# Automating Voltammetry with Flow Technology

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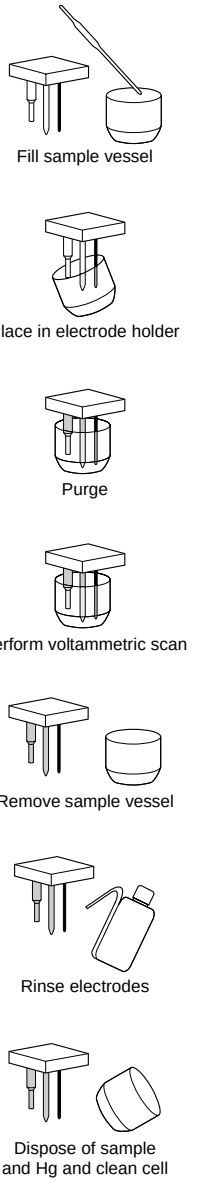
*Electrochemical techniques are versatile, selective, sensitive, and economical. However, the sample handling process used with these techniques has changed very little in the past 25 years, and productivity has not kept the pace with the needs of analytical laboratories. With the development of an efficient and fast on-line deoxygenator, it became possible to automate this sample handling process using flow technology and more than triple sample throughput. The use of on-line deoxygenation, when combined with electrochemical flow detectors, has broad applicability for automating polarography, voltammetry, and stripping techniques. It also extends the availability of LCEC detectors and FIA-EC detectors to the determination of reducible species.*

***F1***

*Steps required to perform a voltammetric analysis using the conventional manual sample handling process.*




Electrochemical techniques are versatile, selective, sensitive, and economical. Their versatility is hard to match with other techniques because one can directly determine organic compounds through reduction or oxidation of their functional groups, organometallic compounds, and inorganic species. They are also versatile because they integrate easily with other analytical instruments.

Electrochemical selectivity is a strength because it can be customized by adjusting the applied voltage, choosing different electrochemical techniques (e.g., dc, pulse, stripping voltammetry), changing the working electrode material, and changing the electrolyte composition (e.g., pH, solvent, complexant addition).

The sensitivity of electrochemical techniques, for this discussion, is equivalent to their limit of detection (LOD). The LOD of pulse (e.g., normal, differential, square wave) and stripping techniques is excellent when compared to other instrumental techniques (***T1***).

The economic advantage that goes along with versatility, selectivity, and sensitivity is becoming even more important as laboratory budgets continue to stagnate or decrease while work loads increase. Electrochemical techniques are among the least expensive to buy and operate, yet their selectivity and sensitivity are comparable to instrumental techniques that cost 2-5 times as much.

To take advantage of these strengths, electrochemical techniques must overcome two drawbacks: poor sample throughput, which is a direct consequence of the manual sample handling process used to do electroanalysis, and the lengthy deoxygenation step required when reducible species are determined. This article will demonstrate how fast and efficient on-line deoxygenation may be used to automate sample handling and deoxygenation. The technology described here requires that one rethink the electrochemical sample handling process. Instead of the manual, step-wise procedure now in use, voltammetry can be performed in a flowing stream that simultaneously performs sample handling and deoxygenation steps.

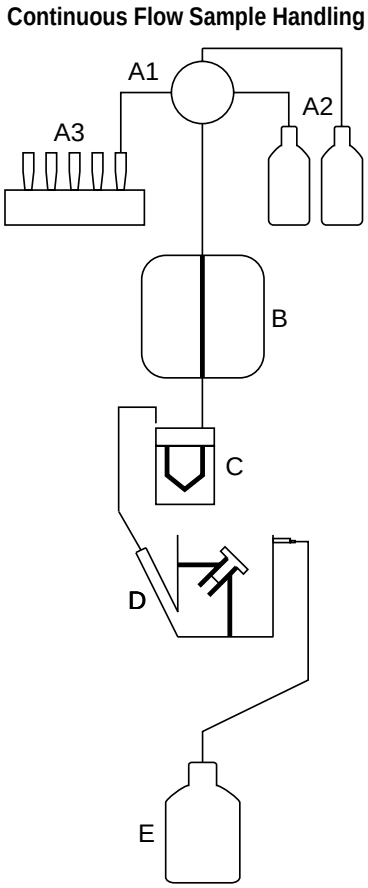
### *Rethinking the Sample Handling and Deoxygenation Process*

Although voltammetric scanning and data collection are highly automated, sample handling and deoxygenation processes have not changed in the past 25 years. These traditional sample handling steps

**F2**

*Schematic diagram of the automated and simpler FAST (Flow Assisted Sampling Technology).*

*A1 - Valve*
*A2 - Sampling station*
*A3 - Autosampler*
*B - Peristaltic pump*
*C - On-line deoxygenation*
*D - Voltammetric flow cell*
*E - Waste*




are shown in ***F1***. An analysis is begun by filling a cell with sample (analyte and supporting electrolyte) and placing it on the electrode assembly. The sample is then purged with an inert gas for 4-10 minutes and the voltammetric scan is run. The sample cell is then removed, electrodes are rinsed, and the analyzed sample and Hg (if a Hg electrode is used) are disposed. This process is too time consuming and manually intensive to use in today's analytical laboratory climate. Autosamplers can be designed to automate this manual process in sequential steps, but they are mechanically complex to build and costly to produce. A faster, simpler, and more economical process is needed and was developed by rethinking how electrochemical sample handling may be done.

