The Effect On Calibration From A Detector's Lack of Sensitivity

Detector sensitivity or minimum detectable concentration (MDC) is defined as the minimum concentration of solute passing through the detector that can be unambiguously discriminated from noise. The size of the signal that will make it distinguishable from the noise (the *signal–to–noise* ratio) is an arbitrary choice. It is generally accepted that with electronic measuring instruments discrimination is possible when the signal to noise ratio is *two* and this criteria has been adopted for chromatography detectors.

Ref: "Gas Chromatography Detectors" By RPW Scott
www.chromatography-online.org/topics/signal-to-noise/ratio.html

The limit of quantitation or LOQ is the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy using the operational conditions of the method. The LOQ is usually defined as a signal to noise ratio of 10:1.

Ref: "How to Choose an ELS Detector"
www.softacorporation.com

"Measurements made at or near the detection limit, however, are not considered to be quantitative. For quantitation (±10%), it is recommended that an element's concentration should be at least five times higher than the detection limit. For accurate quantitation (± 2%), the concentration should be greater than 100 times the detection limit."

Ref: Boss, Charles B. and Fredeen, Kenneth J. (1999) Concepts, Instrumentation, and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry, Second Edition. Published by The Perkin-Elmer Corporation.

The EDL is defined as either the MDL or a level of a compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately 5, whichever is greater.

Ref: EPA Method 515.3, Rev. 1, 1996, page 31, footnote c.

The MRL is the threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample. The MRL should not be established at an analyte concentration that is less than either three times the Detection Limit or a concentration which would yield a response less than a signal-to-noise (S/N) ratio of five.

Ref: EPA Method 515.4, Rev. 1.0, April 2000, section 9.3.

The MRL is the threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample. The MRL may be established at an analyte concentration either greater than three times the MDL or at a concentration which would yield a response greater than a signal to noise ratio of five.

Ref: EPA Method 532, Rev. 1.0, June 2000, section 9.3.

It is important to use a peak height measurement instead of a peak area measurement when looking at minimum detection levels because tailing or fronting peaks are difficult to accurately measure at lower concentrations. Signal to noise ratios are easiest to determine by printing the chromatogram and using a ruler to measure both the noise and the signal.

Ref: "How to Choose an ELS Detector"
www.softacorporation.com

To calculate the signal to noise ratio, measure the peak height in millivolts and divide by the normalized noise value.

$$S:N = \frac{S}{N_D}$$

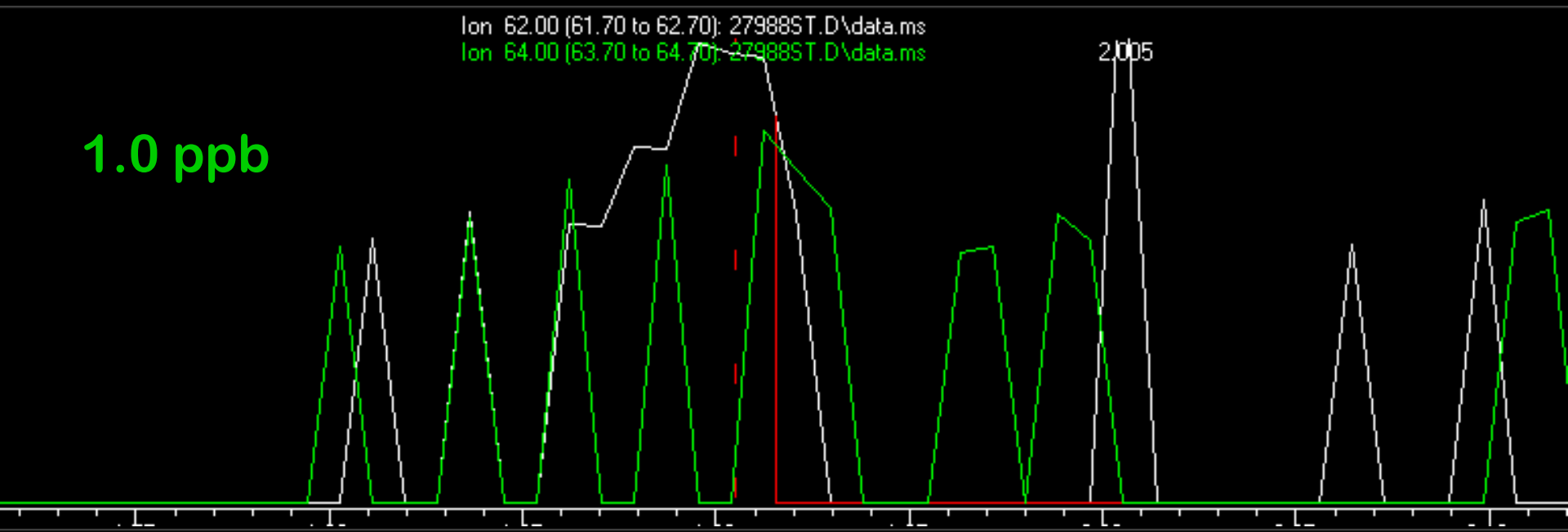
Ref: "*How to Choose an ELS Detector*"
www.softacorporation.com

