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Simultaneous Detection of Organics and Trace Heavy Metals in Tap Water

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14. ABSTRACT

The goal of this study is to determine if organics such as herbicides, pesticides, or toxic industrial compounds can be added to our tap water assay. Results were obtained during a 10-week summer internship by one of the authors. We present data from three model organic compounds in presence of bismuth salts with and without trace amounts of copper. A brief discussion of preliminary results for library based chemical identification and deconvolution of mixtures is included; this was developed from a previously reported algorithm.

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EXECUTIVE SUMMARY

The Naval Research Laboratory (NRL) is developing a portable test kit for the evaluation of drinking water for use by soldiers in the field. The assay leverages developments in bismuth chemistry [1] to achieve the detection of multiple heavy metals at EPA relevant concentrations in a single vial. Construction of a standard addition curve takes roughly fifteen minutes to complete and can be performed on a small, portable instrument. Currently, there are four trace metal targets that can be detected: lead, zinc, copper, and cadmium.

The goal of this study is to determine if organics such as herbicides, pesticides, or toxic industrial compounds can be added to our tap water assay. Results were obtained during a 10-week summer internship by one of the authors. We present data from three model organic compounds in presence of bismuth salts with and without trace amounts of copper. A brief discussion of preliminary results for library based chemical identification and deconvolution of mixtures is included; this was developed from a previously reported algorithm [2].

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1. INTRODUCTION

Contaminated drinking water is an issue that affects communities worldwide. In the United States, it is estimated that 7% of existing municipal water service lines are lead pipes [3]. Furthermore, rural well water can have significant mineral content as well as contamination from farm runoff, mining activity, or other industrial sources. Contaminated drinking water is hazardous to local communities as well as soldiers in the field who must drink available supplies. While a number of portable purification methods exist such as activated carbon filters or chlor-floc tablets, there are currently no portable methods to verify that decontamination was successful. A rapid and portable test kit is desired.

Current gold-standard analytical methods for the evaluation of water quality are ubiquitous but not easily brought into the field. These include various forms of mass spectrometry (GC-MS, LC-MS, ICP-MS), certain optical methods (ICPOES, AAS), and cell culture. Although some portable analysis methods do exist, they are usually targeted for environmental waters, wastewater streams, or analysis of other non-potable types of waters such as swimming pools. In contrast, drinking water is comparably very clean; typical water testing assays such as those for pH, chlorophyll (algae) content, turbidity, and salinity are not useful.

In municipal sources, the only hazardous contaminants that are likely to be found are the heavy metals lead and copper. Electrochemistry is naturally suited to the detection of trace levels of heavy metals in aqueous solution. Unfortunately, the classic method of performing this test involves the use of mercury, which is an acutely hazardous substance. Several years ago it was observed that bismuth salts can serve as a replacement for mercury [1, 4]; bismuth is a much less toxic alternative and is suitable for use by untrained personnel.

Recently, we have developed an assay and a field kit for the analysis of drinking water from municipal taps. The assay can be performed with disposable, screen printed electrodes on a battery powered handheld device [5] connected to a laptop computer. The field kit is based on the method of standard additions. It contains four 50 mL Falcon tubes in a Styrofoam block, each pre-filled with buffer concentrate and bismuth salts. To perform a test, each tube is filled to the 30 mL line with tap water, shaken, and then analyzed with the hand-held instrument by dipping a screen printed electrode (SPE) into the sample. At 3 minutes per tube, the entire test takes roughly 15 minutes or less to complete. Note that standard collection practices such as letting water sit undisturbed in the source pipes for 8-24 hours before testing are typically used in residential dwellings for water quality in order to observe the worst case scenario. In this work, we are more concerned with real time results and post-purification analysis, and such collection practices are not necessary.

The goal of this report is to extend our assay to rural (well) water testing. Compared to municipal supplies, rural water sources may contain additional contaminants from natural mineral deposits as well as organics, especially from farm runoff. However, typical electrochemical testing for organics take place under a very different set of solution conditions than that for trace metals. We desire a single test that can identify both. This report explores two different issues. First, we develop a hybrid assay that can detect both organics and trace metals simultaneously. Second, we describe initial results using an algorithm implemented in Excel to identify and, for mixtures, de-convolute into constituent organics and trace metals.

