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A Comparative Study of Electrode Materials for the Analysis of Tap Water

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14. ABSTRACT

This study reports results obtained during a 10-week summer internship at NRL on two separate topics. First, we perform a comparative study of trace lead detection on nine different commercially available working electrodes using a benchtop potentiostat. Second, we characterize the best performing electrode of the set, the glassy carbon disk electrode, with all four trace metals currently in the assay.

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EXECUTIVE SUMMARY

The Naval Research Laboratory (NRL) is developing an assay and field kit for the analysis of drinking water that is locally sourced by soldiers in the field. The assay is based on square wave anodic stripping voltammetry in the presence of bismuth salts. A standard addition curve can be constructed on a small handheld electrochemical instrument in approximately 15 minutes. Current targets include four heavy metals and three model organic compounds. A library based analysis program provides qualitative identification of contaminants and deconvolution of mixtures, and can easily be expanded with additional compounds. Quantitative analysis is performed on trace heavy metals using dose/response curves.

Initial development of our assay and field kit relied on the use of commercially manufactured screen printed carbon electrodes (SPEs) that contain a pre-plated bismuth thick film. Unfortunately, these electrodes have recently been discontinued and are no longer available for purchase. Two alternative SPEs were tested as replacements, but compared to the original model their performance was poor. For certain contaminants, detection at EPA limits has been difficult to achieve reliably. A replacement working electrode with high sensitivity is needed.

This study reports results obtained during a 10-week summer internship at NRL on two separate topics. First, we perform a comparative study of trace lead detection on nine different commercially available working electrodes using a benchtop potentiostat. Second, we characterize the best performing electrode of the set, the glassy carbon disk electrode, with all four trace metals currently in the assay.

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1. INTRODUCTION

Lack of access to clean drinking water is a global problem. Focusing first on the United States, tap water typically comes from one of two sources: municipal networks and rural groundwater (wells). Municipal water can be drawn from rivers, lakes, or reservoirs; it is purified at a central water treatment plant and certified to be clean before being introduced into a network of water mains and service lines. Many of these networks are quite old. Pipes have historically been made from lead, a toxic material well known to produce negative health outcomes. While there has been a serious effort to eliminate lead water mains over the last century, service lines have proven more difficult to address because they mostly run under private property. Congress banned the use of lead pipes for drinking water in 1986 but existing service lines were allowed to remain in place. As a result, it was estimated in 2016 that nearly 7% of the service lines in the US are still made of lead and that roughly 400,000 schools and childcare facilities are impacted [1].

In addition to buried lead service lines, the interior of many structures contain copper pipes. Copper is less toxic than lead but it can be hazardous in sufficiently large amounts. The concentration of lead and copper in drinking water was formally regulated in the US by the Environmental Protection Agency (EPA) in 1991 through the introduction of the lead and copper rule (LCR). In the current revision, the EPA has set an action level for lead at 15 parts per billion (ppb) and copper at 1300 ppb.

Rural tap water may contain a larger variety of contaminants than municipal tap water. It can suffer from significant natural mineral content as well as contamination from farm runoff, nearby mining activity, or industrial processes such as manufacturing. Some well water systems include conditioning and/or purification steps such as water softening, pre-filtration, or disinfection to address groundwater quality issues, but not all residences choose to implement them. To be sure, the EPA has set numerous limits for metals and other chemicals that might be found in rural drinking water [2]. Yet, while groundwater conditions can change every few months testing for compliance is recommended only once per year for bacteria, nitrates, and nitrites; and once every three to five years for chemicals such as arsenic and radon [3].

Drinking water quality in many locations around the world can be considerably worse than domestic tap water available in the US. This is of significant concern to the military. Soldiers based overseas must drink locally available water. A large number of portable purification methods exist including boiling, chlor-floc tablets, and activated carbon filters. In large, semi-permanent installations routine testing is possible. However, there are currently no portable field tests for use by soldiers on field missions to verify that small-scale purification was successful.

1.1 Background

Tap water analysis typically takes place in central laboratories using various forms of mass spectrometry (GC-MS, LC-MS, ICP-MS), certain optical methods (ICPOES, AAS), and cell culture. Although exquisitely sensitive, this equipment is not portable. Some portable analysis methods for water quality do exist, but they are usually targeted for environmental waters, wastewater streams, or analysis of other non-potable types of waters such as swimming pools. In contrast, tap water is comparably very clean; typical water testing assays such as those for pH, chlorophyll (algae) content, turbidity, and salinity are not useful.

The Naval Research Laboratory (NRL) is currently exploring the use of electrochemistry for drinking water assays. Electrochemistry is naturally suited for the detection of trace heavy metals through the use of the anodic stripping voltammetry technique. Unfortunately, the classical method for performing this analysis uses mercury, a highly toxic material that is not suitable for handling by untrained personnel. Recently it was observed that bismuth can also be used for trace heavy metal detection [4]. Bismuth can

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be pre-dissolved in buffer concentrates or pre-plated onto detection electrodes, allowing it to be used with a minimum of handling. Furthermore, bismuth has very low toxicity compared to mercury, which makes it attractive for use in a field kit.

A second advantage of the electrochemical detection method is that it can be performed with a small number of inexpensive components: a potentiostat, a set of electrodes, and a laptop computer. Recent developments have made further strides in this direction. For example, there has been a trend towards the development of homebuilt miniaturized potentiostats [5] which can be battery powered, handheld, and use wireless communications. Some models completely eliminate the need for the laptop computer and run from either a cell phone or a built-in touchpad with LCD screen. Additionally, a wide variety of inexpensive and disposable screen printed electrodes (SPEs) are now commercially available.

Through the use of a homebuilt potentiostat and commercial SPEs, NRL has developed an assay for drinking water and a preliminary version of a portable field test kit based on the method of standard additions [6]. Initial data for our field kit was collected with pre-plated bismuth thick film disposable electrodes, which were shown to be accurate to about 2 ppb for trace lead detection in two different buffers. Unfortunately, these electrodes have been discontinued and are no longer commercially available. Work continued with an alternative electrode to extend the assay to include simultaneous detection of organics such as herbicides, pesticides, or toxic industrial compounds in the presence of trace metals [7]. Qualitative detection of organics and deconvolution of mixtures take place through the use of a previously published library-based algorithm [8], which can easily be expanded to include additional compounds of interest. Results for organics on the alternative electrode were acceptable. Quantitative detection of trace heavy metals takes place through dose/response curves. While the alternative electrodes were shown to be accurate in the mid to low ppb range, their quantitative performance is considerably worse than the original thick film SPEs.

The two different brands of commercially available carbon SPEs considered as a replacement were Metrohm DropSens bismuth oxide film electrodes and Pine Research large area (bare) carbon electrodes. Because the latter model has no pre-plated bismuth film, it must be used with bismuth salts dissolved in the sample buffer. We have observed that the required protocols and data quality of these two electrodes are very different from our original SPEs. Neither is capable of reliably reaching the 15 ppb EPA action level for lead or the 5 ppb EPA limit for cadmium. However, a review of the scientific literature suggests that it is routinely possible to obtain quantitative detection of lead at or below 1 ppb with a variety of different types of working electrodes (Table 1 in ref [9]). This raises the question: why are the replacement SPEs underperforming?

We have identified several possibilities. It is possible that there is an issue with the production quality of electrodes that we are using. Research groups that rely on screen printing tend to fabricate their own electrodes in house, which are likely to have a much higher quality than a mass-produced product that may have been sitting on a shelf for months. It is also possible that these in-house fabricated screen printed (working) electrodes do not include an embedded reference or counter; the use of high quality external auxiliary electrodes may significantly improve their performance. Other researchers favor more permanent working electrodes such as glassy carbon that are carefully cleaned and polished before use. These extra cleaning procedures may significantly enhance their performance. Finally, there are a large number of studies that focus on custom working electrodes made from a wide variety of chemically modified or nanostructured materials. It may be the case that the extra sensitivity or surface area imparted by these modifications are required to reliably reach detection at EPA limits. Alternatively, it is possible that the problem originates in our homebuilt instrument. That is, the potentiostat could be injecting too much noise into the data to be reliable at very low concentrations.