This reengineered process is built using an on-line deoxygenator to remove dissolved $O_2$ and flow technology, closely related to FIA (flow injection analysis), to collect, transport, and dispose of samples. This new process, Flow Assisted Sampling Technology (FAST), is shown schematically in ***F2***. A sample, already mixed with electrolyte, is chosen from sampling station (***F2A2***) or autosampler (***F2A3***) using a selection valve (***F2A1***). The sample is deoxygenated on-line (***F2C***) and the voltammetric scan is run on the sample as it flows through the voltammetric flow cell (***F2D***). The sample then exits to the waste container (***F2E***). This new approach to automating electrochemical sample handling was made possible by NovaTech's patented on-line deoxygenation technology (1) and can be integrated with most voltammetric flow-through cells, including one developed by NovaTech especially for Hg electrodes (2,3).

**T1**

*Typical limits of detection for selected voltammetric techniques.*

| Voltammetric Techniques | Limit of Detection (*M*) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $10^{-4}$ | $10^{-5}$ | $10^{-6}$ | $10^{-7}$ | $10^{-8}$ | $10^{-9}$ | $10^{-10}$ |
| DC Polarography | | X | | | | | |
| Normal Pulse Polarography/Voltammetry | | | | X | | | |
| Differential Pulse Polarography | | | | | X | | |
| Square Wave Voltammetry | | | | | X | | |
| AC Polarography | | | | X | | | |
| Stripping Voltammetry | | | | | | | X |

**T2**

*Precision of peak height measurements using FAST. Square wave voltammetric measurements were made on 1.0 ng/mL of $Cu^{2+}$, $Pb^{2+}$, $Cd^{2+}$,and $Zn^{2+}$ at a SMDE in a 0.1 M ammonium citrate buffer (pH 3).*

| Run# | Cu (nA) | Pb (nA) | Cd (nA) | Zn (nA) |
|---|---|---|---|---|
| 1 | 236.1 | 43.9 | 66.7 | 114.2 |
| 2 | 243.9 | 44.5 | 67.8 | 115.2 |
| 3 | 242.1 | 44.0 | 67.3 | 114.6 |
| 4 | 240.7 | 43.6 | 67.5 | 113.9 |
| 5 | 240.0 | 43.6 | 67.1 | 114.5 |
| 6 | 236.9 | 43.2 | 66.9 | 113.6 |
| 7 | 241.0 | 43.4 | 67.2 | 113.7 |
| 8 | 235.4 | 42.5 | 66.2 | 112.6 |
| 9 | 236.5 | 42.5 | 66.9 | 112.6 |
| 10 | 228.3 | 41.5 | 66.3 | 111.5 |
| Ave. | 238.1 | 43.3 | 67.0 | 113.6 |
| S. D. | ± 4.5 | ± 0.9 | ± 0.5 | ± 1.1 |

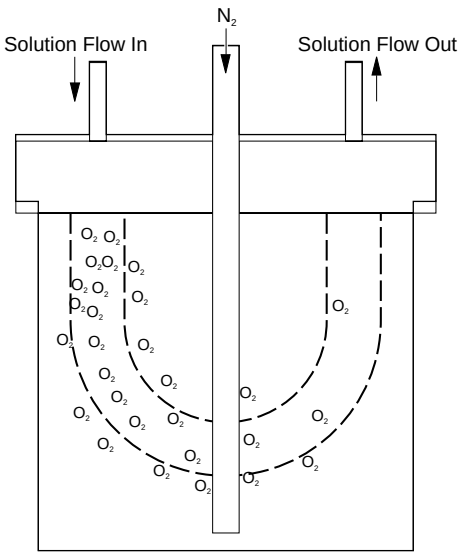
### *On-Line Deoxygenation*

Conventional deoxygenation, which involves purging an inert gas through the sample/electrolyte solution, is a very slow process. It often alters the sample and/or supporting electrolyte composition and is difficult to use in automated systems. Techniques to improve the deoxygenation process have been reviewed by Wallace (4) and include aspiration into a nitrogen atmosphere, coulometric reduction of dissolved $O_2$, use of scrubber columns to remove dissolved $O_2$, voltammetric discrimination, and diffusion through a semipermeable membrane. Of these, only semipermeable membrane deoxygenation has wide applicability, high efficiency, and no drawbacks.