2. MATERIALS AND METHODS

Three separate instruments were used to perform the tests in this study. The main focus of this report is NRL's homebuilt instrument, the CStat Series II v3.875. The commercial instrument used for gold-standard comparisons was a CH Instruments model 760 E. A third instrument, the ACEstat [6], was

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obtained from the Army and tested alongside the other two potentiostats for comparisons and to help evaluate the quality of the CStat.

Screen printed carbon electrodes with a 4x5 mm working electrode, product #RRPE1002C, were obtained from Pine Research Instrumentation (Durham, NC) and used for all experiments without modification. For all three instruments, a Pine Research compact voltammetry grip mount, model #AKSPEGRP1, was used to hold the electrodes. It uses a 5-pin card edge connector with 2.54 mm spacing to make contact with the screen printed electrodes and maps the signals to a USB mini-B female connector as specified in Table 1. Use of this grip mount allows the user to quickly change screen printed electrodes between experiments, and eases the cable requirements necessary to connect it to the chosen instrument. Note that one "spacer" (a piece of another electrode) was used on the bottom side of the SPE for a snug fit in the grip mount.

Card Edge Pin	Electrode	USB mini-B pin & ID	USB Wire Color
1	Counter	Pin 5 / GND	Black
2	Working	Pin 1 / VBus	Red
3	(No Connection)	Pin 4 / ID	(No wire)
4	Sense	Pin 3 / D+	Green
5	Reference	Pin 2 / D-	White

Table 1. A pin and wire map for the construction of custom cables specifically for Pine Research screen printed electrodes in the compact voltammetry grip mount. Electrode orientation in the connector is printed side face up. Card edge pins are numbered left to right. In a 3-wire potentiostat, the sense and working electrodes are identical, although connection 2 is still preferred because D+/D- are a twisted pair.

A standard USB-A to mini-B cable was used to connect the grip mount to the CStat. A custom cable was fabricated to connect the grip mount to the ACEstat, made by clipping the USB-A end of a commercial cable and soldering on a 3-pin Molex female header and pins, DigiKey product #WM8001-ND and #WM2558-ND. A USB mini-B to banana plug cable purchased from Pine Research Instrumentation (product # RRPECBL2, Mini-USB Cell Cable) was used as a breakout for the CH Instrument potentiostat; its factory cables end in alligator clips which were attached to the banana plugs to make the final connections to the grip mount. A photograph of a typical test setup is shown in Figure 1.

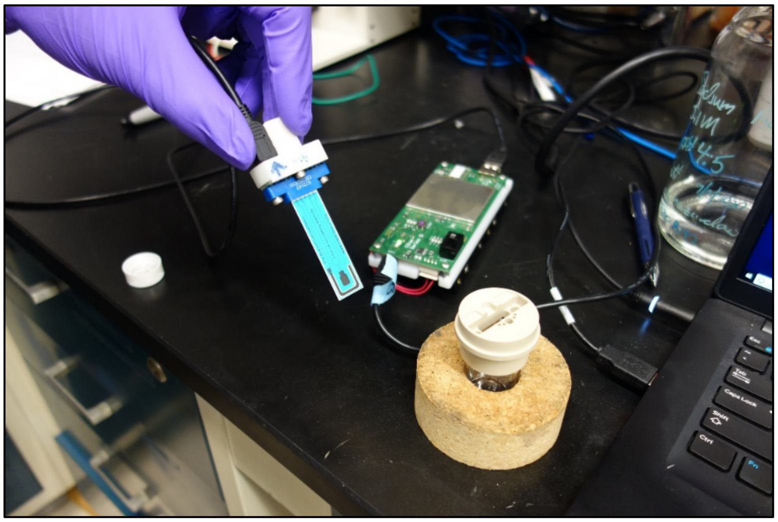

Figure 1. A photograph of a typical experiment. A screen printed carbon electrode (size: 61 x 15 x 0.36 mm) is inserted into a grip mount and is ready to be placed into the test cell, on the bottom right. The CStat Series II instrument connects to the grip mount through a standard USB A to mini-B cable. A laptop computer is used to run the assay.

Trace metal standard solutions of lead, copper, zinc, cadmium, and bismuth, all in nitric acid, were obtained from Agilent (Santa Clara, CA). Paraquat dibromide, diquat dichloride, bisphenol A (BPA), and ferricyanide were obtained from Sigma-Aldrich (St. Louis, MO). 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. Phosphate buffered saline (PBS) at pH 7.4 was obtained from Sigma-Aldrich and used without modification. Testing was performed in glass scintillation vials and used deionized water to minimize the amount of trace metals in the background.