This study is an attempt to find an alternative working electrode for our field kit that can accurately detect lead down to roughly 1 ppb concentrations. To eliminate the possibility of noise in our homebuilt potentiostat, we use a commercially available CH Instruments benchtop unit, model 1040 C. We explore

the performance of nine different commercially available products. This includes both disposable and non-disposable variants, and considers working electrodes made from carbon, gold, and platinum. The use of chemically modified working electrodes is not feasible in a field kit because they are not easily obtained in high volume and there is no data on shelf life or batch-to-batch variation. To minimize the number of data sets required for evaluation, only one heavy metal is targeted in the initial portion of the study: lead at moderate ppb concentrations. The best performing electrode sets were identified and used in additional experiments at lower concentrations. Finally, we perform experiments with glassy carbon to construct dose/response curves for the three other heavy metals currently in NRL's assay: copper, zinc, and cadmium.

2. MATERIALS AND METHODS

Screen printed platinum ceramic electrodes (product #RRPE2001PT-6), screen printed gold ceramic electrodes (product #RRPE2001AU-6) and screen printed carbon electrodes with 4x5 mm working electrode (product #RRPE1002C) were obtained from Pine Research Instrumentation (Durham, NC). Bismuth thick film electrodes (product #DRP-BI10, discontinued), bismuth oxide modified screen printed carbon electrodes (product #DRP-110BI-U50) and gold nanoparticles modified screen printed carbon electrodes (product #DRP-110GNP) were obtained from Metrohm DropSens (Riverview, FL). A 3 mm diameter glassy carbon disk electrode (product #CHI104), a 2 mm diameter platinum working electrode (product #CHI1102), and a platinum wire counter electrode (product #CHI115) were obtained from CH Instruments (Austin, TX). A 6 mm diameter silver/silver chloride refillable reference electrode (product #E-Ag/AgCl_70) was obtained from Redox.me (Norrköping, Sweden). A 1.6 mm gold electrode (product #MF-2014) was obtained from BASi (West Lafayette, IN).

With one exception, all measurements in this study were performed on a benchtop potentiostat, model 1040 C (CH Instruments, Austin, TX). The leads coming from this instrument were terminated with alligator clips. The connection between the instrument and the electrodes was dependent on the form factor of the specific electrodes being used. For discrete electrodes, alligator clips were directly connected to each electrode terminal. In contrast, commercially available SPEs contain working, sense, and reference electrodes on a single compact substrate. Each SPE is terminated with printed electrical contacts designed to be mated to a card edge connector for quick exchange between experiments. A breakout cable is necessary to connect SPEs to the potentiostat; the specific solution depends on the electrode brand.

DropSens SPEs are 34 mm long x 10 mm wide and contain 3 printed contacts. A breakout cable (product #CAC, Metrohm DropSens) terminated with a 3-pin card edge connector on one end and a set of 2 mm banana plugs the other end was used to make a connection between the SPE and the potentiostat leads. Pine Research SPEs are slightly larger at 61 mm long x 15 mm wide and have five electrical contacts instead of three. The breakout cable consisted of two components. First, a Pine Research compact voltammetry grip mount, model #AKSPEGRP1, was used to hold the SPE; it is terminated with a 5-pin card edge connector on one end and a female USB mini-B connector on the other. A USB mini-B to banana plug cable purchased from Pine Research Instrumentation (product # RRPECBL2) was used to make the final connection to the potentiostat leads. A photograph of the two sets of breakout cables described here is shown in Figure 1a.

A Cell Stand from BASi (model #C3) was used with a magnetic stir bar to perform mixing during cleaning and accumulation steps. Stirring was turned off immediately before the square wave voltammetry sweep was performed. A photograph of the experimental setup for discreet electrodes is shown in Figure 1b.

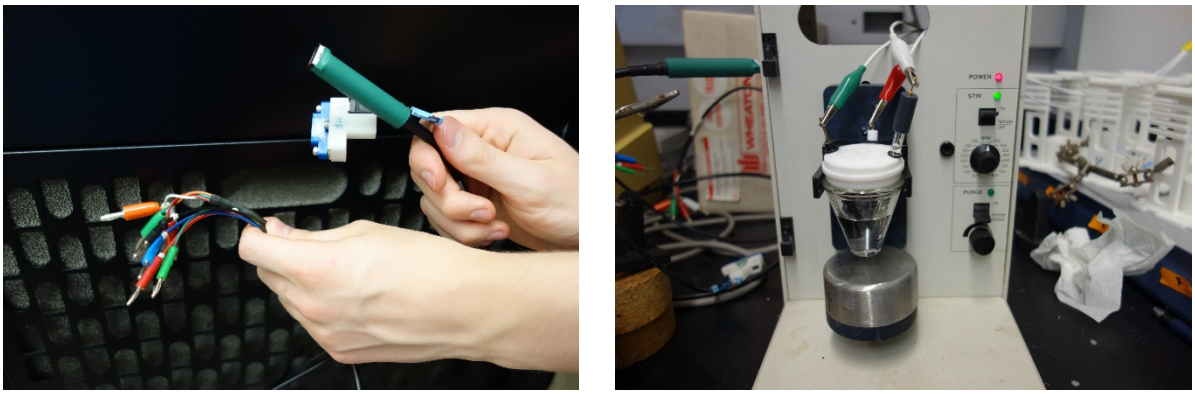

Figure 1. Experimental setup. (a) Breakout cables used for connecting the DropSens and Pine Research screen printed electrodes to the CH Instruments potentiostat leads. (b) Photograph of an experiment set up with discrete electrodes on a C3 Cell Stand for magnetic stirring.

Trace metal standard solutions of lead, copper, zinc, cadmium, and bismuth, all in nitric acid, were obtained from Agilent (Santa Clara, CA). 1 M acetate buffer at pH 4.5 was made from sodium acetate purchased from Sigma-Aldrich, and diluted to 0.1 M for final use. Testing was performed in glass containers and used deionized water to minimize background contamination.

All experiments were performed in 0.1 M acetate buffer at pH 4.5. The buffer was spiked with 500 ppb bismuth for all electrode tests except for the two film SPEs. The square wave anodic stripping voltammetry technique was used for trace metals detection. The procedure has three steps, and other than minor changes in the deposition and cleaning potentials, is identical to that used by Wang and co-workers [4]. First, the electrodes are held at a cleaning potential for 30 s. Next, the electrodes are held at an accumulation potential for 120 s. Finally, a square wave sweep is performed. For most experiments this was 20 Hz with 25 mV amplitude and 5 mV step size. Although most of the data presented in this work was collected over a ten week period, the first three data sets are older. For this reason, there are a few protocol exceptions in some of the older experiments; a partial list of exceptions appears in Table 1. All of the protocol exceptions are published in the Appendix.

Accumulation of heavy metals take place at large negative voltages. However, different electrode materials have different potential windows in which they can operate without solvent breakdown, interference from dissolved oxygen, or producing hydrogen evolution from acidic solutions. Table 1 shows the selected potentials sorted by electrode material.