The operating principle of a semipermeable membrane deoxygenator, shown schematically in ***F3***, is based on the ability of gases (in this case dissolved $O_2$) to diffuse through the membrane while liquids and dissolved solids are not able to pass through. The semipermeable membrane in this on-line deoxygenator is tubular and diffusion takes place while the solution

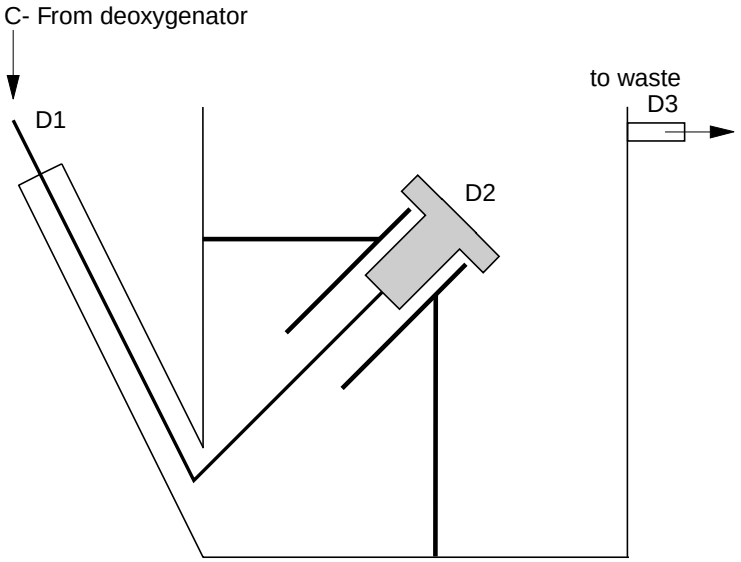
***F3***

*Schematic representation of NovaTech's technology to remove dissolved $O_2$ using on-line semipermeable membrane deoxygenation.*




***F4***

*Schematic drawing of NovaTech's flow-through cell for Hg electrodes.*




flows through it. When optimized, this process makes on-line deoxygenation fast and efficient and is the key technique needed to automate electrochemical analysis.

The efficiency of semipermeable membrane deoxygenation depends on the membrane material's permeability to $O_2$, membrane wall thickness, membrane tubing length, and solution flow rate through the membrane. Deoxygenation efficiency (Eff) is measured using the following equation, where $C(O_2)$ is the concentration of dissolved $O_2$.

Eff = {initial $C(O_2)$ - final $C(O_2)$}/{initial $C(O_2)$}

Eff exceeds 99.9% when four conditions are met: (1) a membrane is used with permeability to $O_2$ of at least 200 micromoles/(m*s*GPa), (2) membrane tubing length is at least 250 cm, (3) membrane wall thickness is less than 0.024 cm, and (4) solution flow rates are less than 3 mL/minute.

The semipermeable membrane used in this on-line deoxygenator has another attribute, its ability to reduce pump pulsations, which is an important factor when high sensitivity and precision is required. The flexibility of the membrane material is responsible for dampening pump pulsations in the flowing stream.

The first application of on-line deoxygenation technology was to extend the use of LCEC detectors to large cathodic voltages where reducible species are detected (5). In this application, minimizing band spreading of separated peaks is critical to preserve peak resolution. This is done by "knitting" the tubular membrane. In one chemical R&D laboratory, several reductive LCEC instruments using this on-line deoxygenation technology have been in use for almost 10 years. The success of on-line deoxygenation for HPLC was a major consideration when developing FAST.