3. RESULTS AND DISCUSSION

Standard electrochemical tests for trace metals use the anodic stripping voltammetry technique, typically in acidic buffer such as 0.1 M acetate at pH 4.5. In this technique, the working electrode is held at a large negative potential for a specified amount of time in order to accumulate metals in solution. Ideally, the solution is stirred during this accumulation step, although we did not stir in the results reported here. Once the accumulation has finished, stirring is terminated and the potential is swept from negative to positive. The current profile resulting from this sweep has peaks in characteristic locations that can be used to identify the type and concentration of any trace heavy metal that might be present in solution. A square waveform (eg, staircase shape) is typically used for this type of analysis, and in order to detect trace metals the sweep typically takes place in the presence of bismuth at a concentration of 500 ppb.

In contrast, organics are often studied by a technique known as cyclic voltammetry (CV) in which the potential is cycled from positive to negative and then back to positive in a linear fashion. PBS at pH 7.4 is an appropriate buffer for many organic compounds.

It was desired to develop a single technique that is compatible with both organics and metals. For this purpose, we settled on the following conditions. All solutions were tested in 0.1 M acetate buffer using cyclic square wave voltammetry. The electrochemical assay has four steps. First, a cleaning step is performed by holding the screen printed electrode at large positive voltage. Second, a square wave sweep (as opposed to a linear CV sweep) from positive to negative voltage is used to identify organics. Third, the electrode is held at a large negative voltage to accumulate metals. Finally, a square wave sweep from negative to positive voltage is used to identify metals. Cleaning and accumulations steps were both 120s in this work. All square waves were implemented at 15 Hz, with 25 mV amplitude and 4 mV step size. These values were selected based on the results of a parametric study with copper at solution concentrations between 100 and 1000 ppb in 100 ppb steps (data not shown). In cases where bismuth was added to solution, the concentration was always 500 ppb.

The exact voltages (vs. Ag/AgCl) used in the sweeps in this study were occasionally varied. Ideal endpoints for screen printed carbon electrodes are +1.0 V for organics and -1.5 V for metals, but unfortunately the ACEstat is not capable of producing voltages beyond ±1.1 V. In order to make accurate comparisons, much of the data collected on all instruments used scan parameters that matched the ACEstat limitations.

To compare the performance of the three different instruments, CV test results for the redox couple ferricyanide are shown in Figure 2. While peak heights are slightly different, the general shape of the compound and location of the peak around 0.4 V are very close, which we interpret as good agreement between the instruments. Note that the CH Instruments data appears to have significantly less noise than the two homebuilt instruments. This may be due to the heavy digital filtering that is applied in software; neither homebuilt instrument has this feature.