Electrode Material	Cleaning Pot. (30 s) (With Stirring)	Accumulation Pot. (120 s) (With Stirring)	Square Wave Sweep (No Stirring)
Bismuth Thick Film SPE	N/A	-1. 0 V (300s)	-1.0 V to 0 V
Bismuth Oxide SPE	-1.2 V (10 minute activation in KOH)	-0.9 V (300 s)	-0.9 V to -0.5 V
Carbon SPE	N/A	-1.5 V	-1.5 V to +0.5 V
Glassy Carbon*	+0.3 V	-1.5 V	-1.5 V to +0.3 V
Gold	+0.3 V	-1.0 V	-1.0 V to +0.3 V
Platinum	+0.5 V	-1.0 V	-1.0 V to +0.5 V

Table 1. Potentials used for the various electrode materials presented in this work. There is one exception: glassy carbon used a +0.5 V cleaning potential and voltammetry endpoint for the 1-10 ppb trace lead experiments only. All potentials are referenced to Ag/AgCl. Note that the scan range for the bismuth oxide SPE was very small to avoid solubilizing the film on the electrode. This allowed one electrode to be used for multiple experiments.

3. RESULTS

Initial experiments were performed to identify which, if any, of the nine different electrodes examined in this work might be sufficiently sensitive to reach 1 ppb detection of trace lead. We attempted to construct dose/response curves for deionized water samples spiked at moderate lead concentrations: large enough that if there was a signal, we could easily find it, but small enough to be relevant to tap water analysis. The data sets varied somewhat between experiments, but in all cases concentrations of spiked lead included some data between 10 ppb and 100 ppb.

Some of the electrodes tested were designed to be disposable. Others were designed to be cleaned and reused. For consistency, dose/response curves were constructed using a single electrode regardless of disposability. Two of the SPEs were film electrodes that required no additional bismuth in solution. Experiments always started at the lowest trace lead concentration and moved sequentially to the highest. An example data set and dose/response curve is presented in Figure 2.

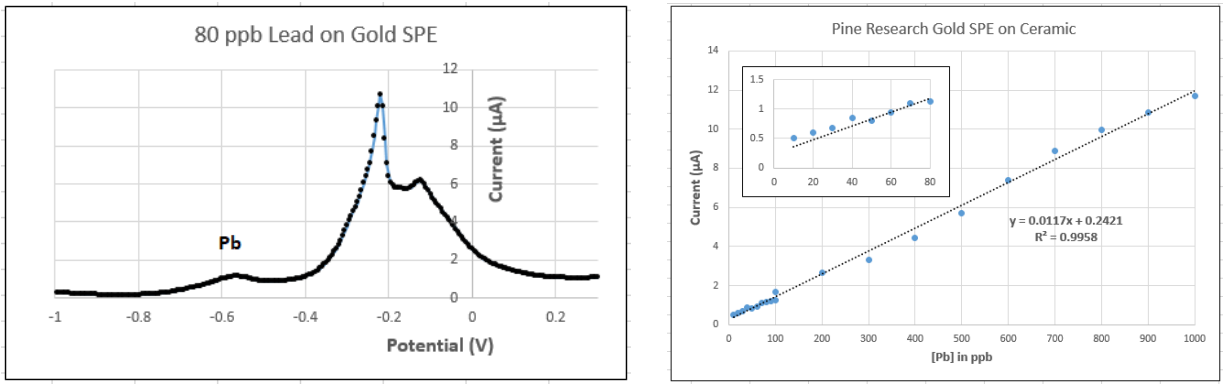

Figure 2. Experimental data collected on a Pine Research gold SPE on ceramic. (a) Raw data for deionized water spiked with 80 ppb lead. The peak sits around -0.565 V, although we believe the reference electrode on this SPE has degraded and shifted all of the peaks to a more negative voltage. This issue will be discussed later in the report. (b) The finished dose/response curve, constructed from raw data. The inset is an expanded view of the 0-80 ppb range.

Although a few of the electrodes completely failed and were deemed unsuitable for trace metals analysis, most performed marginally well and had at least some linear region in their dose/response curve. Whenever possible, limits of detection were calculated. Observations and calculated (or estimated) limits of detection from the experimental series are presented in Table 2. Additional details are provided in the Appendix.

The first entry in Table 2 is the bismuth thick film electrode originally used in our assays. It is no longer available for purchase but is included for data comparison purposes. With the exception of glassy carbon (n=5) and the gold disk electrode (n=1), all of the samples were tested in triplicate in order to obtain error bars and to allow a more quantitative LOD estimation using the formula [10] below, which takes into account the sensitivity of the assay as well as the signal to noise ratio.

$$LOD = \frac{3.3\ \sigma}{m}$$

Here, m is the slope of the best fit linear regression line and σ is the (population) standard deviation of the blank, which in this case is buffer spiked with 500 ppb bismuth but with no lead. Replicate runs were performed in the same solution and with the same electrode; the goal was to eliminate random noise from the instrument rather than to correct for experimental error in the preparation of the sample. In cases where a blank is unavailable, such as the method of standard additions used in our field kit, the standard deviation of the lowest concentration data point may be substituted as an estimate of the blank. It is

important note that we consider this equation to be an estimation because the regression line fit is very sensitive to the specific background subtraction and normalization procedures applied to the raw data.

Electrode Material	Brand	SPE	LOD [ppb]	m (x1000)	Notes
Bismuth thick film on Carbon SPE	DropSens	Yes	2.49	0.2	Electrodes are no longer available. Very steep slope near peak required extra background subtraction step.
Bismuth Oxide film on Carbon SPE	DropSens	Yes	39.9	3.8*	Electrodes require extra activation step in KOH. Ltd scan range to allow electrode re-use; no bismuth peak to scale to. Extra BG subtract step.
Carbon SPE	Pine Res.	Yes	71.4	3.5	Data collected on NRL's custom built potentiostat. Experiment run with n=5.
Glassy Carbon	CHI	No	1.03	9.7	LOD calculated from Figure 3a.
Gold Nanoparticles on Carbon SPE	DropSens	Yes	N/A		Many extra peaks. Results are difficult to interpret.
Gold on Ceramic SPE	Pine Res.	Yes	19.2	5.9	Silver paste reference degraded. LOD calculated from Figure 3b.
Gold Disk	BASi	No	about 90	1.1	LOD could be significantly improved with replicates.
Platinum on Ceramic SPE	Pine Res.	Yes	N/A		Unable to assign a peak for lead.
Platinum Disk Electrode	CHI	No	N/A		Unable to assign a peak for lead.

Table 2. Summary of the trace lead LOD for various electrodes tested in this study. Any electrode that is not an SPE must be used with an external counter and reference. The first two electrodes in the table are bismuth film electrodes. All other electrodes require 500 ppb bismuth spiked into solution. The bismuth oxide electrode had a limited scan range to prevent the film from solubilizing at the end of the scan. Sensitivity is defined as the slope of the regression line; a larger number is better. For meaningful comparisons, regression lines are always fit after the full background subtraction, bismuth normalization, and blank subtraction procedure except for the bismuth oxide SPE, which had no bismuth peak in the data to normalize to. Bismuth exhibited two peaks in all of the experiments with gold electrodes. The more positive of the two seemed to be the most consistent measure for bismuth signal. We were unable to assign a peak for lead on any of the platinum electrodes.

The best two electrodes were identified as the glassy carbon disk electrode from CH Instruments and the screen printed gold on ceramic electrode from Pine Research. An additional data set was collected on each of these electrodes in the 1-10 ppb range. Dose/response curves are shown in Figure 3. For both electrodes, the raw data required background subtraction and normalization to the bismuth peak height in order to remove noise and obtain reasonable error bars. A blank subtraction was also applied in order to get a y-intercept close to zero. The exact procedure is discussed in detail in Section 4.