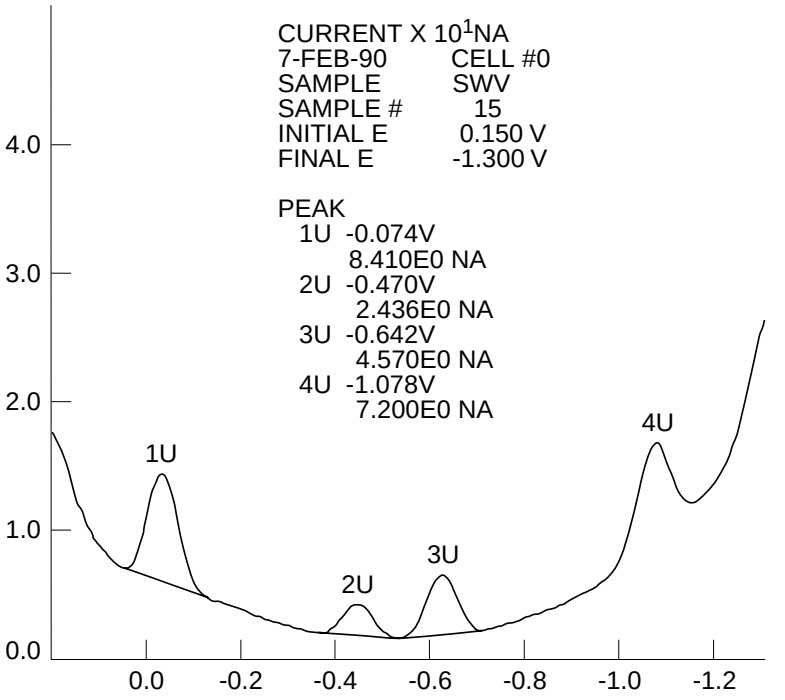
### Hg Electrode Flow Cell

Low-noise and low-dead-volume flow cells are necessary to do LCEC detection or voltammety in a continuously flowing stream. Flow cells for solid electrodes have been available for years, but this is not true for Hg electrodes. NovaTech had to develop its own flow cell for Hg electrodes because none were available with: (1) a cell with a low dead volume, (2) a reliable mechanism to reject dislodged Hg drops, (3) no drop-related noise, (4) simplified operation and maintenance, and (5) minimal IR losses. The flow cell design, which addresses all of these problems is shown in ***F4***.

In this design, sample/electrolyte exits from deoxygenator (***F4C***), flows through tubing impermeable to air (***F4D1***), and enters the cell via the flow inlet assembly (***F4D2***). The flow inlet is angled and has a mesh frit to reject dislodged Hg drops, prevent these drops from blocking the flow path, and direct flow around the Hg drop. The cell is filled with a highly conductive electrolyte, which need not be the same as the sample electrolyte. Excess flow is removed as it exits from this cell through outlet (***F4D3***). Not shown in this schematic is a simple lift mechanism that allows the Hg electrode capillary (or solid electrode) to be easily

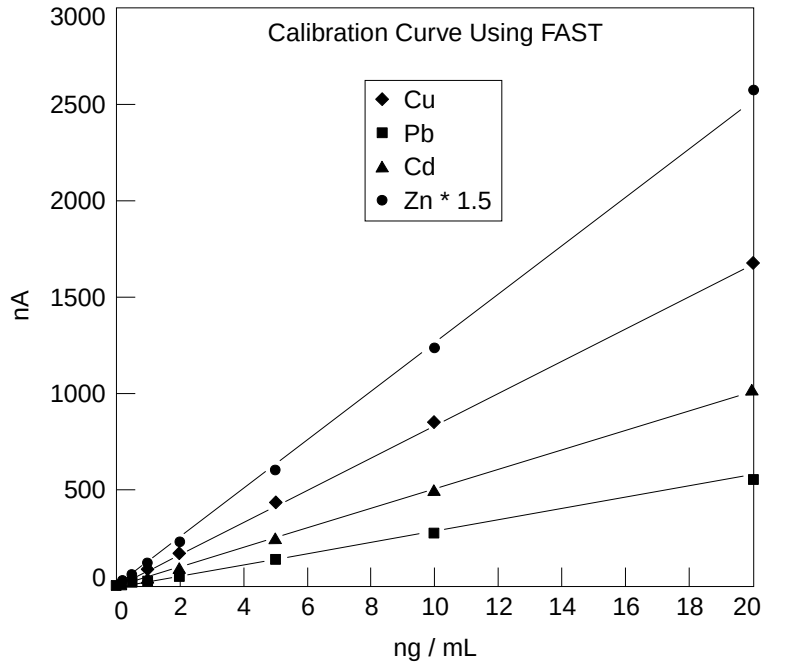
**F5**

*Square wave voltammogram for $Cu^{2+}$, $Pb^{2+}$, $Cd^{2+}$, and $Zn^{2+}$ at a static Hg drop electrode in 0.1 M ammonium citrate (pH 3) buffer. Each metal ion is at 100 ng/mL.*



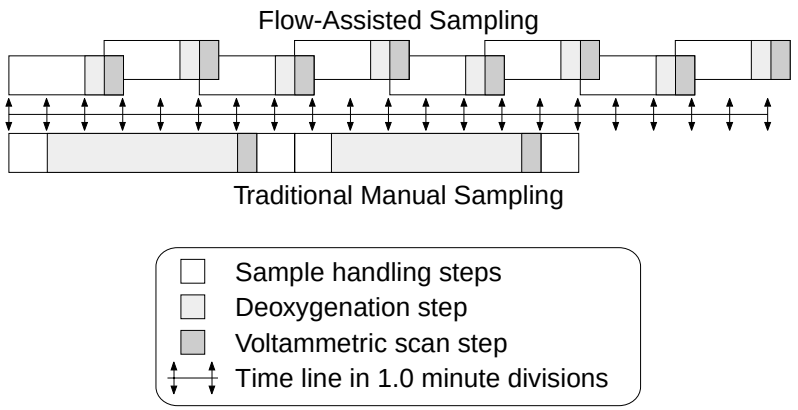

**F6**

*Calibration curve for $Cu^{2+}$, $Pb^{2+}$, $Cd^{2+}$, and $Zn^{2+}$ using the experimental conditions in F5. Note that the data for $Zn^{2+}$ has been multiplied by a factor of 1.5 so that its curve can be distinguished from $Cu^{2+}$.*




