method	Current Method	EPA Method
1. *Title and Description* *List & attach SOPs for new and current.*	Lachat 31-107-06-1-b Adaption of EPA 350.1	Skalar 156-350.1 032593 Adaption of USGS I-2523-85 DEQ has current SOP on file.	EPA 350.1
2. *Procedural differences*	Flow injection technology using same reagents as EPA 350.1	Segmented flow and uses different buffer and hypochlorite concentration compared to EPA 350.1	Segmented flow method
3. *Concentration Range of calibration standards*	0.010 – 0.400 mg/L 6 point calibration	0.02 – 0.100 mg/L 5 point calibration	0.02 – 2.00 mg/L Uses 3 point calibration.
4. *Initial Precision & Recovery*	100+/- 10% allowed (initially 99.3%)	100+/- 10% allowed (103% November 2006)(Currently 98.1%)	100 +/- 10% allowed
5. *Calibration Verification*	Initially and then every 10 samples with recovery 100 +/- 10%	Initially and then every 10 samples with recovery 100 +/- 10%	Every 10 samples with recovery 100 +/- 10%
6. *Method Detection Limit*	.003 mg/L	.004 mg/L	Does not quote one, only the range .02-2.00 mg/L is quoted
7. *Reporting Limit (Practical Quantitation Limit)*	0.010 mg/L	0.020 mg/L	0.02 mg/L (lowest std.)
8. *Correlation coefficient of calibration curve*	≥0.995	≥0.995	≥0.995
9. *Sample matrix and concentration range for each (fresh and saline waters are separate matrices)*	Instrument performs at full range whether saline or fresh up to approximately 35 ppt.	Instrument performs to 0.100 mg/L but method breaks down at salinities approaching those of seawater.	Not designed and does not perform in seawater. Method was designed to have a preceding distillation.
10. *Paired t-test results[i] (per each matrix) A two-sided t-test with p-value of 0.01*	Parallel study results included in Section 17.6 of SOP	First method put in place at DCLS for CBP ammonia so there was no comparison.	Not Quoted in method
11. *Wilcoxin Signed-Rank test[ii] (if paired differences are not normally distributed)*	NA	NA	NA
12. *Other Statistics[iii]*	NA	NA	NA

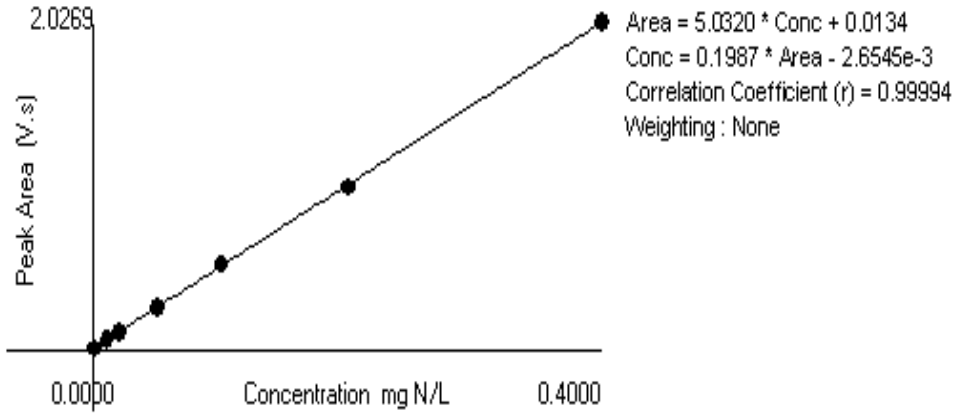
13. Certified reference material results with certified values	See section 13.1 and 13.2 of SOP. 99.3% recovery in reagent water and 103% recovery in approximately 35ppt seawater	See Section 13.1 of SOP. 103% in laboratory reagent water.	Not Quoted but must be in range of 90-110%
14. PT sample and results (USGS, ERA, CBP Blind audit, etc.)	We can run WP, USGS, and blind audit on this instrument because of expanded range and capability.	Blind Audit, no failures last set. Most recent set for Winter 2011 has not been tabulated. WP sample range is to high for this method and does not match daily sample matrix.	No results listed
15. Method blank results	Required ≤ 0.005 mg/L. See section 9.5 for listing of all QC limits.	Required ≤ 0.010 mg/L	Required ≤ 0.010 mg/L
16. Instrument blank (If comparing instruments)	NA (See 15) Lower than EPA requirement.	NA (See 15) Lower than EPA requirement.	NA
17. Spiked sample results (Sample conc. and % recovery of each spike)	CBP Required 100 +/- 20% Study recoveries mean 98.1 % Section 13.3 of SOP	CBP Required 100 +/- 20% Current mean 92%	100 +/- 10%
18. Duplicate sample results (Rep 1, Rep 2 values and RPDs)	RPD ≤ 20% Current study 3.97% Section 13.4 of SOP	RPD≤20% Current mean 8.0%	No requirement listed
19. Raw Data sample pairs (Submit Excel file or equivalent)	File included in email with this file	NA	NA
20. Analyte carry-over	No carryover. Study shown in SOP section 17.5	Can experience carryover when samples are overrange.	No study shown.