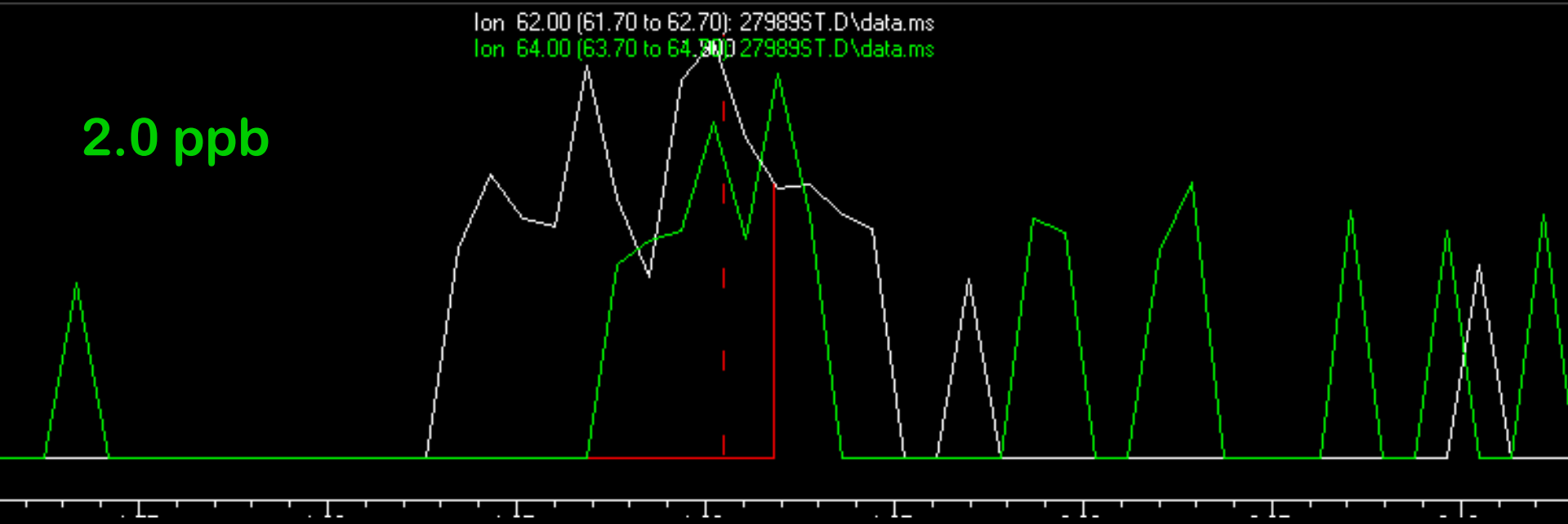
The detector noise is measured by constructing two parallel lines embracing the maximum and minimum signal over the defined time period. The distance between the parallel lines measured in millivolts is taken as the measured noise (v_n), and the normalized noise level (N_D) is calculated with the formula.