**F7**

*A time line comparing length of time required to analyze a sample using flow-assisted sampling versus traditional manual sampling.*




and repeatedly positioned so that the sample/electrolyte flow completely bathes the electrode and isolates it from the cell electrolyte solution. Continuous flow is necessary to this technology to prevent the cell electrolyte and reference electrode filling solution from interfering with the working electrode reaction. The flow, in effect, has the same properties as a salt bridge but without increasing the cell impedance.

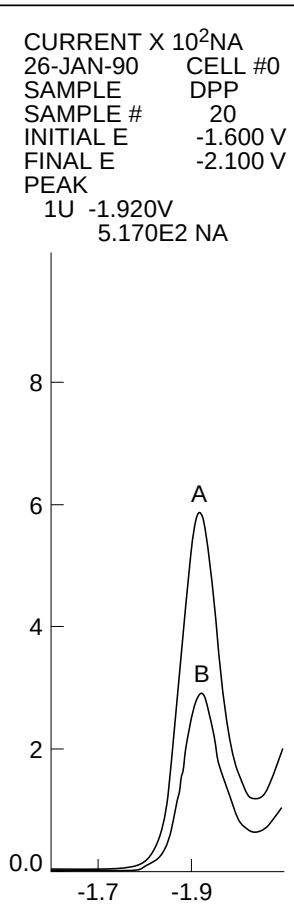
### *Experimental*

In the previous two sections the concept of FAST and the technology behind it were introduced. This section will describe the results of experiments that demonstrate the advantages of FAST over manual sample handling and the other complex automated systems:

- Faster sample throughput because FAST reduces deoxygenation time to under 30 seconds and simplifies sample handling.
- Improved deoxygenation technology that removes dissolved $O_2$ without changing the composition of the sample solution.
- Eliminates contamination sources such as reference electrode leakage, counter electrode reaction products and trace contamination from voltammetric cells.
- Improved stripping voltammetry because hydrodynamic flow is very reproducible and the medium exchange technique is simplified.
- Increased versatility and sensitivity when used as a detector for LC and FIA. On-line deoxygenation makes the entire cathodic voltage range accessible and use of gradients possible.

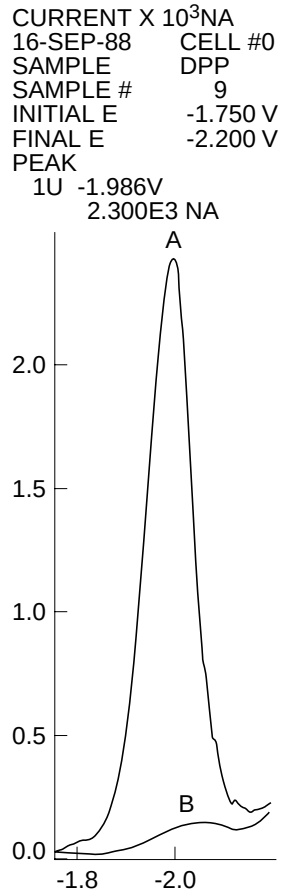
***F8***

*Differential pulse polarogram for 14 mg/L of acetaldehyde in 0.1 M LiOH. Curve A was obtained using FAST. Curve B was obtained using conventional sample handling with a 4-minute inert gas purge.*




***F9***

*Differential pulse polarogram of 0.1 M LiOH. Curve A was obtained using a cell with a conventional saturated KCl-Ag/AgCl reference electrode (no salt bridge) after a 4-minute purge with an inert gas. Curve B was obtained using FAST and the same saturated KCl-Ag/AgCl reference electrode.*




- Safer operation results because smaller sample volumes are used and operators do not have to handle samples during any voltammetric analysis step.

Before comparing sample throughput of FAST versus manual sample handling, a square wave voltammogram (SWV) for four metal ions in an ammonium citrate buffer (pH 3) will be examined (***F5***). This voltammogram shows that the on-line deoxygenator is very efficient and that one can perform voltammetric scans in a flowing stream without adverse effects on peak shape, peak resolution, precision and calibration curve linearity.

If this on-line deoxygenator was not efficient in removing trace concentrations of dissolved $O_2$, peaks would appear near to and possibly interfere with reduction of $Pb^{2+}$ and $Zn^{2+}$. The absence of interfering peaks in these voltage regions is one confirmation that on-line deoxygenation eliminates more than 99.9% of the sample's dissolved $O_2$. Absence of baseline noise is a further indication that dissolved $O_2$ has been eliminated and pump pulsations have been dampened. The precision of peak height measurements and the linearity of calibration curves are shown in ***T2*** and ***F6*** respectively. Both are equal to or better than that which would be obtained in quiescent solutions.

