## CHEM 322 Spring 2013

| Name_ |          |           |        |    |
|-------|----------|-----------|--------|----|
| Due   | In Class | Wednesday | , Jan. | 23 |

Complete the following. Provide answers in the spaces below and attach all work and any computer printouts to this sheet. You may work with a partner on this assignment and turn in a single copy of your results; however, you must ultimately be able to do these calculations yourself.

You have conducted an electrochemistry experiment to determine the quantity of lead in a drinking water sample by driving the reduction of Pb<sup>2+</sup> to Pb<sup>0</sup> at an electrode surface and measuring the flow of electrons (current) that occurs in the process. Over the concentration range that you use, the response of the measurement should be directly proportional to concentration. Using the data for experiments A and B below, evaluate the following items.

- 1. The slope and intercept for the linear relationship describing how current depends on concentration, with the appropriate units and 95% confidence intervals for each.
- 2. The sensitivity of the measurement (with appropriate units)
- 3. The concentration and 95% confidence limit for the unknown in each experiment
- 4. The limit of detection for the measurement (with appropriate units).
- 5. The limit of quantitation for the measurement (with appropriate units).

## **Calibration Data**

| Pb <sup>2+</sup> concentration | Current |  |  |  |  |  |  |
|--------------------------------|---------|--|--|--|--|--|--|
| (ppm)                          | (μΑ)    |  |  |  |  |  |  |
| 10.0                           | 14.6    |  |  |  |  |  |  |
| 20.0                           | 33.1    |  |  |  |  |  |  |
| 50.0                           | 70.1    |  |  |  |  |  |  |
| 75.0                           | 121     |  |  |  |  |  |  |
| 100.0                          | 153     |  |  |  |  |  |  |

## **Unknown Results**

For Experiment A, you measure three replicate unknowns and find their responses to be 41.8  $\mu$ A, 39.4  $\mu$ A, and 43.5  $\mu$ A.

For Experiment B, you measure only one unknown and find its response to be 82.4 µA.

## Answers

|     | wers:   |   |
|-----|---|---|
| 1.  | Slope and intercept at the 95% confidence level: (5)                        | m = $1.5 + /- 0.2_2 \mu A/ppm$<br>b = $-0.6 + /- 13 ppm$                                  |
| 2.  | Sensitivity of the measurement: (2)   | 1.5 +/- 0.2 <sub>2</sub> μA/ppm   |
| 3A. | Concentration and 95% confidence limit for the unknown in Experiment A: (4) | 27 +/- 3 ppm (based on 3 x <sub>calc</sub> )<br>27 +/ 12 ppm (based on y <sub>avg</sub> ) |
| 4A. | LOD for Experiment A: (5)   | $s_{LOD} = 12 \mu A = b + 3s_b$<br>LOD = 8 ppm  |
| 5A  | LOQ for Experiment A: (2)   | $s_{LOD} = 42 \mu A = b + 10 s_b$<br>LOQ = 30 ppm (27)                                    |
| 3B. | Concentration and 95% confidence limit for the unknown in Experiment B: (4) | 50 +/- 10 ppm (54 +/- 14 ppm)   |
| 4B. | LOD for Experiment B: (2 for 4B and 5B combined)                            | Same as 4A  |
| 5B  | LOQ for Experiment B:   | Same as 5A  |