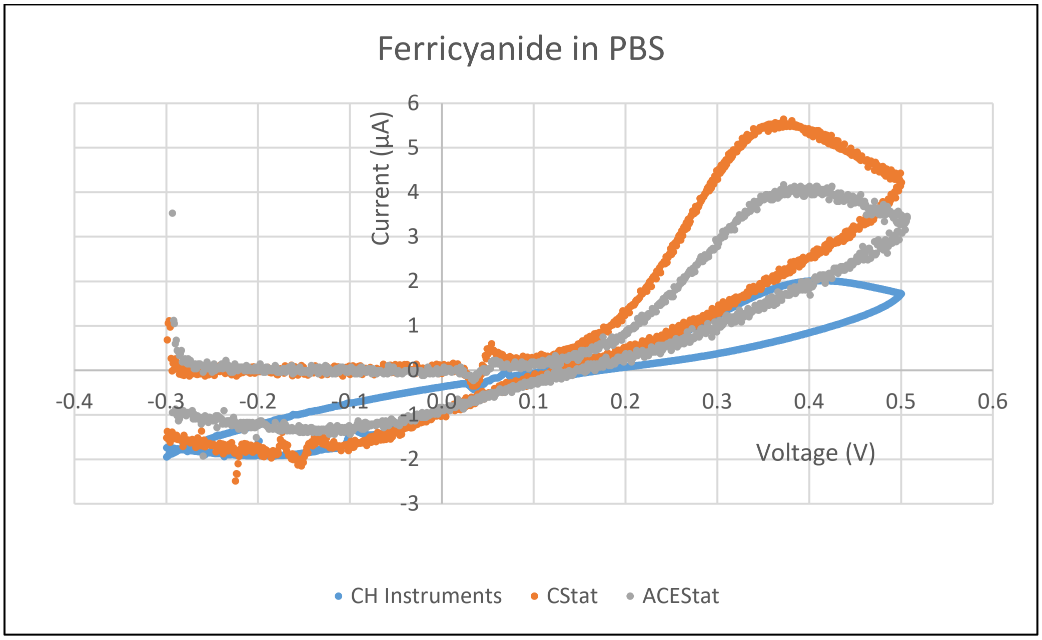

Figure 2. CV scan of ferricyanide by each of the three instruments used in this study. Scans were from +0.5 V to -0.3 V vs. Ag/AgCl and were run at 100 mV/s. The large peak around 0.4 V is characteristic of ferricyanide. The spike at 0.05 V is probably from the carbon ink used to print the electrodes.

Three model organic compounds were selected for this study. Paraquat and diquat are both herbicides. BPA is an industrial chemical sometimes found in plastics used to make water bottles. Voltammograms for these compounds alone, as well as mixed together are shown in Figure 3 in the presence of 500 ppb bismuth. The concentration of all organics was 100 µM.

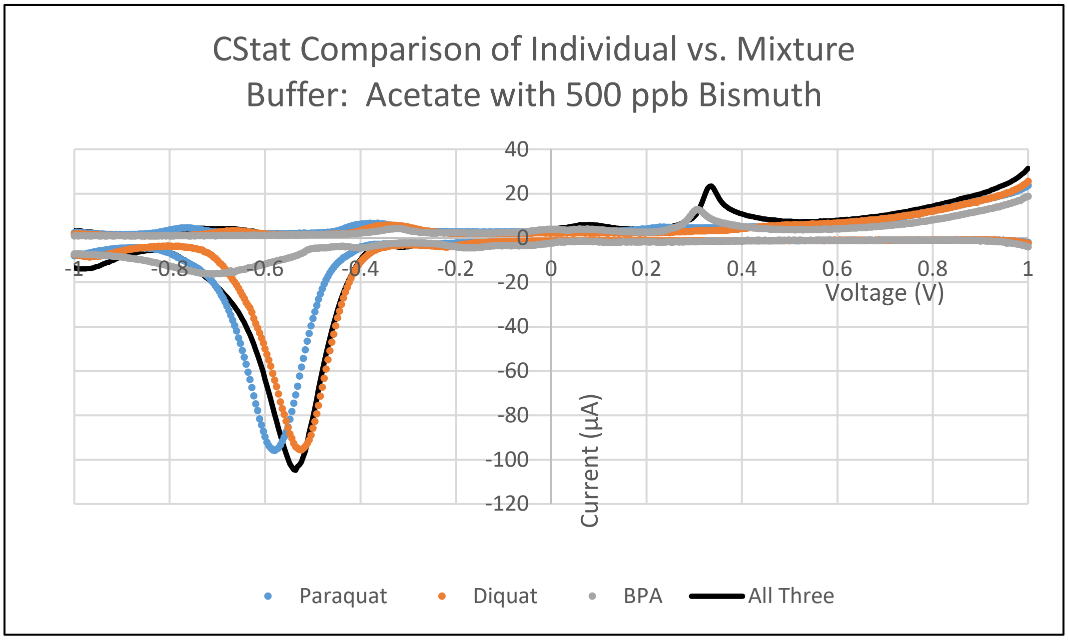

Figure 3. Voltammograms for paraquat, diquat, BPA, and a mixture of all three. All organics were 100 µM concentration in 0.1 M acetate buffer, pH 4.5, with 500 ppb bismuth. Cyclic square wave voltammetry scan parameters were 15 Hz, 25 mV amplitude, 4 mV step size. Applied voltage was +1.0 V to -1.0 V vs. Ag/AgCl.

These data suggest that it is easily possible to detect each of the selected organics at 100 µM concentration in solution conditions that favor trace metal detection. Furthermore, certain peak features such the positive BPA peak at 0.35 V and the positive diquat peak at -0.65 V are also present in the mixture, suggesting that deconvolution may be possible.

