$$\bar{x} = \frac{\sum_i x_i}{n} \qquad s = \sqrt{\frac{\sum_i \left(x_i - \bar{x}\right)^2}{n-1}} \qquad \mu = \bar{x} \pm \frac{t\sigma}{\sqrt{n}} \qquad G = \frac{|value - \bar{x}|}{s}$$

Values of Grubbs Statistic (G)

Number of Observations n	Confidence Level (%) 99.9	99.5	99	97.5	95	90
3	1.155	1.155	1.155	1.155	1.153	1.148
4	1.499	1.496	1.492	1.481	1.463	1.425
5	1.780	1.764	1.749	1.715	1.672	1.602
6	2.011	1.973	1.944	1.887	1.822	1.729
7	2.201	2.139	2.097	2.020	1.938	1.828
8	2.358	2.274	2.221	2.126	2.032	1.909
9	2.492	2.387	2.323	2.215	2.110	1.977
10	2.606	2.482	2.410	2.290	2.176	2.036
11	2.705	2.564	2.485	2.355	2.234	2.088
12	2.791	2.636	2.550	2.412	2.285	2.134
13	2.867	2.699	2.607	2.462	2.331	2.175
14	2.935	2.755	2.659	2.507	2.371	2.213
15	2.997	2.806	2.705	2.549	2.409	2.247

$$F = \frac{s_1^2}{s_2^2}$$

$$t_{calculated} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pooled}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} \qquad s_{pooled} = \sqrt{\frac{s_1^2(n_1-1)+s_2^2(n_2-1)}{n_1+n_2-2}} \qquad \text{d.f.} = n_1 + n_2 - 2$$

$$t_{calculated} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \qquad \text{d.f.} = \left(\frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\frac{\left(s_1^2/n_1\right)^2}{n_1+1} + \frac{\left(s_2^2/n_2\right)^2}{n_2+1}} \right) - 2$$

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln \frac{[\mathrm{Re}d]}{[Ox]} \qquad E = E^0 - (0.0592/n) \log [red]/[ox]$$

Table 4-1 Ordinate and area for the normal (Gaussian) error curve,

$$y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$$

$\|z\|$[a]	y	Area[b]	$\|z\|$	y	Area	$\|z\|$	y	Area
0.0	0.398 9	0.000 0	1.4	0.149 7	0.419 2	2.8	0.007 9	0.497 4
0.1	0.397 0	0.039 8	1.5	0.129 5	0.433 2	2.9	0.006 0	0.498 1
0.2	0.391 0	0.079 3	1.6	0.110 9	0.445 2	3.0	0.004 4	0.498 650
0.3	0.381 4	0.117 9	1.7	0.094 1	0.455 4	3.1	0.003 3	0.499 032
0.4	0.368 3	0.155 4	1.8	0.079 0	0.464 1	3.2	0.002 4	0.499 313
0.5	0.352 1	0.191 5	1.9	0.065 6	0.471 3	3.3	0.001 7	0.499 517
0.6	0.333 2	0.225 8	2.0	0.054 0	0.477 3	3.4	0.001 2	0.499 663
0.7	0.312 3	0.258 0	2.1	0.044 0	0.482 1	3.5	0.000 9	0.499 767
0.8	0.289 7	0.288 1	2.2	0.035 5	0.486 1	3.6	0.000 6	0.499 841
0.9	0.266 1	0.315 9	2.3	0.028 3	0.489 3	3.7	0.000 4	0.499 904
1.0	0.242 0	0.341 3	2.4	0.022 4	0.491 8	3.8	0.000 3	0.499 928
1.1	0.217 9	0.364 3	2.5	0.017 5	0.493 8	3.9	0.000 2	0.499 952
1.2	0.194 2	0.384 9	2.6	0.013 6	0.495 3	4.0	0.000 1	0.499 968
1.3	0.171 4	0.403 2	2.7	0.010 4	0.496 5			

Table 4-2 Values of Student's t

Degrees of freedom	Confidence level (%) 50	90	95	98	99	99.5	99.9
1	1.000	6.314	12.706	31.821	63.657	127.32	636.619
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

Table 4-6 Values of Q for rejection of data

Q (90% confidence)[a]	Number of observations
0.76	4
0.64	5
0.56	6
0.51	7
0.47	8
0.44	9
0.41	10

Table 4-5 Critical values of $F = s_1^2/s_2^2$ at 95% confidence level

Degrees of freedom for s_2	Degrees of freedom for s_1: 2	3	4	5	6	7	8	9	10	12	15	20	30	∞
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79	8.74	8.70	8.66	8.62	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.75	5.63
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.50	4.36
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.81	3.67
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.58	3.51	3.44	3.38	3.23
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.08	2.93
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.86	2.71
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.84	2.77	2.70	2.54
11	3.98	3.59	3.36	3.20	3.10	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.57	2.40
12	3.88	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.47	2.30
13	3.81	3.41	3.18	3.02	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.38	2.21
14	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.31	2.13
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.25	2.07
16	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.19	2.01
17	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.15	1.96
18	3.56	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.11	1.92
19	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.07	1.88
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.04	1.84
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.84	1.62
∞	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.46	1.00