|        | Α                                | В                     | С        | D                      | Е              | F | G                       | Н             | I                  | J                                  | K                           | L        | M                              | N       | 0     | Р   | Q                | R          | S                                       | Т               | U   |
|--------|----------------------------------|-----------------------|----------|------------------------|----------------|---|-------------------------|---------------|--------------------|------------------------------------|-----------------------------|----------|--------------------------------|---------|-------|-----|------------------|------------|---|-----------------|-----|
| 1      |                                  | х                     | у        | ху                     | x <sup>2</sup> | n | <b>y</b> calc           | d             | d²                 | (y-y <sub>bar</sub> ) <sup>2</sup> | <b>y</b> <sub>Unknown</sub> |          |                                |         |       |     |                  |            |   |                 |     |
| 2      |                                  | 10                    | 14.6     | 146                    | 100            | 5 | 14.845                  | -0.2450178    | 0.06               | 4065.3                             | 82.                         | 4        |                                |         |       |     |                  |            |   |                 |     |
| 3      |                                  | 20                    | 33.1     | 662                    | 400            |   | 30.3365                 | 2.7635231     | 7.6371             | 2048.5                             |                             |          |                                |         |       |     |                  |            |   |                 |     |
| 4      |                                  | 50                    | 70.1     | 3505                   | 2500           |   | 76.8109                 | -6.7108541    | 45.036             |                                    |                             | 1        | -                              |         |       | ┷-  |                  |            |   |                 |     |
| 5      | ******************************** | . 75                  | 121      | 9075                   | 5625           |   | 115.54                  | 5.4604982     | 29.817             | 1818.2                             |                             | 180      |                                |         |       |     |                  |            |   |                 |     |
| 6<br>7 |                                  | 100                   | 153      |                        | 10000          |   | 154.268                 |               |                    | 5571.1                             |                             |          | .5491x - 0.6<br>$R^2 = 0.9938$ | 464     | *     |     |                  |            |   |                 |     |
| 8      |                                  |                       |          | 0                      | 0              |   | 0                       | 0             | 0                  |                                    | -                           | 140 - '  | K* = 0.9938                    | /       |       |     |                  |            |   |                 |     |
| 9      |                                  |                       |          | 0                      | 0              |   | 0                       | 0             | 0                  |                                    |                             | 120 -    |                                | •       |       |     |                  |            |   |                 |     |
| 10     |                                  |                       |          | 0                      | 0              |   | 0                       | 0             | 0                  |                                    |                             | 100 -    |                                | /       |       |     | 1                |            |   |                 |     |
| 11     |                                  |                       |          | 0                      | 0              |   | 0                       | 0             | 0                  |                                    | >                           | 80 -     | /                              | •       |       |     |                  |            |   |                 |     |
| 12     | Sums                             | 255                   | 391.8    | 28688                  | 18625          |   | 391.8                   | 7.105E-15     | 84.158             | 13571                              |                             | 60 -     | <b>/</b>                       |         |       |     | LOD/LOG          | Calculat   | ion for                                 | #4/#5           |     |
| 13     |                                  |                       |          |                        |                |   |                         |               |                    |                                    |                             | 40 -     |                                |         |       |     | S <sub>LOD</sub> | 12.3       | = b + 3s                                | b               |     |
| 14     |                                  | D =                   | 28100    |                        |                |   | D = (E12*               | F2)-(B12*B12  | 2)                 |                                    |                             |          | <b>*</b>                       |         |       |     | LOD              | 8.35       | =(s-b)/m                                | 1               |     |
| 15     |                                  | m=                    | 1.54915  |                        |                |   | m = ((D12               | 2*F2)-(C12*B  | 12))/C14           |                                    |                             | 20       |                                |         |       |     | S <sub>LOQ</sub> | 42.5       | = b + 10                                | )s <sub>b</sub> |     |
| 16     |                                  | b=                    | -0.64644 |                        |                |   | b =((E12*               | C12)-(D12*B   | 12))/C14           |                                    |                             | 0        | 50                             | 1       | 00    | 150 | LOQ              | 27.8       | =(s-b)/m                                | 1               |     |
| 17     |                                  | S <sub>y</sub> =      | 5.29647  |                        |                |   | $S_y = SQR$             | T(I12/(F2-2)) |                    |                                    |                             |          |                                | X       |       |     |                  |            |   |                 |     |
| 18     |                                  | S <sub>m</sub> =      | 0.07065  | % S <sub>m</sub> =     | 4.5606         |   | $S_m = SQF$             | RT((C17^2*F2  | 2)/C14)            |                                    |                             |          |                                |         |       |     |                  | İ          |   |                 |     |
| 19     |                                  | S <sub>b</sub> =      | 4.31203  | % S <sub>b</sub> =     | -667.04        |   | $S_b = SQR$             | T((C17^2*E1   | 2)/C14)            |                                    |                             |          |                                |         |       |     |                  |            | *************************************** |                 |     |
| 20     |                                  | S <sub>x</sub> =      | 3.74718  | % S <sub>x</sub> =     | 6.99           |   | $S_x = (C17/A)$         | ABS(C15))*S   | QRT((1/1           | )+(C21^2                           | *F2/C14                     | )+(E12/C | 14)-((2*C2                     | 1*B12)/ | C14)) |     | Calculati        | ion for #3 | В                                       |                 |     |
| 21     |                                  | X <sub>unk</sub> =    | 53.6079  |                        |                |   | x <sub>unk</sub> =(J2-C | C16)/C15      |                    |                                    |                             |          |                                |         |       |     | m                | 1.5491     |   |                 |     |
| 22     |                                  | x-int.=               | 0.41729  |                        |                |   | x-int.=-C1              |               |                    |                                    |                             |          |                                |         |       |     | b                | -0.6464    |   |                 |     |
| 23     |                                  | S <sub>x-int.</sub> = | 2.76761  | %S <sub>x-int.</sub> = | 663.24         |   | $S_{x-int.}=(C1)$       | 7/C15)*SQR1   | Γ((1/F2)+          | AVERAG                             | E(C2:C1                     | 1)^2/(C1 | 5^2*DEVS                       | Q(B2:B1 | 1)))  |     |                  |            |   |                 |     |
| 24     |                                  | R <sup>2</sup> =      | 0.9938   |                        |                |   | $R^2 = 1-(11)$          | 2/J12)        |                    |                                    |                             |          |                                |         |       |     | y1               | 41.8       | x1                                      | 27.4            |     |
| 25     |                                  |                       |          |                        |                |   | t = TINV(0)             | 0.05,F2-2)    |                    |                                    |                             |          |                                |         |       |     | y2               | 39.4       | x2                                      | 25.9            |     |
| 26     |                                  |                       |          |                        |                |   |                         |               |                    |                                    |                             |          |                                |         |       |     | у3               | 43.5       | х3                                      | 28.5            |     |
| 27     |                                  | value                 | unc. (s) | % rel uno              | s              |   |                         | 95% Confide   | ence Inte          | rvals                              |                             | t        | = 3.1824                       |         |       |     |                  |            |   |                 |     |
| 28     | m                                | 1.5491                | 0.071    | 4.5606                 |                |   |                         |               | m=                 | 1.5491                             | +/-                         | 0.224    | 8                              |         |       |     | Average          | 41.6       | uA                                      | 27.2            | ppm |
| 29     | b                                | -0.6464               | 4.312    | -667.04                |                |   |                         |               | b=                 | -0.6464                            | +/-                         | 13.72    | 3                              |         |       |     | Stdev            | 2.1        |   | 1.3             | ppm |
| 30     | х                                | 53.6079               | 3.74718  | 6.99                   |                |   |                         |               | x <sub>unk</sub> = | 53.608                             | +/-                         | 11.92    | 5                              |         |       |     | t                | 4.303      |   | 4.3             |     |
| 31     |                                  |                       |          |                        |                |   |                         |               | x-int.=            | 0.4173                             | +/-                         | 8.807    | 8                              |         |       |     | conf inv.        | 5.1        |   | 3.3             | ppm |