Ammonia by Flow Injection Calibration
Curve 0.010 to 0.400 mg/L

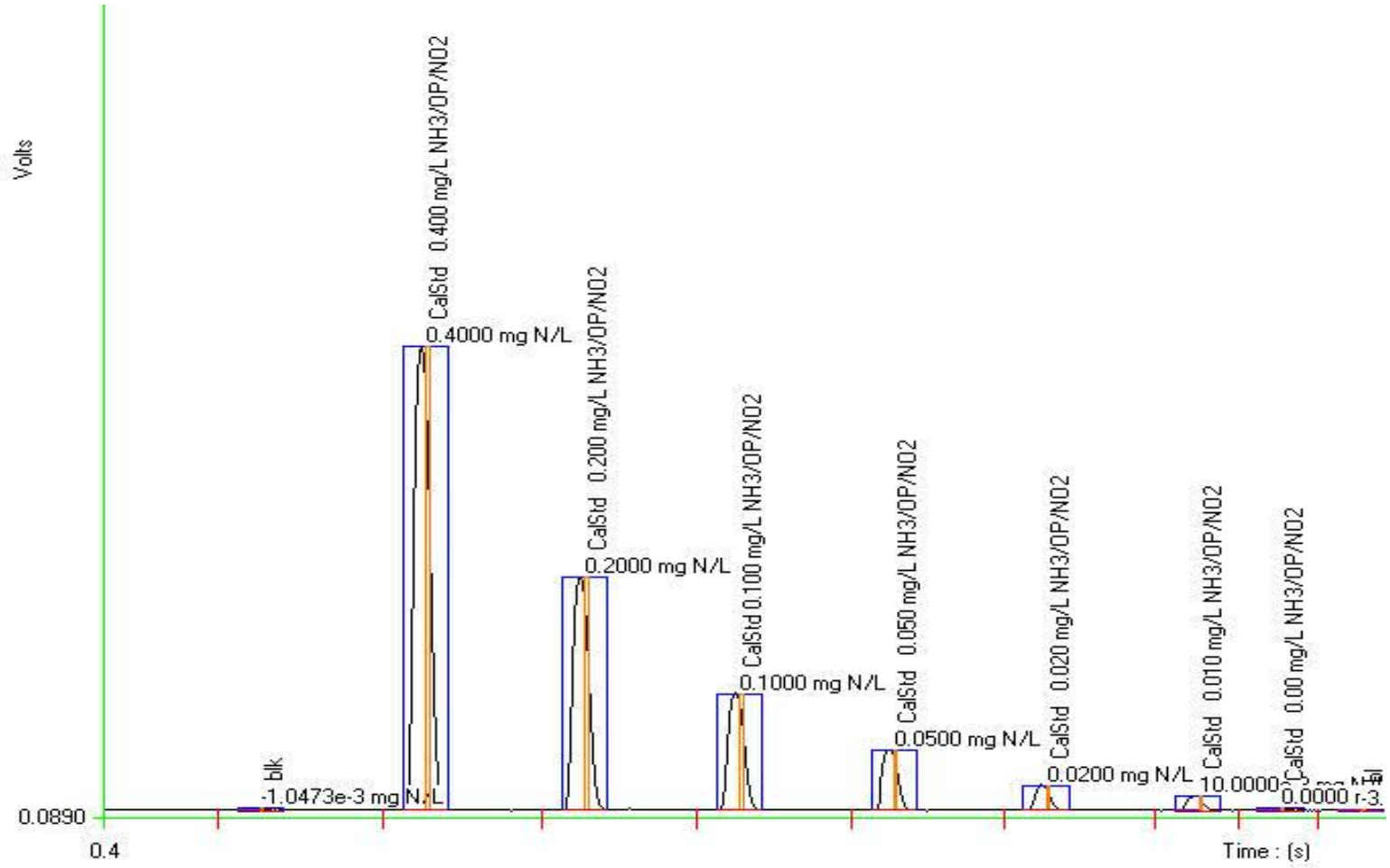
Table : 1 (Ammonia)