$$N_D = v_n A = \frac{V_n}{B}$$

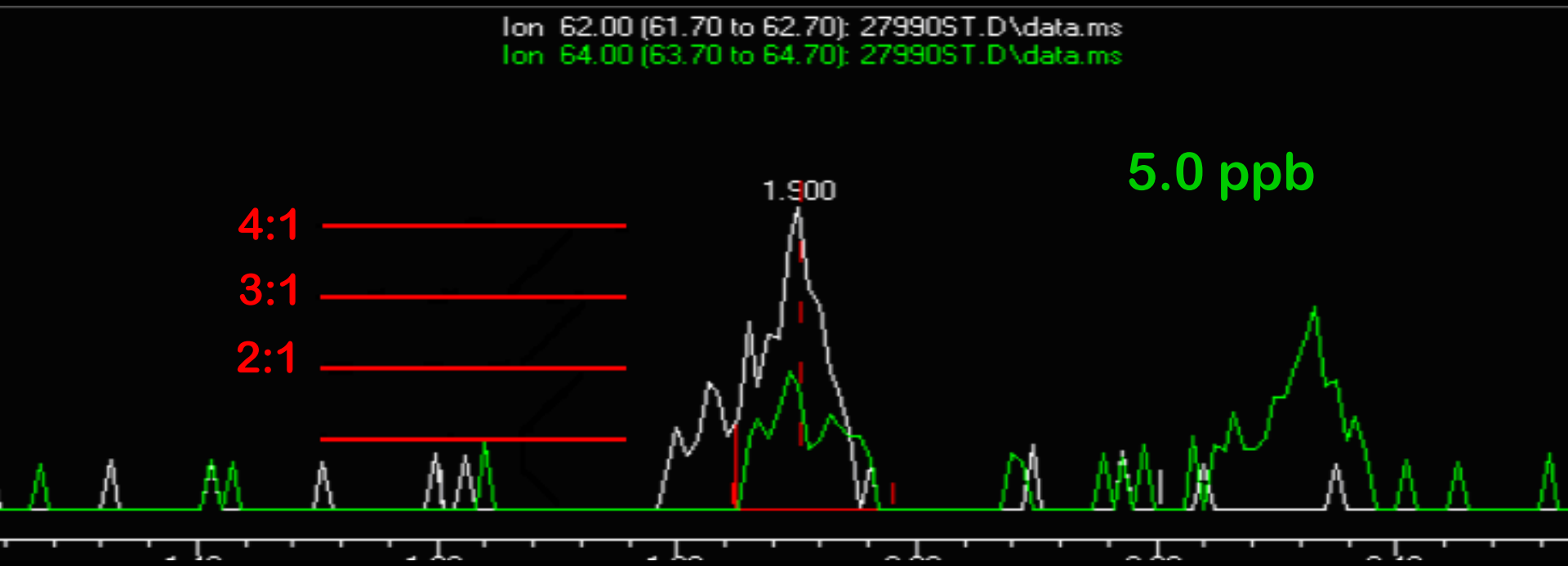
where A is the attenuation factor and B is the amplification factor.

