

# Active voltammetric microsensors with neural signal processing

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## ABSTRACT

Many industrial and environmental processes, including bioremediation, would benefit from the feedback and control information provided by a local multi-analyte chemical sensor. For most processes, such a sensor would need to be rugged enough to be placed *in situ* for long-term remote monitoring, and inexpensive enough to be fielded in useful numbers. The multi-analyte capability is difficult to obtain from common passive sensors, but *can* be provided by an *active* device that produces a spectrum-type response.

Such new *active* gas microsensor technology has been developed at Argonne National Laboratory. The technology couples an electrocatalytic ceramic-metallic (cermet) microsensor with a voltammetric measurement technique and advanced neural signal processing. It has been demonstrated to be flexible, rugged, and very economical to produce and deploy. Both narrow interest detectors and wide spectrum instruments have been developed around this technology. Much of this technology's strength lies in the active measurement technique employed. The technique involves applying voltammetry to a miniature electrocatalytic cell to produce unique chemical "signatures" from the analytes. These signatures are processed with neural pattern recognition algorithms to identify and quantify the components in the analyte.

The neural signal processing allows for innovative sampling and analysis strategies to be employed with the microsensor. In most situations, the whole response signature from the voltammogram can be used to identify, classify, and quantify an analyte, without dissecting it into component parts. This allows an instrument to be calibrated once for a specific gas or mixture of gases by simple exposure to a multi-component standard rather than by a series of individual gases. The sampled unknown analytes can vary in composition or in concentration; the calibration, sensing, and processing methods of these active voltammetric microsensors can detect, recognize, and quantify different signatures and support subsequent analyses. The instrument can be trained to recognize and report expected analyte components (within some tolerance), but also can alarm when unexpected components are detected. Unknowns can be repeat-sampled to build a reference library for later post processing and verification.

**Keywords:** voltammetry, polarography, microsensor, sensor, chemical, intelligent, neural network,

## 1. A BACKGROUND ON GENERAL SENSOR STRATEGIES AND SUPPORT

### 1.1 Active vs. passive sensors

Typical *passive* industrial gas sensors attempt to measure gas presence and/or concentration as a function of a single parameter such as resistance. This is the case in a semiconductor such as tin dioxide ( $\text{SnO}_2$ ), where the presence of a hydrocarbon such as methane ( $\text{CH}_4$ ) will react with the  $\text{SnO}_2$  to cause a measurable rise in electrical conductivity.<sup>1</sup> While this type of resistance measurement "can" be performed over a scanned spectrum of applied voltage, it typically is not. The single reading that is produced is very susceptible to modification by many other external factors such as temperature, pressure, humidity, and/or rate of change of any of these factors. The added complexity of implementing a voltage sweep vs. a single applied potential is usually avoided solely for economical reasons although the additional information gained by actively applying a swept voltage and producing a non-linear spectrum response curve is more beneficial. Similar limitations are seen with strictly *passive* optical sensors, which monitor only the attenuation of a single, narrow-focused, wavelength band.<sup>2</sup> Passive technologies were developed when dedicated microelectronics were expensive, unlike modern Application Specific Integrated Circuits (ASICs) and microcontrollers. These technologies now artificially burden chemical phenomena by attempting to produce linear or near-linear output voltages as a function of a *passive* chemical reaction. This severely limits the phenomena available for modern chemical sensor design.

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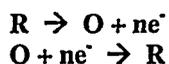
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Active mechanisms, such as voltammetry/polarography and spectrum-response optical sensors, drive an activation signal through a chemical cell<sup>3</sup> while varying that activation signals value (be it an electrical potential or an electromagnetic wavelength). The resultant output signal is sampled and captured in an array format and contains significant additional information that can be used for species identification and quantification. The additional information contained in a spectrum-response can be used to eliminate drift and external influences recorded in the instrument signal.

### 1.1.1 Active voltammetric/polarographic phenomena

Voltammetry involves the production of an electrochemical cell, where an ion-selective electrolyte is sandwiched between two or more electrodes and a measured potential is applied between the electrodes.<sup>4</sup> How the potential is applied to the cell is a characteristic of the exact voltammetric method employed, but in each case, the electrical current driven through the device is measured as a function of reduction or oxidation of the electroactive chemical species present in the supporting electrolyte or on the cell.<sup>5</sup> If the applied potential is scanned through a range of voltages, then the resultant sampled and recorded waveform is referred to as a voltammogram or polarograph.

