The diffusion coefficients of molecules through bulk solution can determine the diffusion coefficient from the slope of a Levich Plot. This method determines the diffusion coefficients, \( D \), from the slope of a Levich plot constructed by measuring limiting currents, \( I_L \), as a function of square root of the rotation rate, \( w \), according to the Levich equation (Equation 1).

\[
I_L = 0.620nFAD^{1/2}w^{1/2}v^{1/3}C
\]

Accurate values for the area of the electrode, \( A \), the number of electrons transferred, \( n \), the concentration of the molecule, \( C \), and the viscosity of the solution, \( \nu \), must also be known in order to effectively determine the diffusion coefficient from the slope of a Levich Plot. The diffusion coefficients of molecules through bulk solution can also be determined quantitatively by wall-jet chronocoulometry, or qualitatively by comparing the CV’s of different compounds because the shape of the CV is related to the diffusion coefficient of the molecule. 

The other primary option for determining diffusion coefficients of a molecule through a membrane coated over an electrode is impedance spectroscopy, where the diffusion of the molecule through a membrane or polymer is related to the impedance of the polymer or membrane to current flow. As such, the diffusion through the polymer is related directly to the resistance of charge transfer (mobility) through the membrane, which is related to its conductivity and directly correlated to the diffusion coefficient by the Nernst-Einstein equation (Equation 2).

\[
D = \frac{\sigma k T}{C q^2}
\]

Conductance, \( \sigma \), can be determined from the charge transfer resistance and related to the diffusion coefficient for the analyte, \( D \), if the concentration, \( C \), the temperature in Kelvin, \( T \), and the charge on the species, \( q \), are also known, where \( k \) is the Boltzmann Constant. The above equation is primarily used when looking at diffusion of ions through solid polymer electrolytes, membranes, and polymer brushes.

Methods using conductance cells for determining the diffusion coefficients of ions in a solution use capillary flow tubes: one capillary containing 25% more concentrated and one containing 25% less concentrated solution than the bulk. The change in the ratio of the resistances of the solutions in the two flow tubes as the ions diffuse from the capillaries into the solution is measured. These ratios can be modeled by Oosgaard-Fuoss to determine the diffusion coefficient of an electrolyte diffusing in bulk solution. There are also non-electrochemical methods for determining diffusion coefficients such as: NMR, field-flow fractionation, and neutron radiography.

These determinations are very involved, as for each candidate an entirely new experiment must be developed, and numerical values for the ancillary parameters must be known, either taken from the literature or measured. For example, the slope of the Levich line depends on viscosity. Slight changes in the viscosity, such as differences in the composition of the supporting electrolyte, can cause shifts in the diffusion coefficient. In addition, this kind of detailed work has only been done for a few probe molecules that are electrochemically ideal in their behavior. For example, the diffusion coefficients of potassium ferricyanide is known in several buffers, but if/when the buffer is changed, the diffusion coefficient must be re-determined. In addition, none of these molecules are typically the desired analytes for electrochemical sensors, where the sensitivity of the sensor is related to the diffusion of the analyte to the electrode or through the membrane coating the sensor. It would therefore be convenient to find a way to determine the diffusion coefficients of Red/Ox analytes in supporting electrolyte solutions.

In this paper we show that there is an existing method in the literature that has been mostly ignored in the thirty years since its development. Electrochemical time-of-flight (ETOF) is a generate-detect experiment in which an analyte is generated either oxidatively or reductively at one electrode, called the generator; it is detected by re-reducing/re-oxidizing the analyte at a second electrode, called the collector (Figure 1). This type of experiment was first reported by Royce Murray, et al., to examine electron diffusion rates through conducting polymers that were inserted between two fingers on an electrode array. The two electrodes are within micrometers of each other and are often members of a microelectrode array. The time it takes the product from the generator to diffuse to the nearest edge of the collector is the time of flight. If a potential pulse is applied to the generator, a burst of product diffuses to the collector (Figure 2), and the time of maximum collection, \( t_{\text{mcc}} \), is measured. The diffusion coefficient of a Red/Ox species can then be calculated using Equation 3.

\[
d = K\sqrt{D t_{\text{mcc}}}
\]
the height of the diffusion layer, the width of the electrodes and the gap between them, and $D$ is the diffusion coefficient. ETOF has the potential to greatly simplify the determination of diffusion coefficients as the concentration of the analyte, the area of the electrode, the viscosity of the solution, and the electron transfer kinetics can remain unknown. This equation is the general form, as presented by Amatore, of an equation that was determined empirically by the Wrighton group for use in modeling diffusion of electro-generated species between electrodes in an array.\(^{35}\)

Another experiment similar to ETOF is the scanning electrochemical microscopy (SECM) experiment. This uses a UME electrode held a short distance vertically from a surface. The surface, or substrate, and the UME, or tip, are used as a generator and a collector electrode and typically biased so that opposing reactions are happening at each electrode.\(^{34-39}\) SECM is typically used for surface imaging of electrode arrays and thin film studies, which both make use of the fact that the tip can be moved and gives spatial data about the resistive or conductive nature of the substrate. It can also be used for kinetics studies and the determination of diffusion coefficients.\(^{34,36,39}\) This is done by determining the diffusion coefficient ratio of the couple in the solution from the limiting currents of the collector and from the feedback to the generator. By knowing the current at time infinity, the electroactive area of the electrode, and the starting concentration of one of the analytes, one can determine the diffusion coefficients for both members of the couple.\(^{35}\) This experiment returns to a methodology that requires knowledge of the electroactive area of the electrode to determine absolute diffusion coefficients, and the initial concentration of one of the species, but no longer requires knowledge of how far the electrodes are separated.