Ref: "*How to Choose an ELS Detector*"
www.softacorporation.com



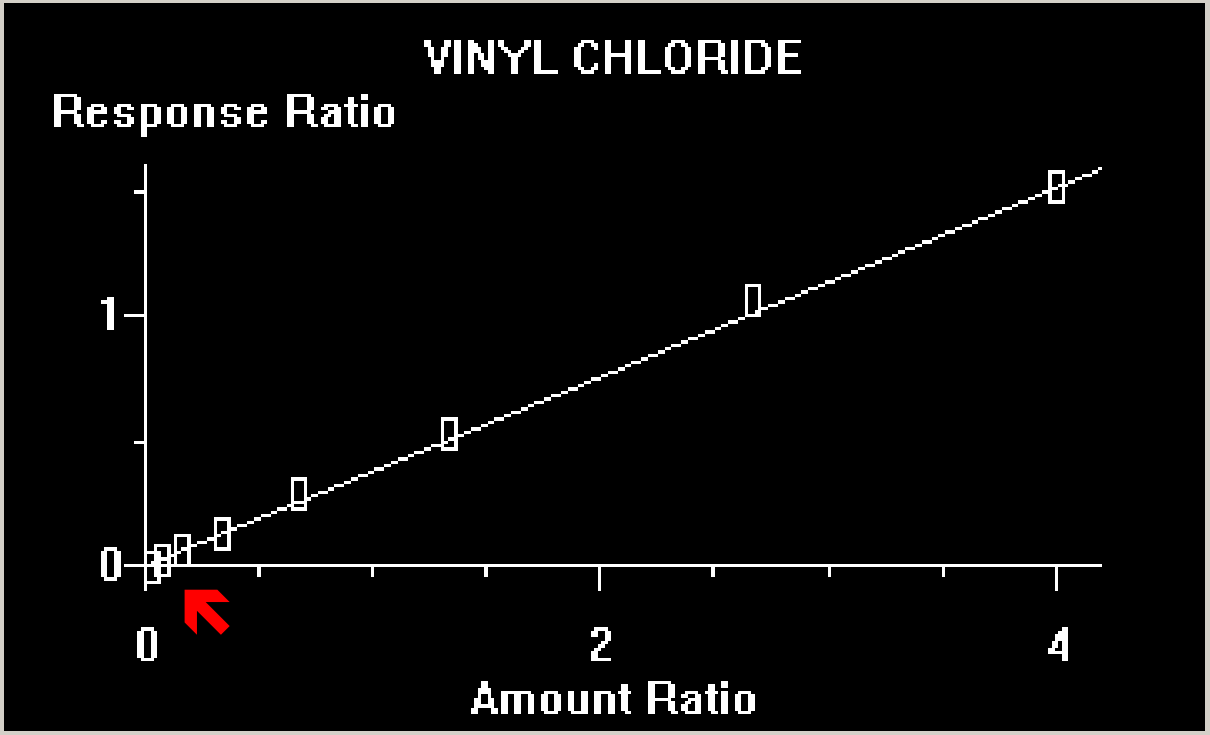


Vinyl Chloride



Vinyl Chloride

Plot Calibration Curve

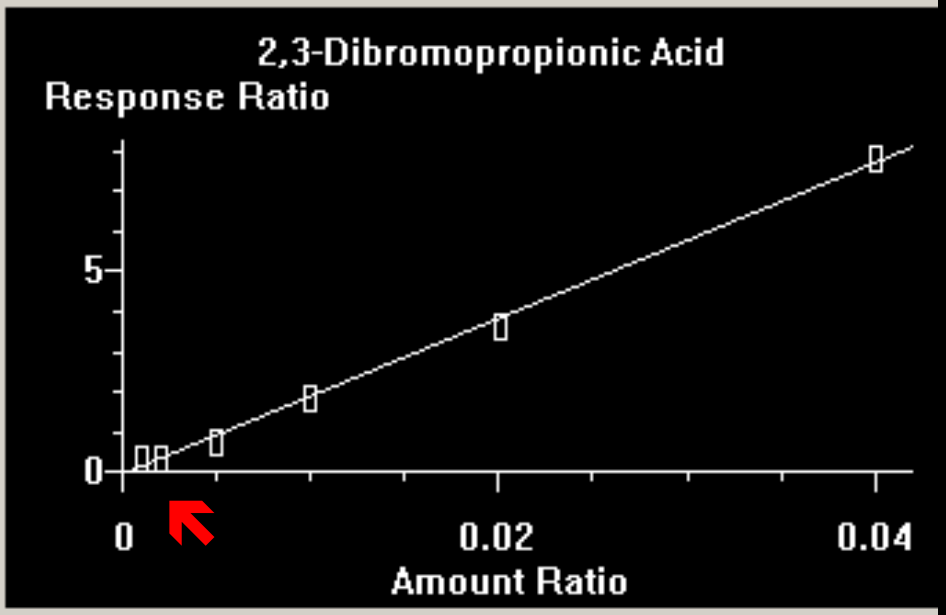


Amount Ratio	Response Ratio
0.16666667	0.07245136
0.33333333	0.13192604
0.66666667	0.28936094
1.33333333	0.53355459
2.66666667	1.06111838
0.06666667	0.02567686
0.03333333	0.00601798