In the case of glassy carbon, we suspect that something happened to the working electrode surface when sampling at 7 ppb concentration. This could be observed directly from the raw data as a large spike (to roughly 130% of previous values) in the height of the bismuth peak, followed by a crash (at 8+ ppb) to values that were sometimes lower than the previous averages. Since all samples contain 500 ppb bismuth, the height of this peak should be steady. The affected data in Figure 3a appear to shift to a new trend line, possibly with a new slope. For this reason, the regression line on glassy carbon was only fit to the first seven data points. Limits of detection were calculated as 1.03 ppb when using the standard deviation of the blank, or 2.59 ppb when using the standard deviation of the 1 ppb data point. However, visual observation of the raw data suggest that there is still about 250 nA of headroom between the signal of the 1 ppb data point and the blank at the lead peak, which we considered to be -0.57 V vs. Ag/AgCl. Most potentiostats can obtain roughly 1-10 nA resolution before external shielding around the sample is

required. This suggests that it may be possible to obtain data in the 0.1 – 1 ppb concentration range with glassy carbon and further improve the LOD. Additional experiments will be necessary to verify this claim.

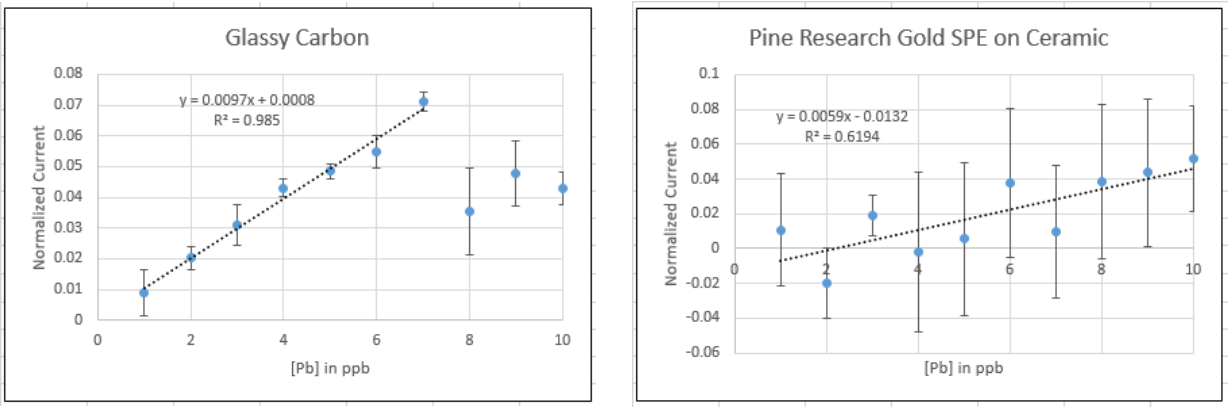

Figure 3. Dose/response curves for lead at 1-10 ppb with (a) a glassy carbon disk electrode, and (b) a Pine Research gold SPE on ceramic. The error bars are ± 1 (population) standard deviation. Background subtraction, normalization to bismuth peak height, and blank subtraction were applied.

In regards to the gold electrode, we noticed in the data from Figure 2a that the bismuth peak on the gold SPE was shifted negative by more than 0.2 V. We suspect that the Ag/AgCl paste reference on this electrode has degraded. For the data shown in Figure 3b, we replaced it with an external Ag/AgCl reference; this shifted all of the peaks back to their proper locations. We did observe a very small shoulder in the data close to -0.38 V vs. Ag/AgCl, but the location of the peak changes voltage slightly as a function of concentration and is very difficult to track. The data in Figure 3b were constructed by assuming all lead peaks were located at -0.38 V and using the same background and normalization procedures that were applied to glassy carbon. The resulting regression line has a positive slope but the error bars on the data are very large, indicating that there is too much noise on this electrode for quantitative detection below 10 ppb. Limits of detection were calculated at 19.2 ppb when using the standard deviation of the blank, or 18.1 ppb when using the standard deviation at the 1 ppb data point. It is possible that a slightly better trend may emerge if peak tracking is implemented, but given our success with glassy carbon this strategy was not pursued.

A final set of experiments was performed with glassy carbon for the three other heavy metals in our assay: cadmium, zinc, and copper. Data are divided into two sets. Data for cadmium and zinc are presented at moderate concentration in Figures 4a and 4b, respectively. For both of these metals, the full background subtraction, normalization, and blank subtraction procedure was applied to obtain the dose/response curves. The cadmium peak was identified at -0.75 V vs. Ag/AgCl, while the zinc peak was identified at -1.025 V vs. Ag/AgCl. In the cadmium dataset, the point associated with the lowest concentration (10 ppb) had a very low bismuth peak height (about 25% of the average) and was discarded from the regression line fit. Similarly, in the zinc dataset the point at 40 ppb had a very low bismuth concentration (about 60% of the average) and was also discarded from the regression line. Furthermore, the zinc data points at 90 and 100 ppb had peaks that shifted significantly from the -1.025 V average. In Figure 4b, these two points were collected at -0.98 V and -0.97 V, respectively.

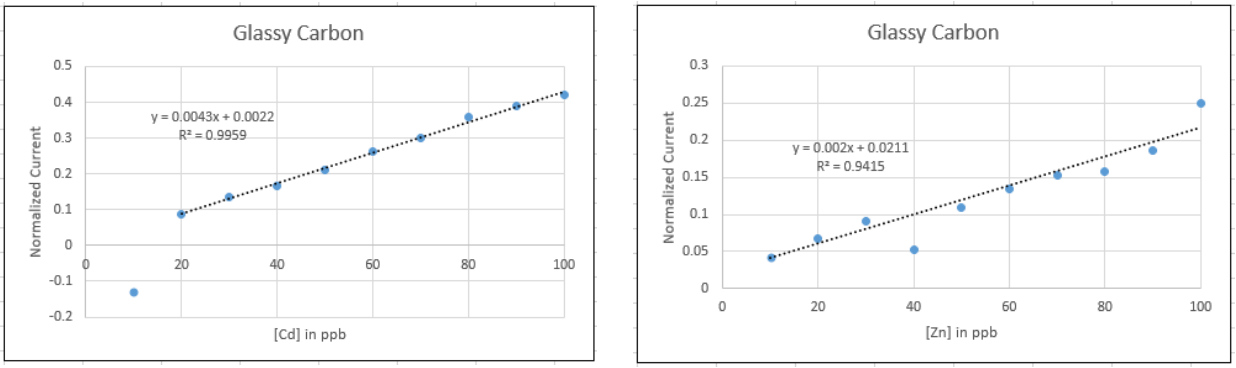

Figure 4. Dose/response curves at 10-100 ppb for (a) cadmium and (b) zinc. Background subtraction, normalization to bismuth peak height, and blank subtraction were applied.

High concentration data for cadmium and zinc are presented in Figures 5a and 5b, respectively. It was observed that at these higher concentrations, the location of the trace metal peaks began to shift. Assuming a constant -0.75 V potential for the cadmium peak and -1.025 V potential for the zinc peak resulted in very poor quality dose/response curves. Instead, peak tracking was required. Interestingly, the location of the bismuth peak remained tightly distributed around -0.14 V vs. Ag/AgCl. In both datasets, normalizing the trace metal peak height to the bismuth peak height reduced the amount of noise present. However, due to the absolute size of the peaks (in µA) the background subtraction and blank subtraction had little effect, and were not used in Figure 5.