Responses from several voltammetric/electrocatalytic sensors using specific analytes are shown in the cyclic voltammograms (performed in triplicate) as reported in the results section. The peaks of the cyclic voltammograms are indicative of electroactive species involved in redox reactions catalyzed by the sensor. These reversible, fast reactions may be represented by the general equations:



where: *R* = reduced electroactive species  
*O* = oxidized electroactive species  
*ne*<sup>-</sup> = number of electrons transferred at electrode (sensor) interface.

Cyclic voltammogram peaks have shown that fast reactions were obtained without the production of intermediates in our sensors. Responses from these sensors are reproducible in nature and are sensitive to the type of analyte *and* to the concentration of the analyte, thus allowing the sensor the ability to completely characterize the gaseous constituent.<sup>6</sup> This is a unique feature of the active sensing process, since most cyclic voltammograms of agents are shaped by kinetics and not by concentrations.<sup>7</sup> The voltammogram itself can be cast as a 1-dimensional array for analysis.

### 1.1.2 Active optical phenomena

There are a great number of different optical sensor configurations and designs, but common themes and strategies can be discussed to illustrate typical operation. A popular strategy involves dual optical chambers where one chamber is filled with a gas-selective reagent, and the other chamber is left alone to serve as a reference cell.<sup>8</sup> Both chambers are exposed to the analyte gas. A common light source (such as an LED) is directed through both chambers, each one terminated with a photodetector. As the reagent reacts with the analyte, specific chemical-reactive wavelengths of light are absorbed. This absorption is detected as an attenuation of the optical signal produced at the photodetector. This attenuation is translated into a change in measured electrical signal. When the supplied activation light from the LED is varied over even a small wavelength range, the final result is a corrected absorption spectrum. This output also can be cast as 1-dimensional waveform for analysis.

## 1.2 Voltammetry as a multi-analyte instrument core

Active measurement, employed by techniques such as voltammetry, can produce responses for multiple analytes. The standard 1-dimensional resultant waveforms can be further altered to change scan rate and ranges to produce response *surfaces* allowing an even larger variety of analytes to be determined. As such, voltammetry and polarography represent very capable tools and have been implemented as parts of larger suites of chemical detection tools in universal instruments.<sup>9</sup> Early attempts displayed limitations that were a function of the mercury electrodes and lack of solid state components, but this shortcoming has been addressed by the fabrication of the ANL prototype with a solid cell and solid state microelectronics.

### 1.3 Data fusion support

The construction of a universal multi-analyte instrument would be supported by the ease of data fusion made available by processing the spectrum-type voltammograms. The voltammograms have been concatenated to produce a larger composite signature; and also have been collected side-by-side to produce a response surface. This has allowed automated (genetic) optimization of processing routines (neural net structures) based upon simple sensitivity analysis performed on the fused data.

Once the response data is cast into a generic 1-dimensional or 3-dimensional format, it can be processed irrespective of its original chemical source. Commercial and research-type signal processing software environments, such as MathWork™'s MatLAB™/Chemometrics Toolbox<sup>10</sup> and ANL's Sensor Algorithm Generation Environment (SAGE<sup>®</sup>)<sup>11</sup>, are available to perform this data analysis. SAGE<sup>®</sup> was designed with this generic waveform processing strategy. SAGE<sup>®</sup> has been built to process waveforms from many classic and experimental chemical sensors including gas chromatography/mass spectroscopy (GC/MS), Fourier Transform Infrared spectroscopy (FTIR), voltammetry, and spectrometry. It even has been scaled up to process spatial versions of hyper and ultra spectral sensor data. SAGE<sup>®</sup> served as a demonstration platform for neural signal algorithms that were produced to support the V/EC microsensors.

These best-performing neural algorithms were produced by simple genetic optimization. The optimization combined various neural schemes into neural structures to produce the most ideal classification algorithm.<sup>12</sup> The number of nodes, interconnection patterns, scaling factors, normalizations, recombinations, activation functions, and training methods were all adjusted during the optimization. Simulated annealing algorithms<sup>13</sup> were coded as example on-board training algorithms.

## 2. V/EC SENSOR PROTOTYPE METHODOLOGY

### 2.1 Solid electrolyte electrochemical cell

For the ANL prototype V/EC microsensor, a solid electrolyte electrochemical cell was fabricated using thick-film screen printing and firing techniques (See Figure 1). Several cell designs were constructed, each with alternative sensing electrode catalysts, electrolytes, and gas-selective coatings. All solid cells employ only two electrodes with the electrolyte sandwiched between them. Shown below are the latest commercially-fabricated devices, both single-element SIP (Single In-line Package) designs and multiple-element BGA (Ball Grid Array) arrays. Also shown in Figure 2 is a typical metallized package used to deploy such a device.