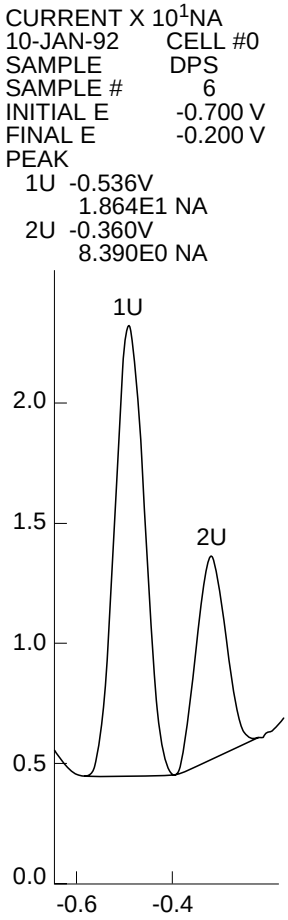
The most important reason to use FAST, however, is the increased sample throughput that is attainable but cannot be seen from figures and tables. A time line, such as the one in ***F7***, can help demonstrate how FAST increases sample throughput. With FAST, the analysis time is the time that a sample flows before switching (***F2A1***) to analyze the next sample. About 2.5 minutes, at a flow rate of 1.0 mL/min., is required to sweep out the last sample and achieve the maximum analyte concentration at the working electrode for the next sample. The SW scan is initiated at the 2.5 minute mark and is completed 0.5 minutes later. The advantage of FAST is that one can switch to the next sample WHILE finishing the analysis of the current sample. Manual sample handling requires about one minute to fill the voltammetric cell and place it in the electrode holder. Deoxygenation takes 5 minutes and the SW voltammetric scan 0.5 minutes. The clean up steps take another one minute for a total of 7.5 minutes compared to 2.5 minutes for a FAST analysis. The reduced analysis time of FAST is attained because sample transport, deoxygenation and cell cleanup occur simultaneously, but at different places along the sample's flow path. The low dead volume of this flow system, <0.9 mL, ensures that the rapid sampling rate can be maintained without carry over from one sample to the next. For techniques with short scan times, such as SWV, the analysis time is a function of the flow rate and system dead volume. For techniques with long scan times, such as DPP, the analysis time will depend, to a greater extent, on the length of the scan time.

### Improved Deoxygenation Technology

An advantage of on-line deoxygenation is illustrated in ***F8,*** which shows an overlay of two differential pulse polarograms for acetaldehyde (14 mg/L) using the on-line deoxygenator (***F8A***) and inert gas purging (***F8B***) to remove dissolved $O_2$. With on-line deoxygenation, dissolved $O_2$ selectively passes through the walls of the semipermeable membrane tubing and prevents the loss of volatile analytes, such as acetaldehyde, that occurs when inert gas purging is used. Inert gas purging requires at least 4-minutes and causes a 50% loss of acetaldehyde which makes this technique unsuitable for volatile analytes.

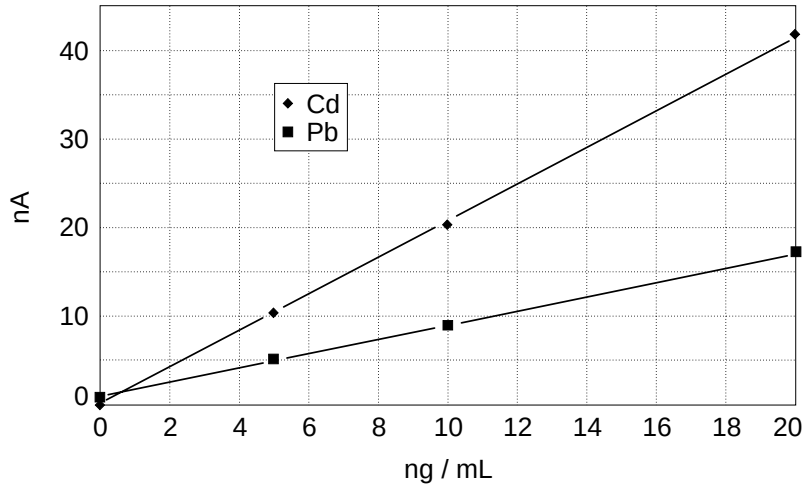
**F10**

*Differential pulse anodic stripping voltammetry of 10 ng/mL of $Cd^{2+}$ and $Pb^{2+}$ using FAST. Deposition was done in 1% $HNO_3$ at -0.8 V. vs Ag/AgCl and stripping, after switching to 0.1 M ammonium citrate (pH 3) buffer, using a differential pulse scan.*