Resp Ratio = 3.76e-001 * Amt

RF Rel Std Dev = 21.7% Curve Fit: Avg RF

t Calibration Curve

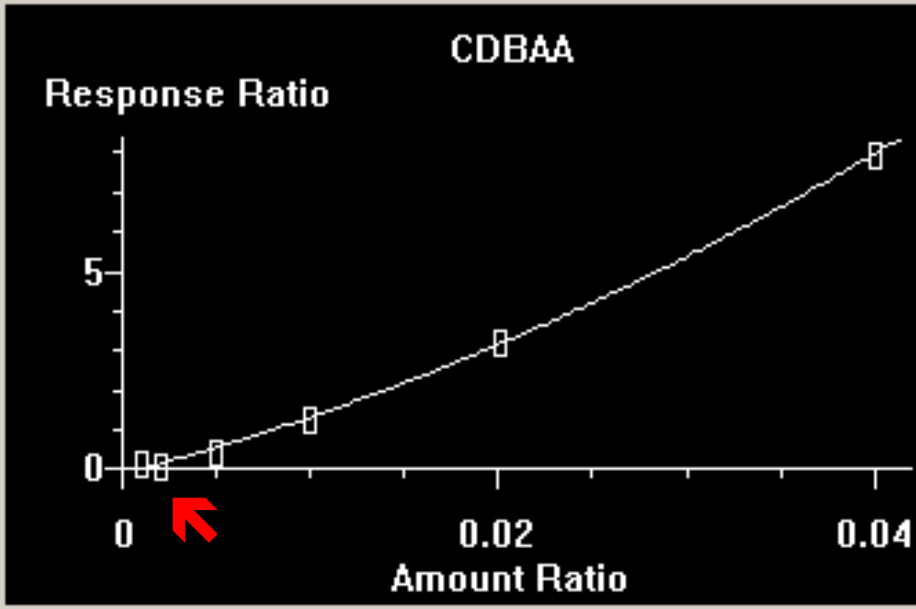


Amount Ratio	Response Ratio
0.00100000	0.37574992
0.00200000	0.34124722
0.00500000	0.78283251
0.01000000	1.85402583
0.02000000	3.62955801
0.04000000	7.82171699