	Known Conc. (mg N/L)	Rep	Peak Area (V.s)	Peak Height (V)	% RSD	% Residual	Det. Conc (mg N/L)	Detection Date	Detection Time
1	0.4000	1	2.0269	0.6524	0.0	0.0	0.4001	8/26/2010	2:46:57 PM
2	0.2000	1	1.0111	0.3265	0.0	0.9	0.1982	8/26/2010	2:49:50 PM
3	0.1000	1	0.5332	0.1698	0.0	-3.2	0.1033	8/26/2010	2:52:39 PM
4	0.0500	1	0.2630	0.0850	0.0	0.8	0.0496	8/26/2010	2:55:26 PM
5	0.0200	1	0.1121	0.0363	0.0	1.7	0.0196	8/26/2010	2:58:12 PM
6	10.0000e-3	1	0.0623	0.0204	0.0	2.3	9.7227e-3	8/26/2010	3:00:58 PM
7	0.0000	1	0.0105	3.9222e-3			-5.7712e-4	8/26/2010	3:02:27 PM

Figure : 1 (Ammonia)



Carryover Study



Qc L Standard Identifier	Replicate Result mg/L	True Value mg/L	% Recovery	Matrix
#417 INO-R/S 2008-2	0.0382	0.04	95.5	DI
#417 INO-R/S 2008-2	0.0819	0.08	102.375	DI
#417 INO-R/S 2008-2	0.0358	0.04	89.5	DI
#417 INO-R/S 2008-2	0.0825	0.08	103.125	DI
#417 INO-R/S 2008-2	0.0405	0.04	101.25	DI
#417 INO-R/S 2008-2	0.0813	0.08	101.625	DI
#417 INO-R/S 2008-2	0.0804	0.08	100.5	DI
#417 INO-R/S 2008-2	0.082	0.08	102.5	DI
#417 INO-R/S 2008-2	0.0411	0.04	102.75	DI
#417 INO-R/S 2008-2	0.083	0.08	103.75	DI
#417 INO-R/S 2008-2	0.077	0.08	96.25	DI
#417 INO-R/S 2008-2	0.0702	0.08	87.75	DI
#417 INO-R/S 2008-2	0.0367	0.04	91.75	DI
#417 INO-R/S 2008-2	0.0364	0.04	91	DI
#417 INO-R/S 2008-2	0.0738	0.08	92.25	DI
#417 INO-R/S 2008-2	0.0716	0.08	89.5	DI
#417 INO-R/S 2008-2	0.0771	0.08	96.375	DI
#417 INO-R/S 2008-2	0.0388	0.04	97	DI
ERA P152-739b 1/25	0.348	0.327	106.42	DI
ERA P152-739b 1/100	0.078	0.082	95.12	DI
ERA P152-739b 1/25	0.339	0.327	103.67	DI
ERA P152-739b 1/25	0.341	0.327	104.28	DI
ERA P152-739b 1/25	0.3378	0.327	103.30	DI
ERA P152-739b 1/25	0.3406	0.327	104.16	DI
ERA P152-739b 1/100	0.0835	0.08	104.38	DI
ERA P152-739b 1/100	0.0838	0.08	104.75	DI
ERA P152-739b 1/100	0.0848	0.08	106.00	DI
ERA P152-739b 1/100	0.0833	0.08	104.13	DI
Absolute Grade 090808	0.0807	0.08	100.88	DI
Absolute Grade 090808	0.0401	0.04	100.25	DI
#288 INO R/S 2009-13	0.038	0.04	95	DI
#288 INO R/S 2009-13	0.0808	0.08	101	DI
#288 INO R/S 2009-13	0.0389	0.04	97.25	DI
#288 INO R/S 2009-13	0.08	0.08	100	DI
#288 INO R/S 2009-13	0.0372	0.04	93	DI
#288 INO R/S 2009-13	0.0795	0.08	99.375	DI
#288 INO R/S 2009-13	0.0784	0.08	98	DI
#288 INO R/S 2009-13	0.04	0.04	100	DI
#288 INO R/S 2009-13	0.0433	0.04	108.25	DI
#288 INO R/S 2009-13	0.0803	0.08	100.38	DI
Absolute Grade 090808	0.077	0.08	96.25	dI
		Avg Rec	99.28	%
		SD	5.12	%