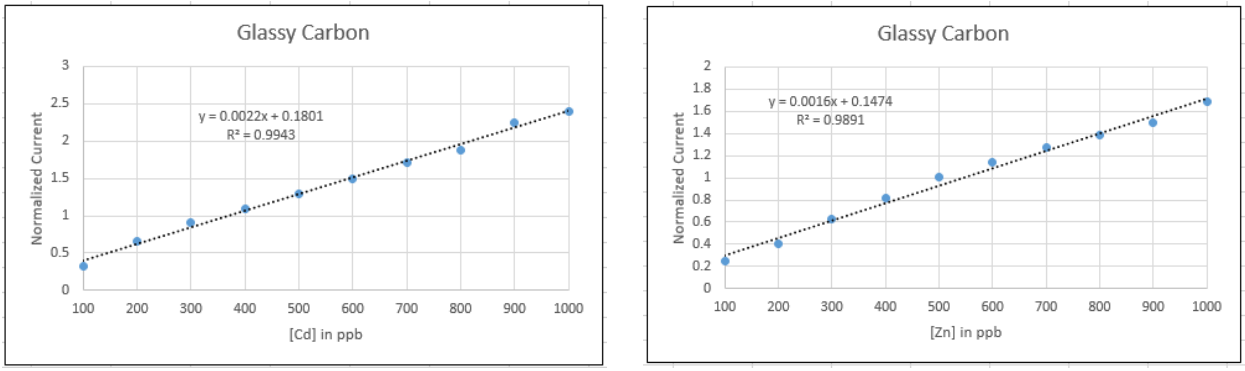

Figure 5. Dose/response curves at 100-1000 ppb for (a) cadmium and (b) zinc. Peak tracking was implemented in order to obtain this data as well as a normalization to the height of the bismuth peak. No other background subtraction or blank subtraction was needed, probably due to the size of the peaks as compared to the background.

Unlike all other heavy metals considered in this study, copper dose/response curves proved challenging to construct. An example is presented in Figure 6. Interestingly, while the copper peaks all maintain a tight distribution around +0.015 V vs. Ag/AgCl, the bismuth peak changes both location and size, eventually shrinking down to a very small value. If a background subtraction is performed first, then scaling to the bismuth peak essentially divides the highest concentration data by a number very close to zero, causing the dose/response curve to diverge. As a result, the normalization procedure was applied to low concentration data only, as shown in Figure 6a. In the absence of bismuth normalization, the data in Figure 6b appear to level off around 800 ppb concentration, although there is a significant amount of scatter.

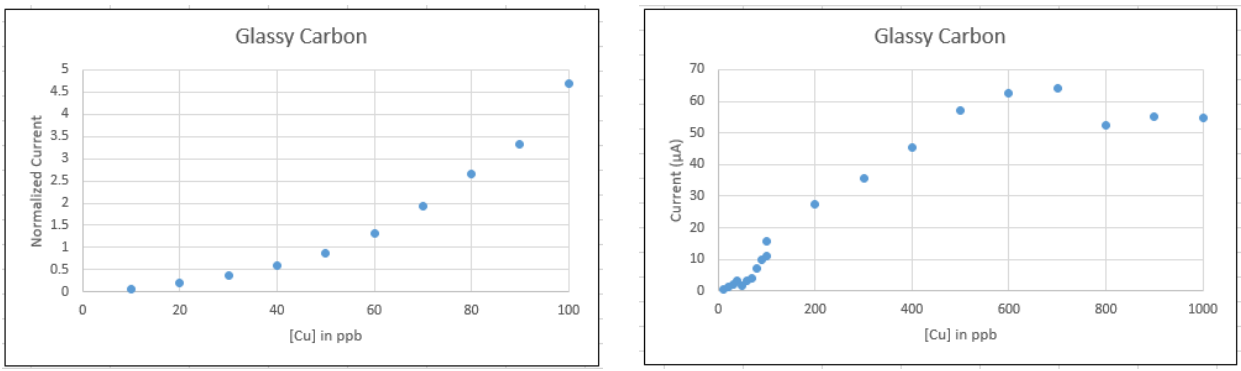

Figure 6. Dose/Response curves for copper (a) at moderate concentrations with normalization to the bismuth peak, and (b) the full data set out to 1000 ppb but without normalization to the bismuth peak. Significant scatter was observed in the lower concentration data without bismuth normalization. Background subtraction was performed in both cases, but the blank was not subtracted.

4. DISCUSSION

The goal of this study was to identify a replacement electrode(s) for our field kit capable of trace lead detection at 1 ppb. Our data suggest that this goal can be achieved, but it is highly dependent on electrode material and form factor, data normalization procedure, and instrument noise.

We found that glassy carbon performed better than any of the other materials considered in this study, including the discontinued bismuth thick film SPE. However, this type of electrode is not disposable and would be challenging (though by no means impossible) to implement as part of a field kit because it requires cleaning and polishing before use. Considering only disposable electrodes, gold on ceramic from Pine Research outperformed all of the other replacement candidates. We note that the particular gold SPE used in this study was old and likely had a degraded Ag/AgCl electrode. It is possible that fresh electrodes may have better performance. However, it is unclear if the other three trace metals in our assay will show up on gold. This is especially important for zinc given that it requires a large negative potential for detection and gold has a reduced accessible potential window with a negative limit of -1.0 V vs. Ag/AgCl in aqueous solution as compared to -1.5 V for carbon. We intend to further study these particular gold electrodes in the future. Interestingly, the addition of gold nanoparticles to the SPEs did not seem to positively affect any of the limits of detection for trace metal analysis, and instead introduced a variety of other peaks that were detrimental to the study (data not shown).

In regards to data analysis, quantitatively estimated limits of detection were found to be highly dependent on the background and normalization procedure implemented. We tried a number of different approaches but settled on the following procedure in this work. All implemented steps are based on experimental observations. The first observation is that voltammograms have a background that varies from scan to scan; on some of the SPEs this background can be larger than the signal. That is, regions in the voltammogram that have no signal associated with the sample can still have a non-zero current, and it is not necessarily the same from sample to sample. To eliminate this, we implement a simple single-point background subtraction procedure. We set the signal at the most positive voltage in each scan to be zero by subtracting it from the value at every voltage in the scan. Then, bismuth and trace metals are assigned a peak signal (in µA). This procedure is repeated for each data point. A list of peak signals is tabulated.

The resulting data from the background subtraction step typically show reasonable linearity. However, they are only relevant to the working electrode on which they were collected. Different working electrodes have different amounts of surface area, and will require separate calibration curves. We note that all experiments are run with 500 ppb bismuth. The height of this peak should be uniform for each electrode and vary between different electrodes based on the amount of active area. The idea of using the bismuth peak as a "built-in" internal standard was originally proposed by Wang [4]. Following

this theory, we hypothesize that the height of all trace metal peaks will scale with the active area of the electrode in the same way that bismuth does. Then, by normalizing all of the tabulated data (including the blank) to the height of the bismuth peak, it may be possible to create a calibration curve that will work for other types of carbon electrodes. At the very least, it should be capable of adjusting for errors due to batch to batch variations in active area of the same type of SPE, or changes in active area due to the polishing and cleaning procedure used with permanent electrodes. Interestingly, implementation of this procedure did allow us to use the 7 ppb data point in the regression line for glassy carbon in Figure 3a, and it also somewhat linearized the 8-10 ppb data points, albeit with large error bars and on a trend line that may have a different slope. The ultimate test of the bismuth normalization procedure will be using pre-constructed calibration curves to make predictions about unknown samples. We intend to pursue this idea in future work.

The third observation is that, even after background subtraction and normalization, the signal of the background subtracted and normalized blank (buffer with 500 ppb bismuth but no trace metal) at voltages where a trace metal peak should appear is non-zero. We subtract this blank signal from the signal of the sample in the tabulated data. This procedure should set the intercept of the dose/response curve regression line very close to zero. Note that we did not force the intercept to be zero in any of the data presented here. Doing so will slightly change the slope and R-squared value, and may have a small effect on the LOD calculations.

We observed that implementing the bismuth normalization is not always effective. In some cases it reduces noise in the data; in other cases it increases it. However, in all cases except copper, monitoring the bismuth peak height for outliers seems to be an effective method of data rejection. Further studies including the identification of unknowns will be required to refine and finalize the background and normalization procedure used to create dose/response curves for our assay.