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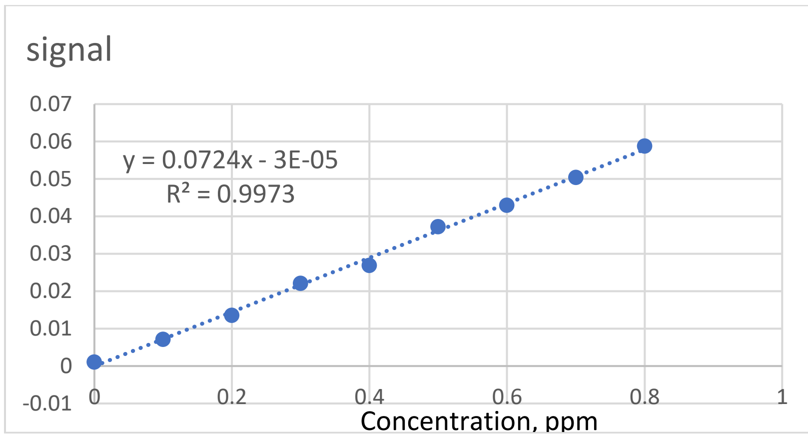
Name____

80 points total – 10 points each.

1) A LOD was measured for a lead analysis method. Below left are nine measurements for a blank and low Pb concentration signals. Their averages and standard deviations are show in each respective column. A calibration curve is on the right with a least squares best fit line shown. What is the LOD for this method? [1]

	blank	low conc
	0.0006	0.0045
	0.0012	0.0052
	0.0022	0.0062
	0.0005	0.0061
	0.0016	0.0047
	0.0008	0.0056
	0.0017	0.0053
	0.001	0.0041
	0.0011	0.0052
std dev	0.000556	0.000701
avg	0.001189	0.005211



2) Sketch and label a diagram that illustrates the concepts of [2]

a) linear range
b) sensitivity
c) dynamic range
d) background

3) What is the 95% confidence limit for the following set of data? [3]

Sample	Signal
1	21.56 mA
2	27.25 mA
3	25.53 mA
4	24.99 mA
5	24.43 mA
Average	**24.75 mA**
s	**2.07**

4) Which if any of the following measurements can be excluded with 95% confidence? 4

0.5980, 0.5993, 0.5995, 0.5997, 0.6010, 0.6400
Average = 0.6062 s = 0.0166

5) Arsenic in blood was measured by atomic absorption spectroscopy (AAS) and an electrochemical sensor (ES). The results are reported below with the standard deviations.

	AAS	ES
As	0.069±0.005 ppb (n = 7)	0.063±0.008 ppb (n = 5)

Are the standard deviations significantly different at the 95% confidence interval? Show your work. 5

6) For $Fe^{3+} + e- \rightarrow Fe^{2+}$ $E^0 = -0.441$ V

What is the single electrode potential if $[Fe^{3+}] = 0.0013$ M and $[Fe^{2+}] = 0.015$ M? 6

7) What is E^0_{cell} for the reaction below? 7

$Hg_2SO_4(s) + 2e- = 2Hg(l) + SO_4^{2-}$

Given:

$Hg_2^{2+} + 2e^- = 2Hg(l)$ $E^0_{red} = 0.796$ V

$Hg_2SO_4(s) = Hg_2^{2+} + SO_4^{2-}$ $K_{sp} = 7.4e-7$

8) In the following series which is the 8

a. Strongest reducing agent? ______________________

b. Strongest oxidizing agent?______________________

c. Is NAD^+ a strong reducing agent than NADH? _______

Table 14-2 Reduction potentials of biological interest

Reaction	$E°$ (V)	$E°'$ (V)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229	+0.816
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771	+0.771
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.535	+0.535
Cytochrome *a* (Fe^{3+}) + e^- $\rightleftharpoons$ cytochrome *a* (Fe^{2+})	+0.290	+0.290
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.695	+0.281
Cytochrome *c* (Fe^{3+}) + e^- $\rightleftharpoons$ cytochrome *c* (Fe^{2+})	—	+0.254
2,6-Dichlorophenolindophenol + $2H^+ + 2e^-$ $\rightleftharpoons$ reduced 2,6-dichlorophenolindophenol	—	+0.22
Dehydroascorbate + $2H^+ + 2e^-$ $\rightleftharpoons$ ascorbate + H_2O	+0.390	+0.058
Fumarate + $2H^+ + 2e^-$ $\rightleftharpoons$ succinate	+0.433	+0.031
Methylene blue + $2H^+ + 2e^-$ $\rightleftharpoons$ reduced product	+0.532	+0.011
Glyoxylate + $2H^+ + 2e^-$ $\rightleftharpoons$ glycolate	—	−0.090
Oxaloacetate + $2H^+ + 2e^-$ $\rightleftharpoons$ malate	+0.330	−0.102
Pyruvate + $2H^+ + 2e^-$ $\rightleftharpoons$ lactate	+0.224	−0.190
Riboflavin + $2H^+ + 2e^-$ $\rightleftharpoons$ reduced riboflavin	—	−0.208
FAD + $2H^+ + 2e^-$ $\rightleftharpoons$ $FADH_2$	—	−0.219
(Glutathione-S)$_2$ + $2H^+ + 2e^-$ $\rightleftharpoons$ 2 glutathione-SH	—	−0.23
Safranine T + $2e^-$ $\rightleftharpoons$ leucosafranine T	−0.235	−0.289
$(C_6H_5S)_2 + 2H^+ + 2e^- \rightleftharpoons 2C_6H_5SH$	—	−0.30
$NAD^+ + H^+ + 2e^-$ $\rightleftharpoons$ NADH	−0.105	−0.320
$NADP^+ + H^+ + 2e^-$ $\rightleftharpoons$ NADPH	—	−0.324
Cystine + $2H^+ + 2e^-$ $\rightleftharpoons$ 2 cysteine	—	−0.340
Acetoacetate + $2H^+ + 2e^-$ $\rightleftharpoons$ L-β-hydroxybutyrate	—	−0.346
Xanthine + $2H^+ + 2e^-$ $\rightleftharpoons$ hypoxanthine + H_2O	—	−0.371
$2H^+ + 2e^- \rightleftharpoons H_2$	0.000	−0.414
Gluconate + $2H^+ + 2e^-$ $\rightleftharpoons$ glucose + H_2O	—	−0.44
$SO_4^{2-} + 2e^- + 2H^+ \rightleftharpoons SO_3^{2-} + H_2O$	—	−0.454
$2SO_3^{2-} + 2e^- + 4H^+ \rightleftharpoons S_2O_4^{2-} + 2H_2O$	—	−0.527

Answers

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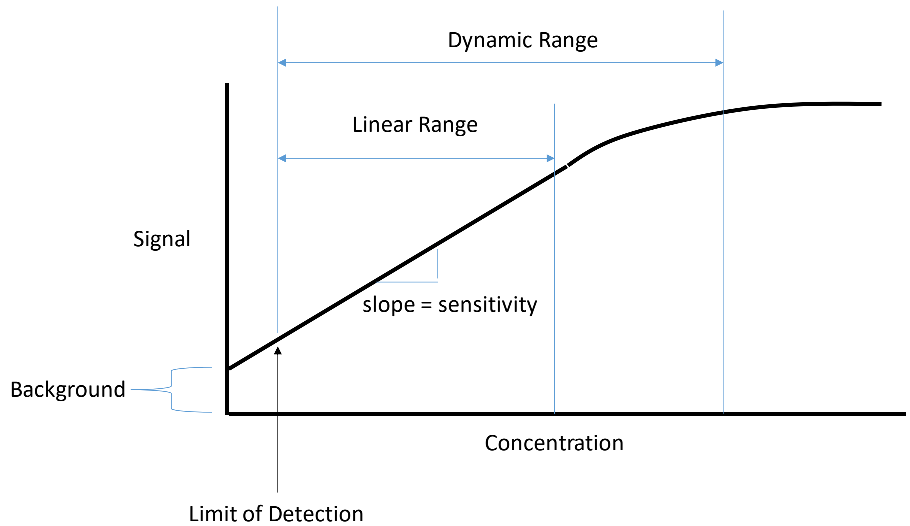
[1] LOD = 3s/m = 3*0.000701/7.24e-2 = 0.029 ppm

[2]



[3] μ = x-bar ± (ts/√n)   C.L. = ±(2.776)*(2.07/√5) = 2.56

There's a 95% chance that the true mean lies in the interval 24.75 ± 2.56

[4] Use Grubbs Test for this,   G-calc = (0.6400 – 0.6062) / 0.0166 = 2.04
Locate G-Table for n = 6   G-table = 0.1822

G-calc > G-table   we may discard 0.6400 with 95% confidence

[5] Use F-test for this question.

F-calc = $(0.008/0.005)^2$ = 2.6

F-table = 4.53   4 d.f. & 6 d.f.   F-calc < F-table

The s are not significantly different.

[6] Use the Nernst Equation: $E = E^0 – (0.0592/n) \log [red]/[ox]$

$E = -0.441 -0.0592 \log [0.015]/[0.0013] = -0.504$ V

[7] $E = 0.796 – 0.0592/2 \log 1/[Hg_2^{2+}]$
$K_{sp} = 7.4e\text{-}7 = [Hg_2^{2+}][SO_4^{2-}]$

$[Hg_2^{2+}] = 7.4e\text{-}7/[SO_4^{2-}]$

$E = 0.796 - 0.0592/2 \log [SO_4^{2-}]/7.4e\text{-}7 =$ **0.615 V**

8

a. Strongest reducing agent? ________$S_2O_4^{2-}$_________
b. Strongest oxidizing agent?__________O_2__________
c. Is NAD^+ a strong reducing agent than NADH? ___No____

NADH is the reducing agent.