Saline Quality Control Sample Recovery in Synthetic Seawater

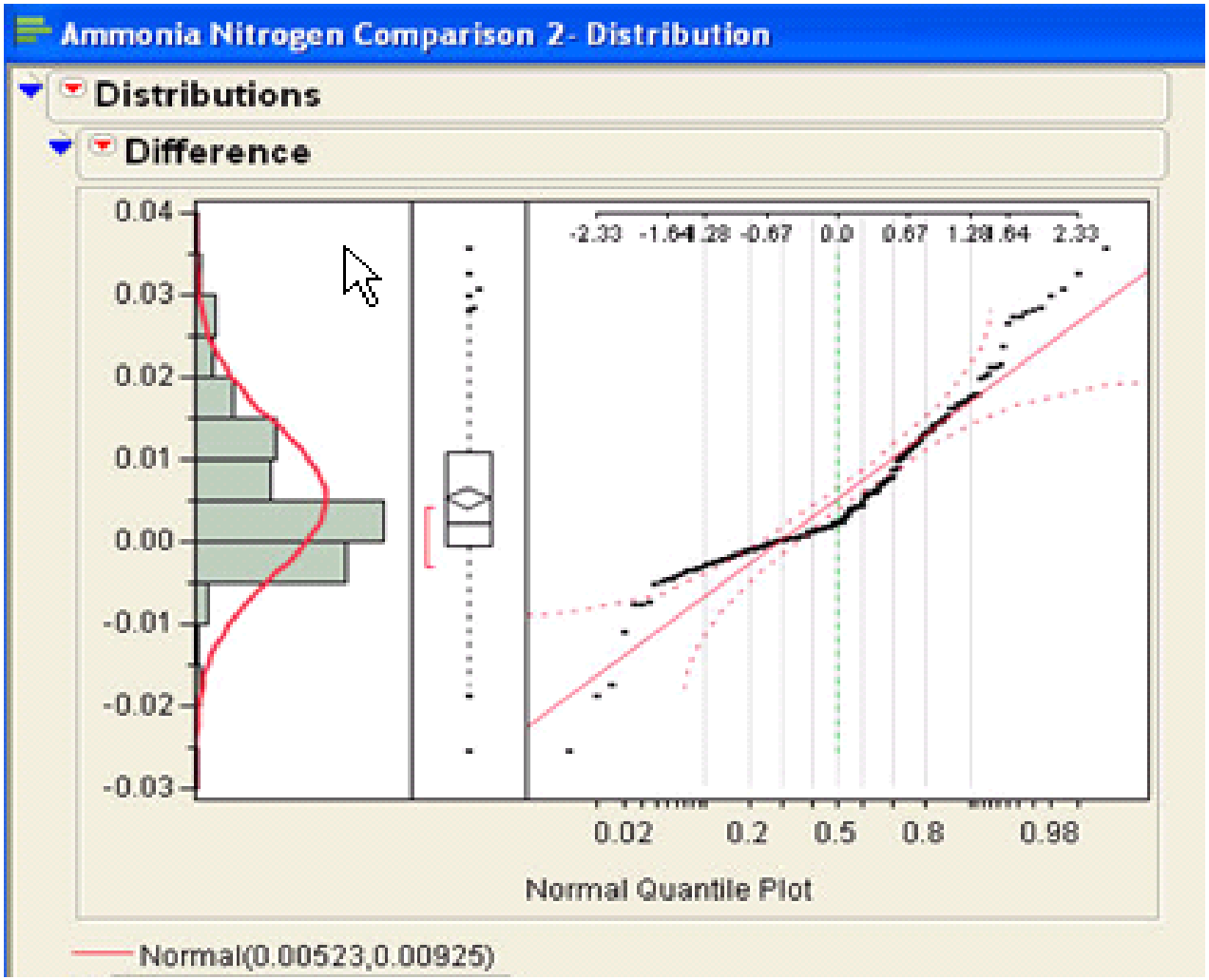
Identifier	Qcs Saline Standard Replicates Result mg/L	True Value mg/L	% Recovery	Matrix
#417 INO-R/S 2008-2	0.0394	0.04	98.5	saline
#417 INO-R/S 2008-2	0.0841	0.08	105.125	saline
#417 INO-R/S 2008-2	0.0408	0.04	102	saline
#417 INO-R/S 2008-2	0.0866	0.08	108.25	saline
#417 INO-R/S 2008-2	0.0422	0.04	105.5	saline
#417 INO-R/S 2008-2	0.0882	0.08	110.25	saline
#417 INO-R/S 2008-2	0.0789	0.08	98.625	saline
#417 INO-R/S 2008-2	0.0382	0.04	95.5	saline
ERA P152-739b 1/25	0.329	0.327	100.61	saline
ERA P152-739b 1/100	0.088	0.082	107.32	saline
ERA P152-739b 1/100	0.0868	0.08	108.5	saline
ERA P152-739b 1/100	0.0877	0.08	109.625	saline
ERA P152-739b 1/100	0.0875	0.08	109.375	saline
ERA P152-739b 1/100	0.088	0.08	110	saline
ERA P152-739b 1/25	0.306	0.327	93.58	saline
ERA P152-739b 1/25	0.315	0.327	96.33	saline
ERA P152-739b 1/25	0.322	0.327	98.47	saline
		Avg Rec	**103.39**	%
		SD	**5.74**	%