In regards to instrument noise, we found that replicate measurements were required to get the error bars small enough to obtain quantitative estimates of the LODs near 1 ppb, even with a commercial benchtop potentiostat. There are two impacts of this observation. The first is that any homebuilt potentiostat used in our field kit must be carefully designed to minimize noise issues if 1 ppb detection limits are desired. The second is that the time to complete the assay will be impacted if replicate measurements are necessary. The goal for the field kit is to get from sample to answer in less than one hour. At just under 4 minutes per experiment, a standard addition curve with four data points can be constructed in approximately 15 minutes. To do this in triplicate would require 45 minutes, but if additional data is required due to a noisy handheld instrument it is possible that we may not meet the one hour target. One possible solution is multiplexing, although implementing simultaneous measurement capabilities in our homebuilt instrument will require additional hardware development.

4.1 Detection at Higher Concentrations

The data collected in this work can be broken into three decades based on the spiked concentration: low (approx. 1-10 ppb), medium (approx.10-100 ppb), and high (approx. 100-1000 ppb). Interestingly, the amount and type of normalization required to eliminate excessive noise in dose/response curves constructed over these ranges on glassy carbon electrodes is different. For detection in the lowest range, the three step procedure outlined above is necessary, although as discussed earlier the bismuth normalization does not always help. In contrast, in the mid concentration range simply plotting the raw data is usually sufficient to obtain linear results, although they do benefit from the full normalization procedure. At high values, we observe that the assigned locations of the trace metal peaks begins to shift with concentration. Linear regression line fits can usually still be obtained, but it requires going through the raw data and picking the actual peak height regardless of where it is located, rather than assigning a fixed peak voltage location. In some cases such as Figure 9 in the Appendix, two separate regression lines are required to fit the data. At very high concentrations the slope can level off to zero. Normalizing to bismuth does not fix these issues. One possibility is the formation of metal complexes in solution that

behave differently than single ions. Another is that the active area of the working electrode may be getting saturated. A third is that there might not be enough bismuth in solution to form a fused alloy with such large concentrations of metals. Regardless of the cause, given that most EPA limits for trace metals fall in the low to medium ppb range, one can conclude that if the concentration of any metal (except possibly copper) is above 100 ppb, there is no need to quantitate the data. Don't drink the water.

4.2 Reference Electrodes

Electrochemistry is typically performed with three separate electrodes. The counter electrode sources and sinks current to the experiment, and is typically made from an inert material. The reference electrode provides a stable and known reference voltage for the experiment. The working electrode can be made from a variety of different materials and is typically the location of any chemistry that is taking place.

Up to this point, this report has been concerned with the composition and performance of the working electrode. However, some of the data collected in this study were impacted by the type or condition of the reference electrode. Screen printed electrodes are composite structures that include a counter, reference, and working electrode in a single compact package. The DropSens electrodes in this work use a pseudo-silver reference. The Pine Research electrodes in this work use a reference made from Ag/AgCl paste. In contrast, the disk electrode setup relies on a high quality external reference, a single-junction Ag/AgCl electrode.

In cases where a reference electrode goes bad, we observe that all of the assigned peaks shift their location, and not necessarily by the same voltage. That is, the distance between individual peaks (eg, the voltage difference between the bismuth and lead peaks) may also change. When this happens, the resulting peak heights and ratios may be affected. We observe that the pseudo-silver reference electrodes used in most DropSens SPEs are particularly bad; while there is batch to batch variation we observed the failure rates as high as 10-20%. In contrast, most Pine Research SPEs use Ag/AgCl paste electrodes. When used only once or just a few times before disposal, the paste electrode performs very well. However, it will eventually degrade if re-used enough times; this is what we observed with the gold SPE on ceramic in Figure 2.

For a field kit, it may be the case that the use of an external Ag/AgCl electrode is necessary to ensure high quality results, even with an SPE. The disadvantage of this approach is that single-junction reference electrodes are fragile, and they cannot be allowed to dry out. They must be stored in KCl buffer in order to maintain their performance. Alternatively, it might be possible to verify the accuracy of a silver paste reference on an SPE by including a small amount of trace silver in the buffer; this should give a signal at 0 V vs. Ag/AgCl. Any significant shift in the location of this peak can be used to reject data sets.

4.3 Copper

The results for cadmium and zinc are straightforward and appear similar to lead. For all three of these metals on glassy carbon, the bismuth peak was always tightly located between -0.13 V and -0.15 V vs. Ag/AgCl and its size did not change as a function of metal concentration. In contrast, copper shows some interesting trends. The bismuth peak location is variable and shifts from -0.15 V to almost -0.23 V as the copper concentration is increased, and its size decreases to almost zero as this happens. This suggests that the two metals are interacting with each other beyond the formation of a fused alloy, and it makes fitting a linear regression line to dose/response curves difficult. Also of note is that, unlike every other metal considered, the copper peak appears at a more positive potential than bismuth. This issue is discussed at length by Wang and co-workers [11]. It is suggested that while bismuth forms a fused alloy with lead and cadmium, copper and bismuth compete for the same surface sites on carbon. Furthermore, the presence of copper in solution will completely mask the appearance of a zinc signal due to the formation of a Zn-Cu complex at copper concentrations as low as 100 ppb. In these cases, Wang suggests

that the addition of gallium in the buffer at 1000 ppb will create Ga-Cu complexes and unmask the Zn peaks, although this is not necessary unless solution levels of copper are sufficiently high.

Wang has suggested that it may be possible to get a linear dose/response curve at moderate copper concentrations if peak area is considered instead of peak height [11]. However, we performed this analysis and found that it gave a modest improvement at best (data not shown).

4.4 Recommendations for the NRL Field Kit

Based on the results of this study, we make the following three recommendations for NRL's field kit. First, while commercially available SPEs are easy to use and disposable, none of the replacement models we tested were suitable for trace metal detection at very low levels. We suggest implementing glassy carbon electrodes, albeit with a custom made holder that is capable of fitting inside of the Falcon tubes currently used in the field kit. This will require the inclusion of a small tube with KCl for reference electrode storage as well as a polishing kit. Second, in order to facilitate noise reduction replicate measurements are necessary; we suggest multiplexing NRL's homebuilt potentiostat so that it is capable of taking four measurements simultaneously. Finally, based on our observations on copper as well as a review of the work by Wang and co-workers [11], we suggest placing an upper limit of 100 ppb on the amount of copper allowed in the drinking water analysis. Any values higher than this should result in the water being rejected, even though the EPA limit for copper is 1300 ppb. This is due to both the difficulty of obtaining a quantitative prediction for copper over 100 ppb as well as the ability of copper to completely mask zinc and more generally to displace bismuth from the assay, which may affect the detection of other trace metals. In cases where high concentrations of copper are impossible to remove from tap water, the option to repeat the analysis with 1000 ppb gallium in the buffer may be necessary. Note that these guidelines will also affect the composition of the stock solutions used for constructing the standard addition curve in the field. We suggest keeping the concentration of all metal standards well below 100 ppb.

5. CONCLUSIONS

The performance of nine different working electrodes was studied with a goal of selecting a replacement for NRL's field kit capable of detection limits of 1 ppb for trace lead spiked into deionized water in the presence of bismuth. Glassy carbon was found to meet this requirement, with a quantitative LOD estimated at 1.01 ppb from this study. Further refinements and additional data may push this limit lower. Background subtraction and normalization procedures were discussed. These procedures were also found to be relevant to trace cadmium and zinc, although quantitative predictions of copper at higher concentrations will be challenging due to interactions between itself and bismuth, and its ability to form complexes with zinc and therefore mask the peak. Based on the observations in this study, recommendations were made for NRLs field kit for tap water testing.