Resp Ratio = 1.94e+002 * Amt - 5.45e-002

Coef of Det (r^2) = 0.997 Curve Fit: Linear

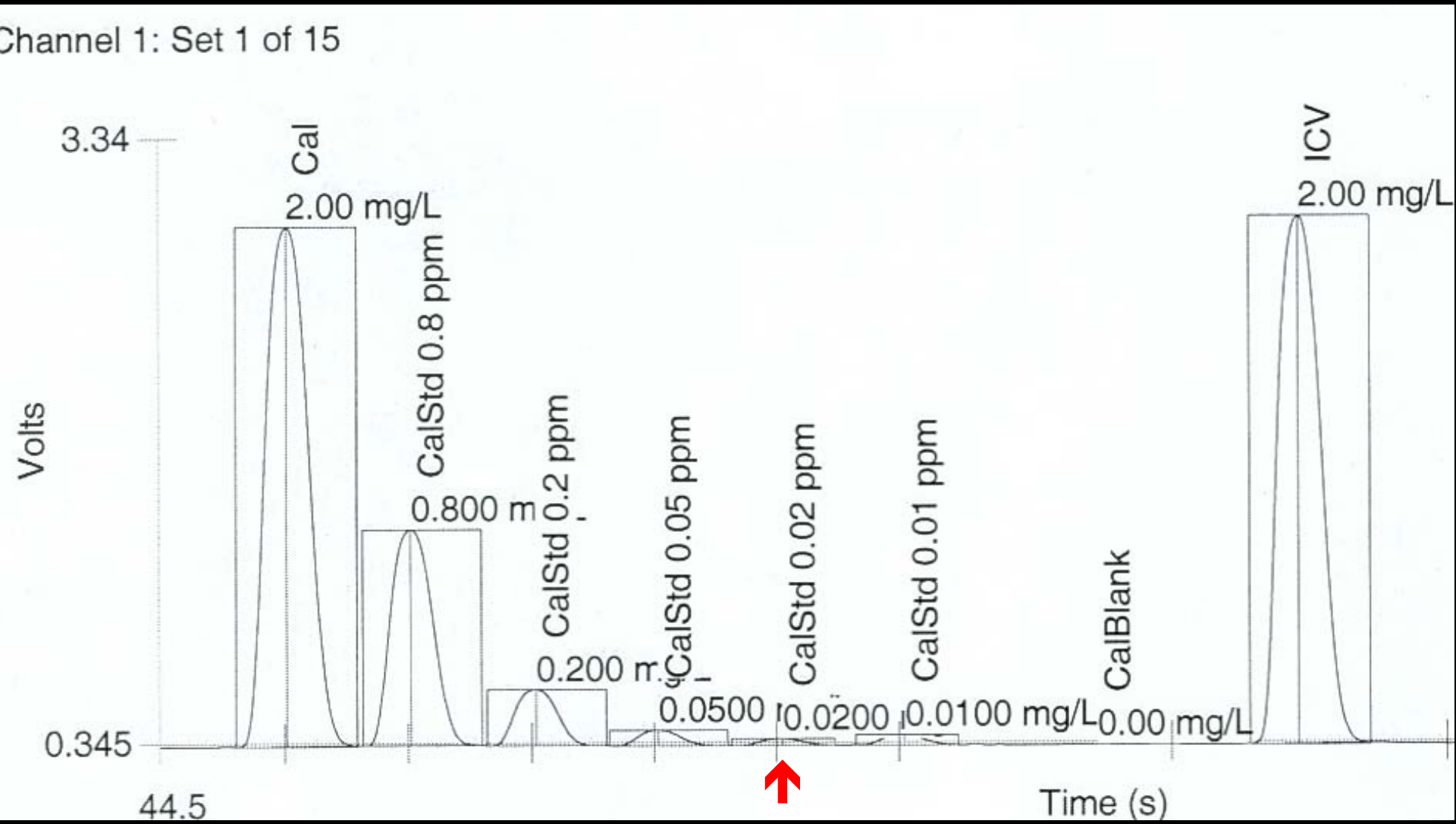
Calibration Curve



Amount Ratio	Response Ratio
0.00100000	0.12703862
0.00200000	0.09135492
0.00500000	0.41457116
0.01000000	1.24084806
0.02000000	3.22677675
0.04000000	7.94040903

R = 1.94e+003 A*A + 1.25e+002 A - 1.37e-001

Coef of Det (r^2) = 0.999 Curve Fit: Quadratic


Channel 1: Set 1 of 15
3.34
0.345
Volts
Cal
2.00 mg/L
CalStd 0.8 ppm
0.800 m
CalStd 0.2 ppm
0.200 m
CalStd 0.05 ppm
0.0500
CalStd 0.02 ppm
0.0200
CalStd 0.01 ppm
0.0100 mg/L
CalBlank
0.00 mg/L
ICV
2.00 mg/L
44.5
Time (s)

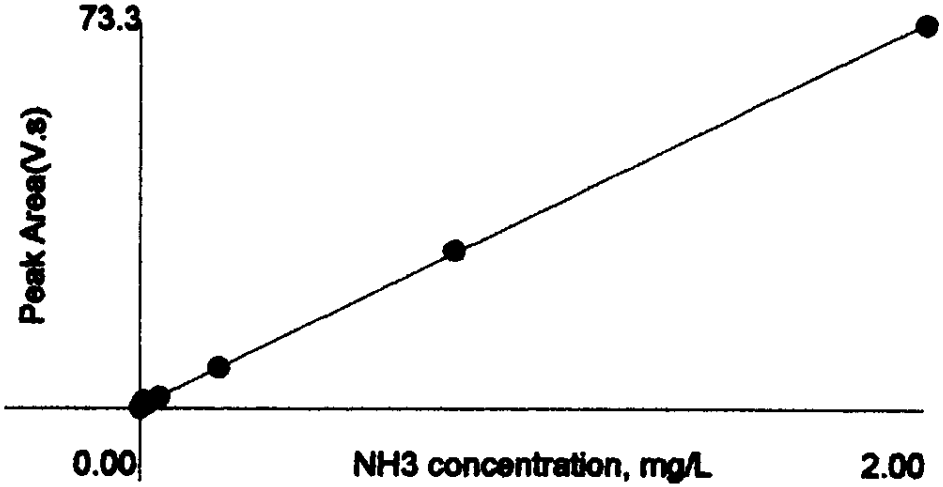
Author [redacted]

Date : 7/14/2004

Table 1: NH3

	Conc. (mg/L)	Rep	Peak Area (Volt-s)	Peak Height (Volts)	% Residual	Detection Date	Detection Time
1	2.00	1	73.3	2.57	0.3	7/14/2004	10:52:30 AM
2	0.800	1	30.2	1.07	-1.9	7/14/2004	10:53:44 AM
3	0.200	1	7.73	0.274	0.4	7/14/2004	10:54:58 AM
4	0.0500	1	2.08	0.0728	8.6	7/14/2004	10:56:11 AM
5	0.0200	1	0.925	0.0319	21.8	7/14/2004	10:57:23 AM
6	0.0100	1	1.41	0.0504	-72.7	7/14/2004	10:58:36 AM
7	0.00	1	1.84e-4	6.03e-4		7/14/2004	10:59:49 AM

Figure 1: NH3



Area = 36.5 * Conc + 0.452
Conc = 0.0274 * Area - 0.0123
Correlation Coefficient (r) = 0.99989

No Weighting

Ammonia