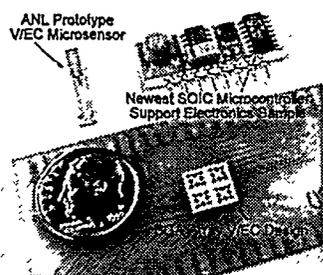


Figure 1. Prototype SIP V/EC sensor, sample electronics package (S-SEP), coin (for scale), and BGA V/EC array sensor design.

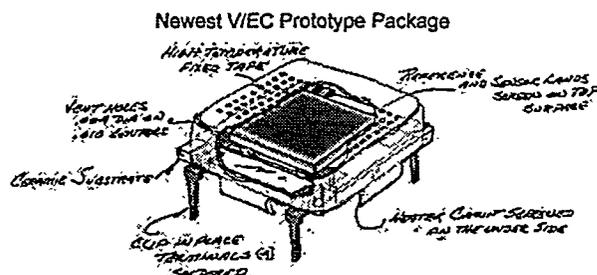


Figure 2. V/EC microsensor package design (stamped metal enclosure).

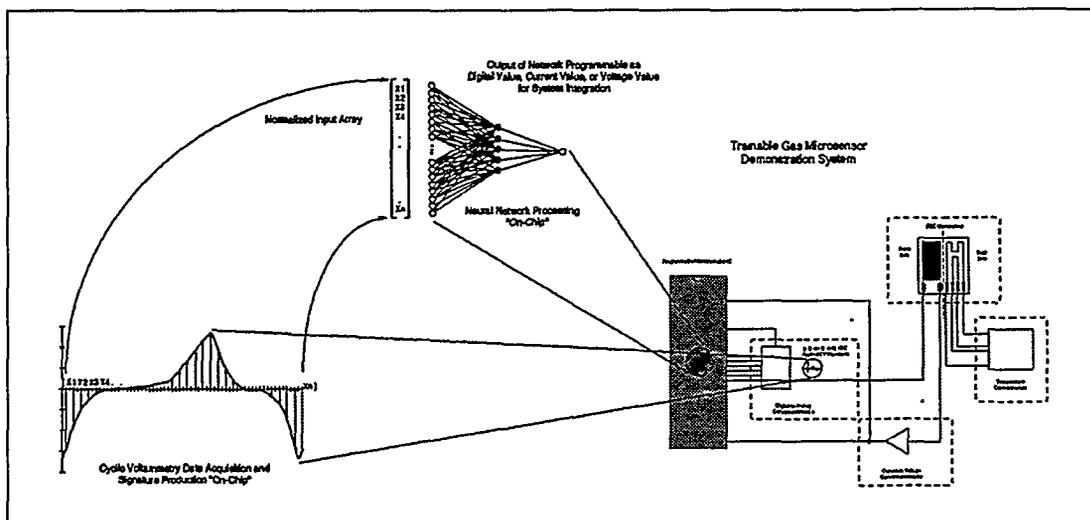
## 2.2 Voltammetry application

Demonstration electronics packages were produced that combined data acquisition hardware for generating cyclic voltammetry waveforms, along with a simple programmable LED thermometer-bar-type interface. The microcontrollers selected for the first prototype were PIC™ Micro 16C74s in a 40-pin dual in-line package (DIP) package. These micros were capable of pulse-width modulation (PWM) output and 8-12 bit analog-digital (A/D) input with 2K or 4K of on-board random access memory (RAM) and read-only memory (ROM) for data and code storage. Also interfaced were several instrument amplifiers to perform the signal conditioning required for current-voltage conversion of the voltammetry waveform. After the prototype was bread-boarded and tested, a complete multi-layer printed circuit board (PCB) was produced. This first generation board used a single 9V battery for powering the electronics. The micros allowed implementation of a serial communication interface, so the unit could be attached to a more capable notebook PC for reprogramming (See Figure 3).



**Figure 3. Prototype V/EC analytical instrument (printed circuit board + notebook host).**

Code representing several different staged (or gated) networks<sup>14</sup> was produced in an external neural modeling environment such as NeuralWare™ Pro II or MatLAB™ Neural Net Toolbox. It was then exported as "C" language code and ported/converted to 16C74 assembly code and then written to each microcontroller or to an accompanying serial programmable read-only memory (EPROM). Algorithms for implementing several forms of cyclic voltammetry were tested. A simple triangular (0 → +1 → 0 → -1 → 0 Volts DC) wave was selected and implemented using either the micro's built-in PWM support or an external digital-analog conversion (DAC) integrated circuit to produce the driving signal to the V/EC microsensor. The code made (24) output voltage steps and sampled and stored the resultant current at each step. A generic feedforward<sup>15</sup> neural network structure was coded on the microcontroller, with the process weight values read from a ROM or RAM storage location. This allowed bench retraining for different gases, and field replacement of the information representing a specific gas or set of gases. A system diagram of the prototype is shown in Figure 4 below.