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7. APPENDIX

Dose/response curves and additional information are presented for each of the entries in Table 2 from which a LOD could be calculated. All potentials listed in the Appendix are referenced to Ag/AgCl.

Bismuth thick film SPEs were obtained from Metrohm DropSens. These were the original electrodes used with the NRL field kit, and at least for trace lead detection, they were shown to be capable of attaining reliable data to very low ppb levels. The electrodes are no longer commercially available and therefore no data has been collected to evaluate their suitability for cadmium, zinc, copper, or any of the model organics considered in NRL's previous studies. Typically, film electrodes are designed to be single use. However, we have found that these particular thick film electrodes could be re-used multiple times with minimal loss of performance.

The data in Figure 7 was collected on July 6, 2022. Solution conditions were slightly different from the current study; the buffer also had 0.2 M NaCl added. No electrode cleaning step was performed. Accumulation time was 300 s at -1.0 V. Square wave voltammetry parameters were -1.0 V to 0 V, 15 Hz, 25 mV amplitude, 4 mV step size. In order to obtain reliable data, an additional slope subtraction was required in a region where there was no activity from the metals. In this case, slope and intercept were obtained from the region between -0.6 V and -0.5 V vs. Ag/AgCl. Then the analysis procedure consisted of four steps instead of three, as follows: first, the background was subtracted (in this case, the value of the signal at -0.5 V vs. Ag/AgCl). Next, the data between -0.6 V and -0.5 V was fit to a regression line. The value of this regression line (the baseline) was subtracted from each point in the voltammogram. The lead peak was identified at -0.448 V, and data were tabulated for each concentration tested. Third, the signal of the blank was subtracted. It is important to note that the data had no actual bismuth peak because the potential was not swept sufficiently positive to create one. However, the signal was estimated to be roughly 150 µA based on the potential at or near 0 V for each voltammogram. This is significantly larger than any bismuth peaks from any of the other electrodes considered in this study (typically 30 µA or less), probably due to the density of the bismuth in the film on the electrode. As a final step, normalized current was created by dividing the actual current by 150 µA. While this has absolutely no effect on the fit of the regression line, it does normalize the slope and therefore allow direct comparisons to other calculated sensitivity values in this work.

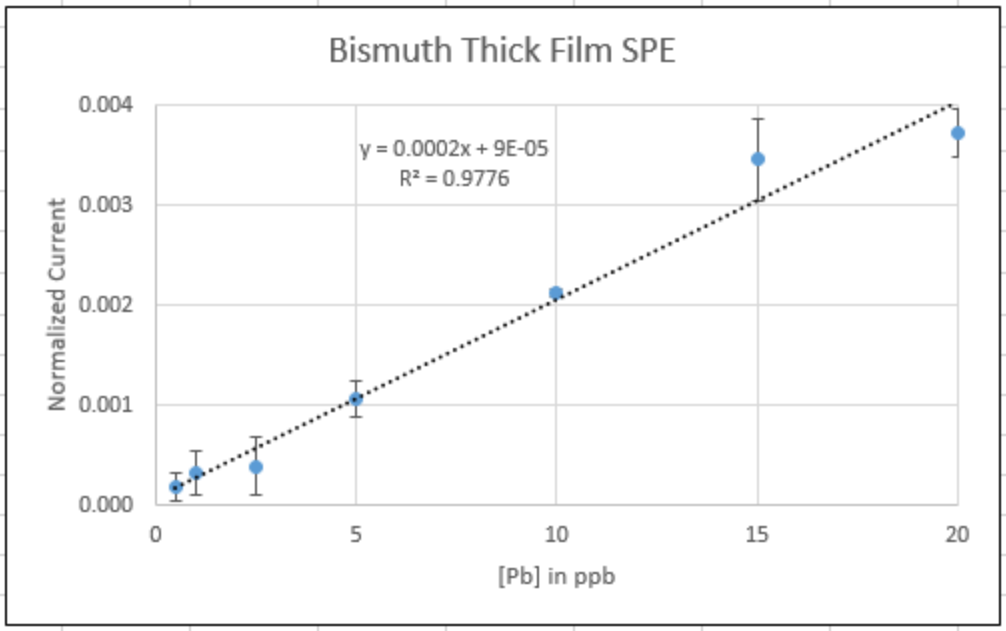

Figure 7. Dose/response curve for bismuth thick film SPE. LOD calculated to be 2.49 ppb based on the (population) standard deviation of the blank. The error bars are ± 1 standard deviation.

Bismuth oxide film SPEs were also obtained from Metrohm DropSens. They were originally selected because they were a logical drop-in replacement for the (now obsolete) bismuth thick film SPEs. However, their usage and performance is quite different. The bismuth oxide electrodes must first be activated in 0.1 M KOH for 10 minutes at -1.2 V. Once this has been performed, the electrode potential must remain more negative than the bismuth peak in order to prevent the film from solubilizing and dissolving into the sample. This peak is typically located at -0.14 V on carbon, but the pseudo-silver reference on the DropSens electrodes was found to be unreliable and bismuth could be shifted as far negative as -0.45 V. These electrodes are inherently designed for single use scenarios, although we found that as long as the applied potential was kept sufficiently negative, they could be re-used.

The data in Figure 8 was collected on November 22, 2022. Data was collected in 0.1 M acetate buffer at pH 4.5, but with no bismuth added. There was no cleaning step, although a separate 600 s activation step in 0.1 M KOH at -1.2 V as outlined above was necessary. Accumulation time was 300 s at -0.9 V. Square wave voltammetry parameters were -0.9 V to -0.5 V, 15 Hz, 25 mV amplitude, 4 mV step size. Similar to the bismuth thick film SPEs, in order to obtain reliable data an additional slope subtraction was required in a region where there was no activity from the metals. In this case, slope and intercept were obtained from a regression line of the data in the region between -0.8 V and -0.75 V vs. Ag/AgCl. First, background subtraction took place at -0.8 V. Next, the baseline subtraction took place. Data were tabulated and the blank was subtracted. There was no bismuth peak to normalize to. In fact, it was impossible to make any kind of estimate as to how large it might be. Therefore, sensitivity listed in Table 2 for bismuth oxide SPEs cannot be directly compared to other values in the table.

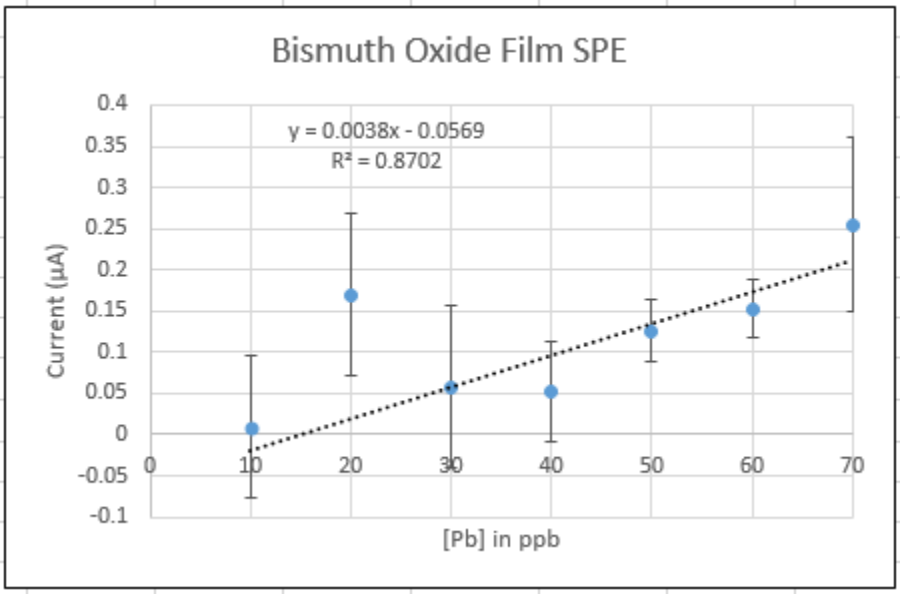

Figure 8. Dose/response curve for bismuth oxide film SPE. LOD calculated to be 39.90 ppb based on the (population) standard deviation of the blank. The 20 ppb data point has been assumed to be an outlier and was not included in the regression line calculation, although there is no rigorous mathematical basis for making this choice. The error bars are ± 1 standard deviation.