Figure 4 shows sample results for mixtures of organics and metals, also taken on NRL's CStat instrument. In this case, a mixture of copper and paraquat is shown, along with the resulting dose/response curve for quantitative predictions.

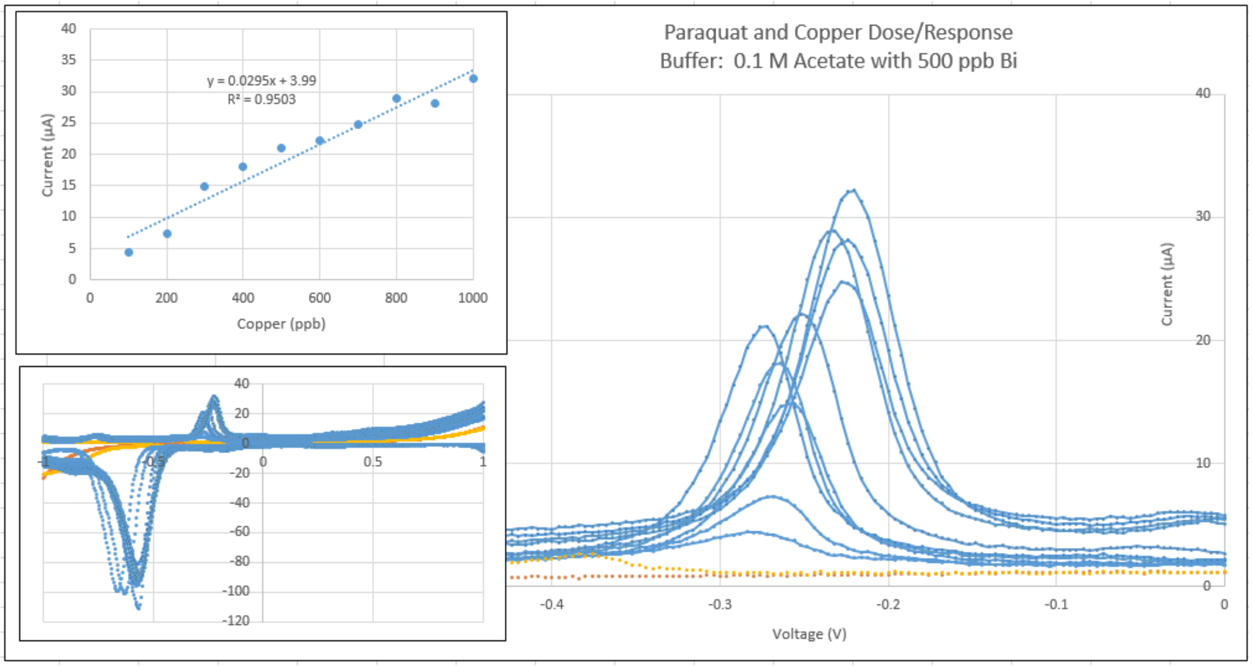

Figure 4. Results for mixtures of trace amounts of copper and the herbicide paraquat in 0.1 M acetate buffer with 500 ppb bismuth. The orange and yellow data contain no copper; they are buffer and bismuth only, respectively. The bottom left inset is the full data scan. The main plot is an exploded view of the copper peak, which sits between -0.2 V and -0.3 V vs. Ag/AgCl. The top left inset is the resulting dose/response curve, which can be used for predictions. We suspect that the small copper peak shifts in voltage are a result of excessive capacitance in the CStat hardware.

We have attempted to perform chemical identification of the samples and de-convolute mixtures using a previously reported Excel algorithm [2]. Briefly, two sets of coefficients are generated in this procedure. The first set is generated from a least squares fitting from a library of organics and metals to the sample scan using the solver function from Excel. The second set is generated through a calculation comparing the sample to the library using a correlation function. The two sets of coefficients are multiplied together to arrive at a final score. A large score indicates a high likelihood of that particular library compound being present in the sample. If two or more scores are high, the sample is likely a mixture. While much optimization work remains to be done, preliminary results are presented in Figure 5. In this case, the analysis algorithm was able to correctly identify both bismuth and diquat in the sample.