**Figure 4. System operation diagram (on-chip cyclic voltammetry and neural processing to support V/EC sensor).**

### 2.3 Neural identification and quantification

Each cycle of the scan/store/process/idle procedures was initiated with an external momentary switch. The produced signature waveform was preprocessed before initiating the neural pattern recognition. The preprocessing consisted of normalization and storage of each point as a scaled integer. Several successive signatures could be stored locally for historic comparison.

For the normal prototypes' hardware, all neural algorithm "training" was performed on a notebook PC, with only the feedforward portion coded on the micro. During the processing stage, the stored signature waveform was fed as input to a simple multi-layer feedforward neural network. A typical network structure consisted of (24) input nodes, (15) hidden processing nodes, and (1-2) output nodes. The internal processing was performed both as 24-bit floating-point values and as scaled integer values. For most purposes, performance was nearly identical. The output nodes contained values that were a function of the concentration of a specific gas to which the sensor was trained to respond. This value was converted to an appropriate value on the LED thermometer-type display. On the notebook systems, all the inter-process numbers were kept as floating point numbers and stored and processed appropriately. The voltammograms shown in Figures 5-9 are MS Excel charts of the raw, unfiltered voltammetric responses.

The entire signal generation, conditioning, and processing routines are generic in that they do not consider the chemical source of the values. This makes this method equally applicable to any active sensor technology that is capable of producing a similar waveform. It also supports the eased integration of several distinctly different sensor types, into a more capable suite.

## 3. V/EC ACTIVE MEASUREMENT RESULTS

The voltammetric measurement techniques employed by the ANL prototype have been used to identify and characterize a significant number of species and mixtures. The following voltammograms in Figures 5-9 illustrate the variety and reproducibility of the technique. Each of the voltammograms shown is composed of triplicate/superimposed captured waveforms. In most cases, the curves traced out are indistinguishable from a single voltammogram outline. The examples illustrate the distinct shapes taken on by different analytes, supporting the use of the active voltammetry for chemical species

identifications. The examples also illustrate the voltammetric signature changes that take place when the concentration of the analyte changes. These changes are not linear, and have been historically difficult to quantify, but the neural network processing utilizes the entire waveform for this analysis, generalizes the response characteristics, and is effective.

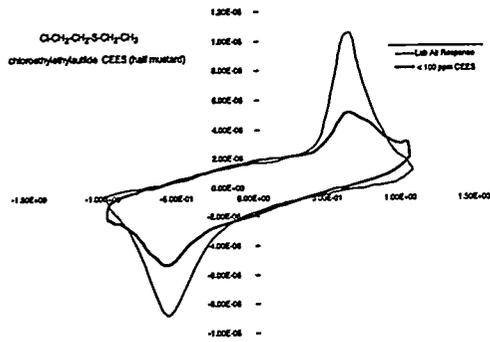


Figure 5a. V/EC sensor response to chloroethylethylsulfide.

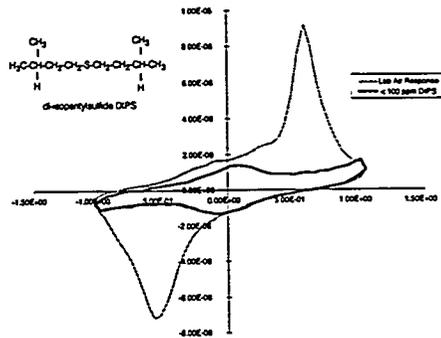


Figure 5b. V/EC sensor response to di-isopentylsulfide .

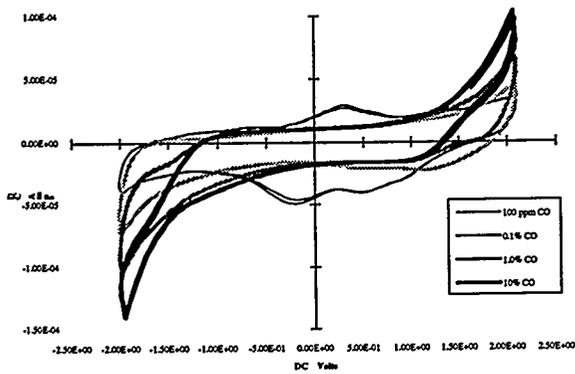


Figure 6. V/EC sensor response to carbon monoxide.