Large area carbon SPEs were obtained from Pine Research Instruments. These electrodes were selected after it was observed that the DropSens bismuth oxide SPEs were not performing well. There were two reasons for this choice. First, we wanted to eliminate the 10 minute activation step required for the bismuth oxide, which was cutting into the already short 1 hour time limit for the full standard addition field assay. Secondly, we hoped to be able to more easily re-use the carbon electrodes. Since there is no film pre-plated on the electrode, the sample buffer must contain bismuth at 500 ppb. Even though bismuth is solubilized and stripped from the working electrode at potentials more positive than about -

0.14 V, in this case it simply goes back into solution and can be re-adsorbed during subsequent accumulation steps.

The data in Figure 9 were collected between June 9-11, 2023 on NRL's homebuilt CStat Series II instrument. Note that the CStat has significantly more noise than the CH Instruments 1040 C potentiostat, and therefore it is likely that the calculated LODs could be improved. However, based on our observations from using these electrodes over a six-month period, we find it unlikely that the data will achieve the 1 ppb LOD sought in this work no matter which instrument it is collected on.

In the data presented in Figure 9, there was no cleaning step, which may also contribute to lower LODs. Accumulation took place over 120 s at -1.5 V. Square wave voltammetry parameters were -1.5 V to +0.5 V, 15 Hz, 25 mV amplitude, 4 mV step size. The standard background subtraction, blank subtraction, and bismuth normalization procedure described in this report was applied to the data. Interestingly, the data shows two separate slopes: one at concentrations below about 100 ppb, and a second one at higher concentrations. However, in this particular case no peak tracking was necessary. The slope of the regression line in the lower concentration series was used to calculate the LOD. All lead peaks showed up at roughly -0.852 V. The bismuth peak showed up at roughly -0.46 V. For this particular experiment, five replicates were performed instead of the standard three.

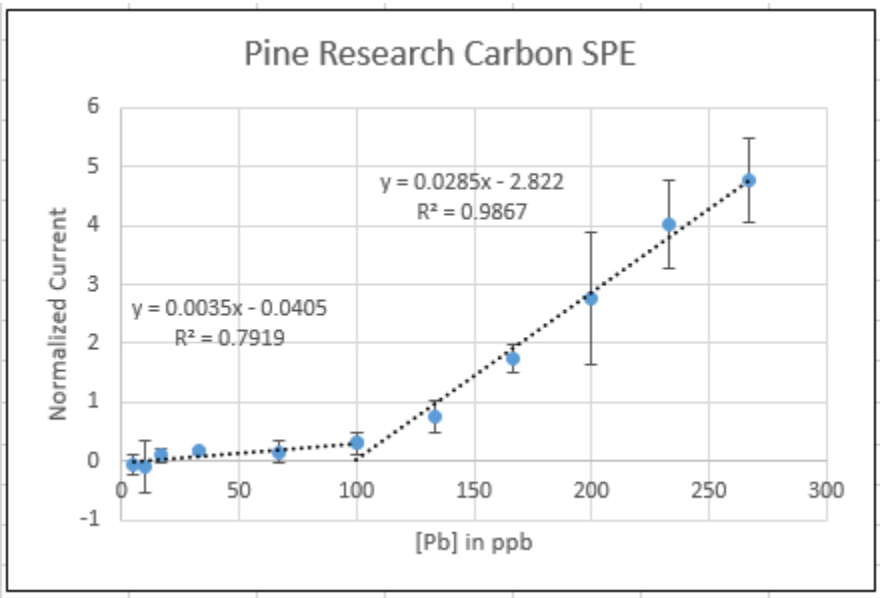

Figure 9. Dose/response curve for carbon SPE. LOD calculated to be 71.40 ppb based on the (population) standard deviation of the blank. Note that this could be significantly improved by applying a cleaning step before metal accumulation, and by collecting data on a lower noise instrument. The error bars are ± 1 standard deviation.

Data for the glassy carbon electrode (August 15, 2023) and the Pine Research gold on ceramic SPE (August 16, 2023) are shown in Figures 3a and 3b, respectively.

The final electrode in Table 2 that was capable of providing a LOD was the gold disk electrode by BASi. This electrode was selected based on our observation that glassy carbon was a significant improvement over carbon SPEs, possibly due to the external Ag/AgCl reference electrode and the ability to clean (polish) before use. Given that the gold (on ceramic) SPE performed significantly better than screen printed carbon, we hypothesized that the gold disk electrode would be the best performing electrode of the set. Unfortunately, it turned out that this was not the case. It appears that the high concentration data is very linear, but there is significant scatter at lower concentrations. Unlike all other electrodes, only one data point was obtained for each concentration. As a result, there are no statistics on these data and the LOD had to be qualitatively estimated. Based on experience with other electrodes, we suspect that replicate measurements will significantly improve the LOD.

The data in Figure 10 was collected on August 9, 2023. Figure 10a shows the full range of data. Figure 10b presents the 10-100 ppb concentration range, which has significantly more scatter. Accumulation took place over 120 s at -1.0 V. Square wave voltammetry parameters were -1.0 V to +0.3 V, 20 Hz, 25 mV amplitude, 5 mV step size. The standard background subtraction, blank subtraction, and bismuth normalization procedure described in this report was applied to the data. LOD was qualitatively estimated to be 90 ppb.

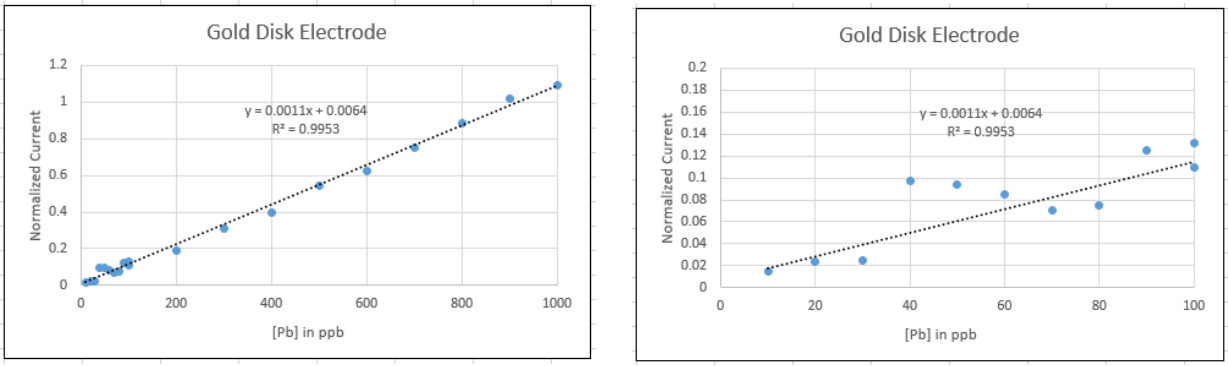

Figure 10. Dose/response curve for the BASi gold disk electrode. (a) Full range of collected data. (b) Data over 10-100 ppb. LOD estimated from the lower concentration data to be about 90 ppb. This could be significantly improved with replicate data sets.