**F11**

*Three standard calibration curves for $Cd^{2+}$ and $Pb^{2+}$ using DPASV with medium exchange under the conditions in **F10**.*




run in 0.1 *M* LiOH using a saturated KCl Ag/AgCl reference electrode and no salt bridge (***F9***). Peak A is caused by $K^+$ from the reference electrode filling solution that has leaked into the sample solution during the inert gas purging step. When FAST is used to run the DP polarogram, no peak for $K^+$ is observed (***F9***). Because of the unique design of the flow cell and flow inlet adapter, the flowing solution envelopes the electrode and prevents contaminants from the reference electrode, counter electrode and/or cell electrolyte from diffusing back to the working electrode and interfering. In effect, the flow inlet adapter and solution flow act as a "salt bridge" without the IR loss normally associated with these bridges.

### Improved Stripping Voltammetry

Stripping voltammetry is a two-step analysis comprised of a hydrodynamically enhanced (stirred) preconcentration step and a stripping step under quiescent conditions. Deposition and stripping are done in a voltammetric cell with mechanical stirring, which has two disadvantages. First, it is very difficult to perform medium exchange, in which deposition occurs in one electrolyte and stripping in a second electrolyte, with conventional batch sample handling. Medium exchange is very advantageous because one rarely encounters a sample matrix or electrolyte for which deposition and stripping are optimal. Second, hydrodynamic flow to the working electrode is difficult to control using mechanical stirring devices (e.g., magnetic stirring bars) in voltammetric cells and this causes poor precision. The benefit of doing stripping voltammetry in a flowing stream, using flow injection technology, is known for solid electrodes (6,7), but is not as well known for Hg electrodes because it is more difficult to produce flow cells for them.

To demonstrate that FAST solves these two disadvantages, differential pulse anodic stripping voltammetry (DPASV) was run on solutions containing $Cd^{2+}$ and $Pb^{2+}$ using a hanging Hg drop electrode. The standards and samples were prepared in 1% $HNO_3$ and deposited from this matrix. Stripping was performed in 0.1 M ammonium citrate (pH 3) buffer. A stripping voltammogram with medium exchange is shown in ***F10*** and was obtained with a 100-second deposition at -0.8 V. vs Ag/AgCl followed by a DP stripping scan. This DPAS voltammogram is no different than one that would be obtained without medium exchange using conventional sample handling until one looks at the quantitative data summarized in ***T3***. A three-standard calibration curve (5, 10, 20 ng/mL of each metal ion in 1% $HNO_3$) was run and the standard curve is shown in ***F11***. This standard curve was used to analyze tap water spiked with four concentrations of $Cd^{2+}$ and $Pb^{2+}$ and the calculated results are compared to the spiked concentrations in ***T3***. The precision of stripping voltammetry using FAST is good enough to use standard curve calibrations which would be impossible with mechanical stirring techniques in conventional cells.

### Elimination of Contamination Sources.

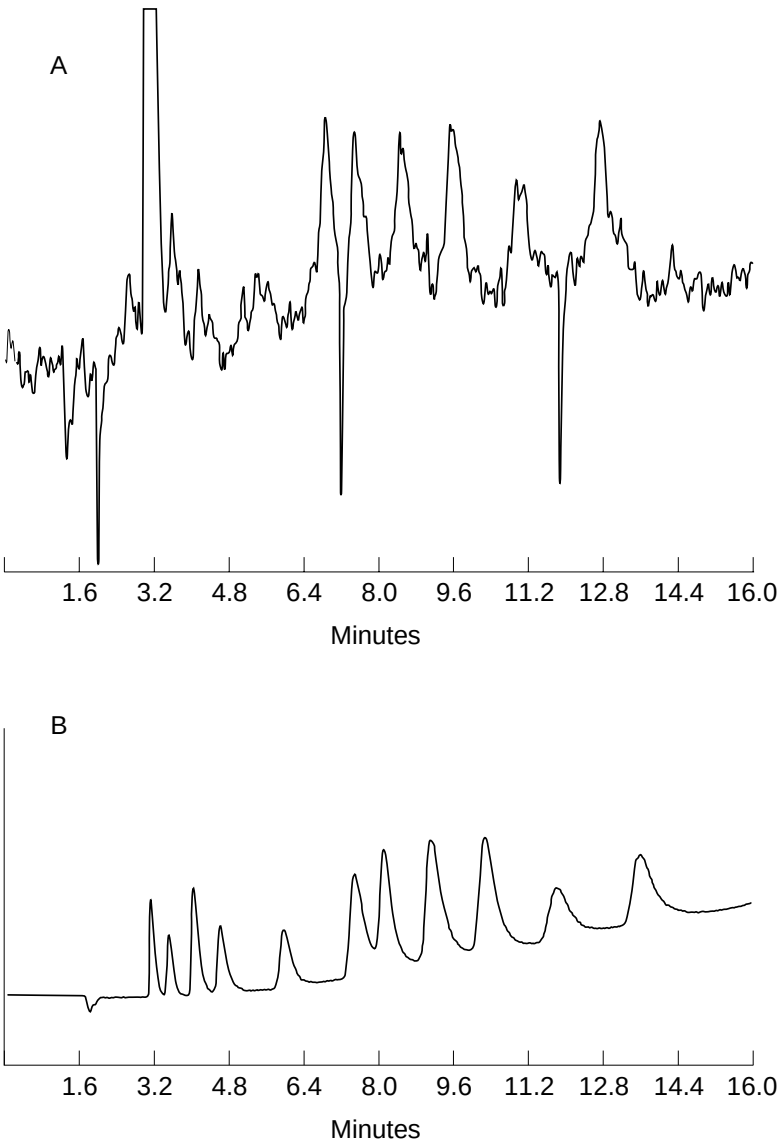
FAST has the ability to eliminate several sources of contamination that can cause loss of precision and accuracy. One such source of contamination is caused by reference electrode filling solution leaking into the sample solution. To illustrate this, a DP polarogram was