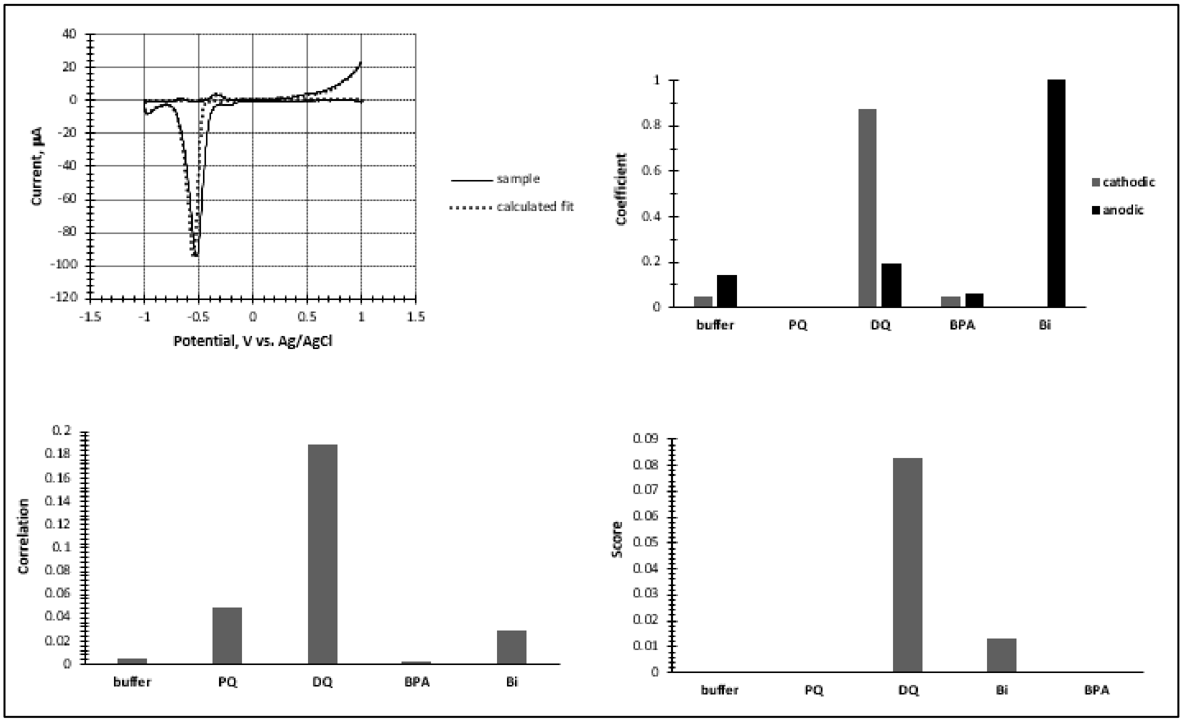

Figure 5. Data analysis for a solution containing diquat and 500 ppb bismuth in 0.1 M acetate buffer. The top left figure is a voltammogram of the sample (solid line) along with a best calculated fit based on a linear least squares comparison to the library using Excel's solver function (dotted line). The resulting coefficients for this fit are shown in the top right figure. The bottom left figure is the coefficients for the library correlation function calculation. The final score is the bottom right figure, showing a likely mixture of diquat and bismuth.

Future work will explore the effect of background subtraction and normalization on data analysis. In the results presented in Figure 5, each scan was first broken into forward and reverse components. The current at the first data point in each segment was assigned to be zero, and then the actual value at the endpoint was subtracted from the rest of the segment. In this way, the samples and library components could be compared directly. It may be the case that an alternative or supplemental background subtraction will make the analysis more accurate. In addition, we plan to explore the possibility of normalizing all scans to the 500 ppb bismuth peak. In Figure 2, it was observed that different instruments reported different peak heights for the same compound. This procedure may remove variation between instruments, as well as electrode-to-electrode variation to account for different amounts of surface area, broadening the applicability of library data.

4. CONCLUSIONS

The results of this study show that it is possible to detect organics and trace heavy metals in the same sample using a homebuilt handheld potentiostat. We have developed hybrid scan parameters that contain elements of both the cyclic voltammetry procedure standard for electrochemical detection of organics and the anodic stripping voltammetry procedure for trace heavy metals. Three model organics and their mixtures were studied in acetate buffer and in the presence of bismuth. We demonstrated that it is possible to obtain a dose/response curve for trace metals in the presence of an organic. Finally, preliminary results of a library based data analysis algorithm capable of both chemical identification and deconvolution of mixtures were presented.

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