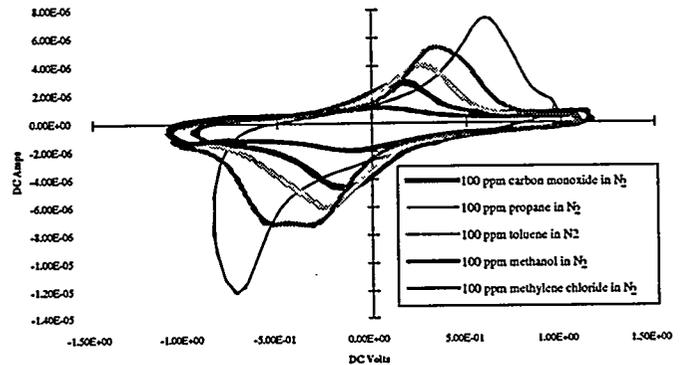


Figure 7. V/EC response to various hydrocarbons demonstrating multi-gas response capability.

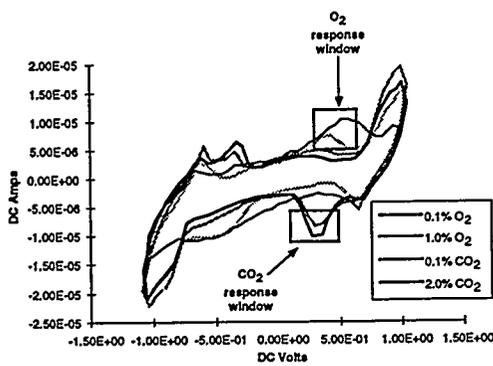


Figure 8. V/EC response to O<sub>2</sub> and CO<sub>2</sub> demonstrating selective response windows.

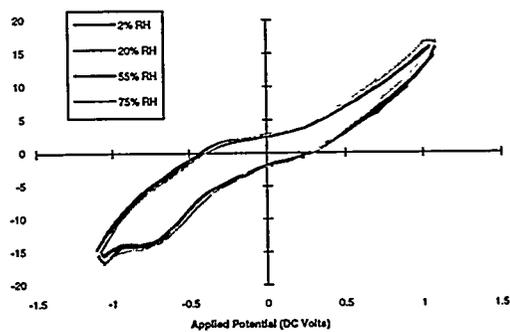


Figure 9. V/EC sensor response to humidity. The signal does not change or drift with increased humidity.

#### 4. DISCUSSION, CURRENT EFFORTS, AND FUTURE DIRECTION

The prototype devices combined the simplest forms of each of the subordinate technologies (ceramic-metallic materials, voltammetry, and neural analysis). The original data, gathered by employing simple linear sweep cyclic voltammetry, results in typical detection levels as illustrated in the Table 1.

methane (> 0.1%)	methanol (> 100 ppm)	oxygen (> 100 ppm)	ammonia (> 100 ppm)
methylene chloride (> 100 ppm)	chlorine (> 10 ppm)	carbon monoxide (> 10 ppm)	hydrogen sulfide (> 10 ppm)
benzene (> 10 ppm)	propane (> 1 ppm)	carbon dioxide (> 0.25%)	formaldehyde (> 10 ppm)
ethanol (> 10 ppm)	Toluene (> 10 ppm)	nitric oxide (> 1 ppm)	chloroethylethylsulfide (CEES) (< 100 ppm)
xylene (> 5 ppm)	Acetone (vapor test)	dichloroethane (vapor test)	di-isopentylsulfide (DIPS) (< 100 ppm)
dichloromethane (vapor test)	isopropyl alcohol (vapor test)	smoke (particulate test)	

() Represents lowest concentration tested. Most gases can be detected from their lower limit to 100%.

These values do not necessarily represent the detection limits or the entire range of possible analytes, but they do illustrate useful detection levels that are able to serve a variety of applications. The square wave voltammetry being employed now is a technique ported over from liquid chemical cell systems. It is common to see dramatic improvements in both detection levels and sampling time through this simple change.<sup>16</sup> Two to three order of magnitude improvements are not uncommon, nor are reductions in sampling rates from minutes to fractions of a second. Typical detection limits for liquid cells consist of fractions of ppm or ppb, levels. In fact, historically, voltammetry has found its most effective use in the detection of contaminants, where threshold detection of minute amounts far outweighs more accurate measurement of larger quantities. Scan rate increases to around 200 Hz will be established and demonstrated at the completion of the current projects. The reduction in overall sampling times will have a marked effect on the usefulness of a small miniature monitor. The reduced sampling time will indirectly improve temperature stability during measurement and dramatically reduce power consumption required for sensor element heating to operating temperatures.

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