### Increased Versatility When Using LCEC.

The last example shows how on-line deoxygenation can expand the use of LCEC. ***F12A*** and ***F12B*** were obtained using a BAS Hg-

**F12**

*Reductive LCEC detection of nitroaromatic compounds after gradient separation on a polymeric 5 micron LC column. Gradient conditions: 50% acetonitrile - 70% acetonitrile both containing 0.1 M $NaClO_4$/0.01 M $H_3PO_4$. EC detector was a BAS thin-film Hg-plated Au electrode held at -0.90 V. vs Ag/AgCl. Curve A was obtained without an on-line deoxygenator. Curve B was obtained with an on-line deoxygenator. Nitroaromatic compounds injected (30 - 80 ng) were p-nitrobenzoic acid, o-nitroaniline, p-nitroaniline, m-nitroaniline, p-nitrophenol, o-nitrophenol, m-dinitrobenzene, 4-Cl-2-nitroaniline, 2,6-dinitrotoluene, o-nitrotoluene and 1-Cl-3-nitrobenzene.*




**T3**

*Precision of stripping voltammetry with medium exchange. $Cd^{2+}$ and $Pb^{2+}$ were spiked into simulated, acidified tap water (1% $HNO_3$) at 2, 5, 10 and 20 ng/mL of each metal ion. A three-point calibration curve was used to do the quantitation. Deposition was done at -0.8 V. vs Ag/AgCl in 1% $HNO_3$ and stripping with a DP scan using 0.1 M amonium citrate (pH 3) buffer.*

Calibration Data

| | Cd | Pb |
|---|---|---|
| Slope | 2.078 | 0.81 |
| Intercept | -0.14 | 0.96 |
| $R^2$ | 0.99978 | 0.99958 |

Concentration in ng/mL

| Conc. Spiked | Cd Found | Pb Found |
|---|---|---|
| 10.0 | 9.9 | 10.3 |
| 5.0 | 5.1 | 4.2 |
| 2.0 | 2.1 | 1.7 |
| 20.0 | 19.9 | 20.4 |
| 10.0 | 9.6 | 9.1 |
| 10.0 | 10.1 | 10.5 |

plated Au working electrode and a BAS LC-4A Amperometric Detector to detect eleven nitroaromatic compounds after gradient separation on a polymeric 5 micron column. The Hg-plated Au electrode was held at -0.9 V vs Ag/AgCl. Without the on-line deoxygenator (***F12A***), the peak caused by dissolved $O_2$ in the sample interferes with the detection of several nitro compounds and traces of dissolved $O_2$ remaining in the eluent causes severe baseline noise. Both of these interferences disappear when an on-line deoxygenator is placed between the LC column and EC detector (***F12B***).

### Safer Operation

The use of flow technology (FAST) provides safer operation of voltammetry, especially when deoxygenation and Hg electrodes are used. With conventional purging, the inert gas bubbles through the sample solution, releasing volatile species into the laboratory air. With FAST, the inert gas and sample solution are separated by a semipermeable membrane which keeps volatile species from being released. The Hg electrode flow cell used to obtain these data separates used Hg drops from the liquid portion of the waste stream, facilitating recovery of waste Hg for recycling.

## *Summary*

The purpose of this work is to describe how flow technology can be used to automate voltammetry and demonstrate its benefits. The use of semipermeable on-line deoxygenation is introduced and its benefits shown. LCEC detection, polarography, voltammetry and stripping voltammetry examples are utilized to illustrate that FAST — Flow Assisted Sampling Technology — makes electroanalytical techniques even more versatile, selective, sensitive, and economical.

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