Real world Sample performance:

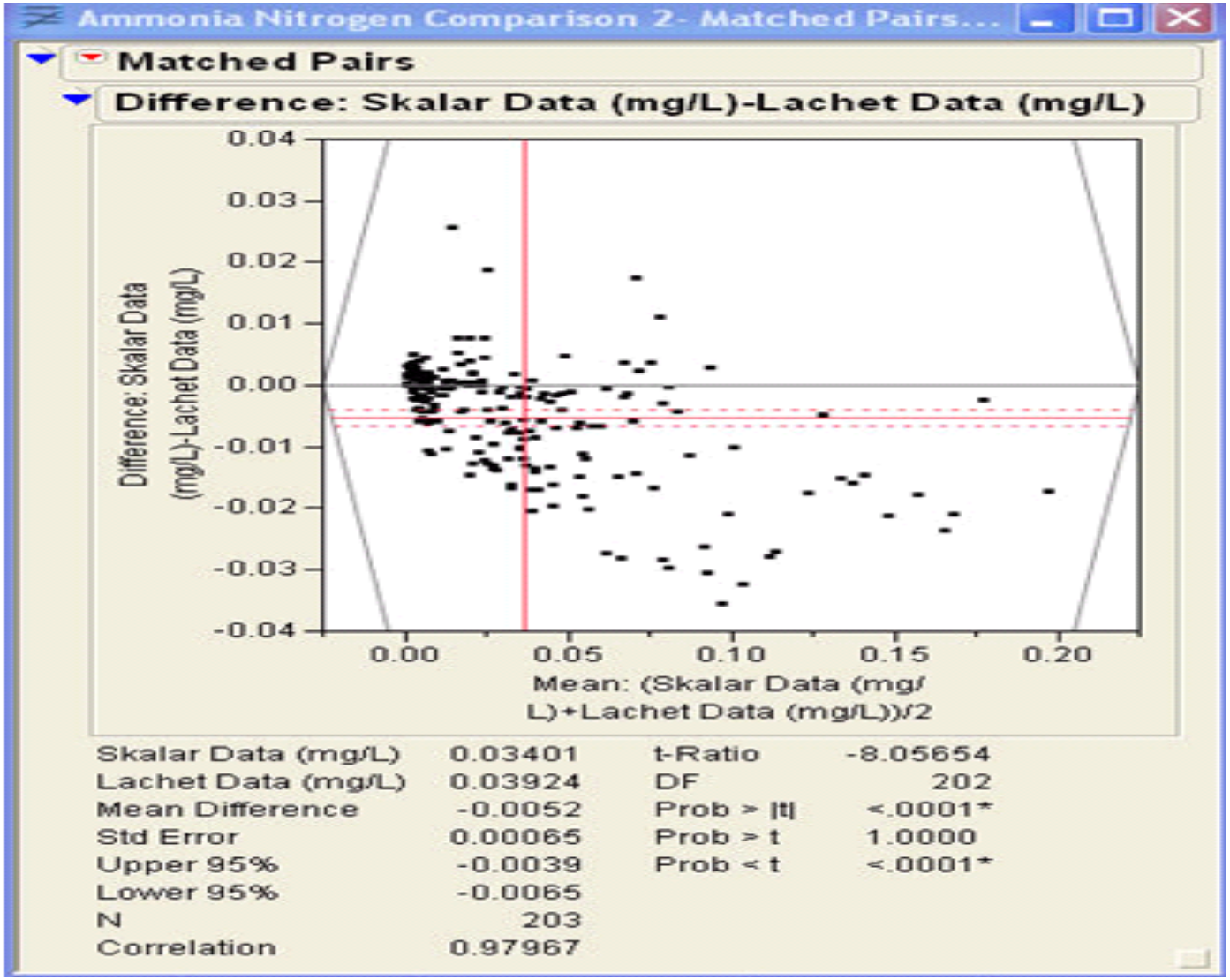
Sample Spike Recovery : 98.1% with S.D of 5.8%

Duplicate RPD: Avg 4.0%

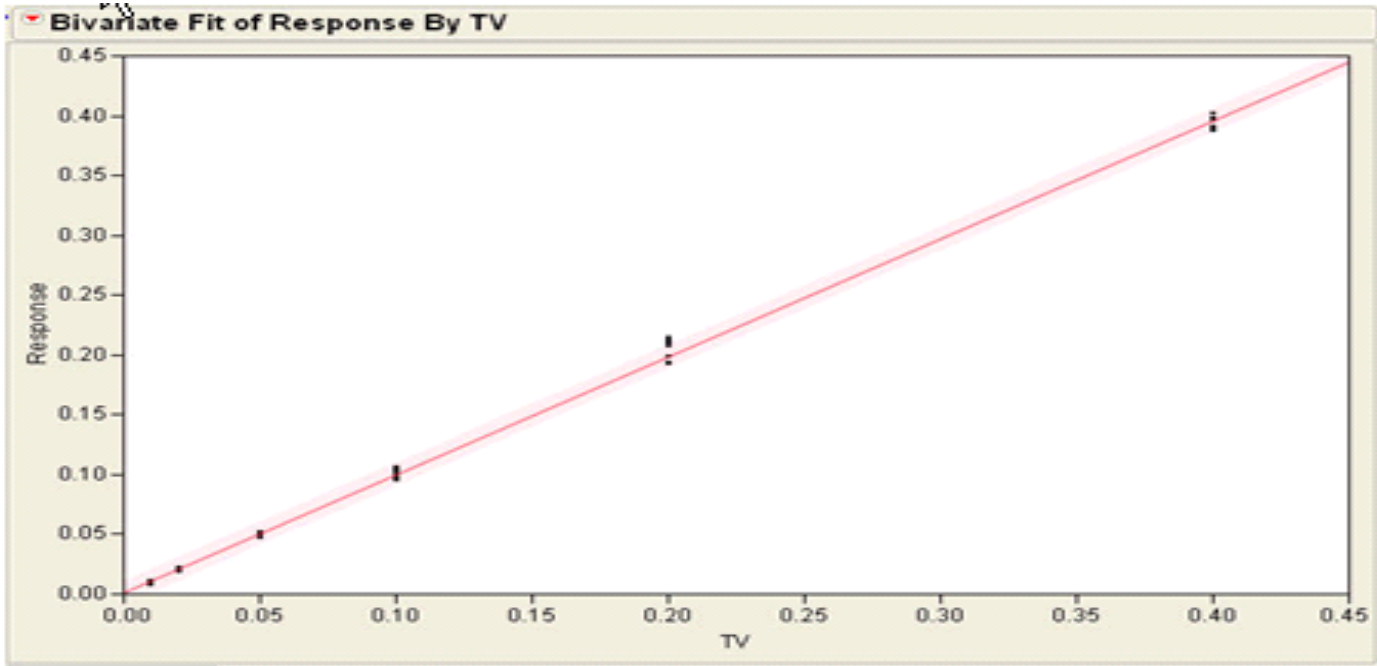
Differences of the Lachat Result – Skalar Result indicates a normal distribution with a slight high bias on the Lachat.



Matched pairs differences plot showing the small positive bias of the Lachat.



Variability of the Curve Standards.



Linear Fit

Response = 0.0009444 + 0.9876946*TV

Summary of Fit

RSquare	0.998535
RSquare Adj	0.998514
Root Mean Square Error	0.005043
Mean of Response	0.131014
Observations (or Sum Wgts)	71

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	4	0.00025398	0.000063	2.7500
Pure Error	65	0.00150076	0.000023	Prob > F
Total Error	69	0.00175473		0.0354*
				Max RSq
				0.9987

The standard deviation associated with ten replicate readings of each standard over several runs and days. Concentration in mg/L

CONC	0.01000	0.02000	0.05000	0.10000	0.20000	0.40000
SD	0.00112	0.00109	0.00175	0.00367	0.00891	0.00563
VAR	0.0000013	0.0000012	0.0000031	0.0000134	0.0000794	0.0000317

Advantages of the flow injection and EDTA buffer:

*Faster reaction and time of flight reducing the amount analyte and sample that spreads into the adjacent wash solution while flowing through the analyzer. Contributes to a sharper more well defined peak.

•Can make calibration standards in DI water and use to analyze salinities equivalent to ocean water. EDTA buffer helps mitigate the negative bias produced by high concentrations of magnesium.

•Uses peak integration instead of height to determine results. By integrating only a slice of the peak we can eliminate the interference from the refractive index/ carrier to sample interface. Use of smaller flow cells with high color producing reactions also reduces refractive index effects.

•The use of smaller flow cells with digital detector technology allows the lab the ability to analyze a wider range without the need for dilution.

•No carryover issues leading to peak shoulder reruns.

Conclusions from statistical analysis:

- Results from the flow injection are biased high in comparison to the segmented flow results. Avg. bias is on the order of 0.005 mg/L. While the result is statistically significant it is not practically significant.

- Based on analysis by Elgin Perry the T-Test overstates the statistical significance and a more valid test would have been to use a nested analysis of variance test for this type of population (203 samples). The second test indicates that the difference is slightly significant, p=0.0458, and shows a mean bias of 0.005 mg/L.

*Elgin's analysis concluded that the interval from 0.0 to 0.030 mg/L could be considered equivalent. Above 0.030 mg/L a correction factor may be needed should there be a step trend. Those factors are stated with his analysis and filed with the validation.

- There were conclusions drawn from experimental design that deserve discussion in an upcoming AMQAW meeting.