The previous literature concerning ETOF is mostly theoretical work modeling the diffusion of a single molecule and then comparing the model to empirical data, where distance $d$ was varied and the time of maximum collection measured at each distance. The geometric constant, $K$, was determined for a single molecule but never empirically proved to be a constant; especially for the case of multiple molecules diffusing in different buffer solutions. A key contribution in this paper is the rearrangement of Equation 3 into Equation 4, as an alternative data analysis treatment for ETOF data.

$$\sqrt{t_{mc}} = \frac{d}{K\sqrt{D}} + B$$  \[4\]

If $K$ is constant, and $d$ is held constant, then by selecting molecules with various and known diffusion coefficients, it would be possible to construct a curve with slope, $\frac{1}{K}$, and with an intercept $B$, which is a consequence of the x-intercept which occurs at the fastest diffusion rate able to be differentiated from $t_{mc} = 0$ s. This “calibration curve” for the geometry of the array could then be used to determine the diffusion coefficient for any molecule in any solution. This experiment can be done without experiencing the loss of signal that occurs when $d$ increases while performing a typical multiple distance experiment.

**Experimental**

*Generator controller and LabView software.*—Amatore used a multistat (Autolab PGstat 20 and GEPES software from Ecochemie, Metrohm Switzerland) to perform ETOF experiments. There are commercial instruments with the needed capability (Bio-Logic, Grenoble, France), but they are expensive. The bipotentiostats available in our lab, were not capable of leaving the second working (generator) electrode open circuit, nor of providing a potential pulse. Our solution was to modify our existing bipotentiostat. The second working electrode from a CHI 750 potentiostat (CHInstruments, Austin, Texas, USA) was used to provide the potential to the generating electrode. As with most commercially available bipotentiostats the second working electrode only provides a static potential that is applied when the experiment initiates.

For the application described here, the generator is at open-circuit save for a brief potential pulse. To accomplish this, a relay was spliced into the second working electrode lead (Figure 3, Generating Electrode Controller, GEC). Timing and control of the relay was established by LabView software, and a National Instruments CompactDAQ 9417 controller using a 9403 digital I/O module (National Instruments, Austin, Texas, USA), attached to a laptop computer (Figure 3). A circuit board was constructed to connect the relay and control and capture the digital signals between the potentiostat and the digital I/O module. The GEC went through several iterations before arriving at a final design shown in Figure 4. The D-flip-flop captures the downward “start-scan” pulse from the CHI 750a, latches the prompt so it will not be missed by the LabView software loopng until the digital I/O line associated with the start trigger changes state. A software timer (seconds) selected by operator input, starts and at time-out, a second I/O output line, relay trigger, triggers the one-shot. The one-shot energizes the relay for a brief 15 ms period, momentarily applying a potential to the generator. The NPN transistor at the Q output of the one-shot, shown in Figure 4, provides sufficient drive to close the relay. Setting the generator pulse width by the one-shot’s RC time.

Figure 1. The Electrochemical Time of Flight experiment (ETOF). A) Oxidized form (O) in solution and generator (red) at open circuit, the collectors (blue) are polarized to an oxidizing potential. B) The generator is briefly polarized to a reducing potential, converting the O to its reduced form (R). C) R travels from the generator over to the collectors and is reoxidized to O. D) A representative electrode array, 25 micron width electrodes, with a 25 micron separation, and 2 mm long. (Two of the array members on this array have been platinum.)

Figure 2. Chronoamperometric transients for the ETOF experiment in ferrocyanide: the ferricyanide reduction current at the generator (red curve and axis) and the ferrocyanide reoxidation current at the collector (blue curve and axis). The generator is briefly polarized, after this point the oxidative collector current increases until it reaches a maxima. The time between these two points is the time of maximum collection.
Figure 3. The connections between the Generation Electrode Controller (GEC) to the National Instruments cDAQ modules and the 750a potentiostat to produce a pulsed potential waveform at the second working electrode that would otherwise be impossible with the CHI 750a alone.

constant ensures that generator pulses are always a constant width free from software timer and I/O uncertainties. The combination of the GEC and LabView software allows the collection of 10 sets of 10 generate-detect replicates, signal averaged over about 25 minutes.

Working electrode array.—The electrode array was fabricated at the University’s HiDec microfabrication facility. An array of 16 interdigitated, 25 μm by 2 mm gold band working electrodes with a 25 μm separation were constructed using standard photolithography procedures on silicon wafers, then diced. In ETOF experiments, one micro-band electrode served as the generator, with flanking bands, serving as the collector electrodes.

Chemicals.—5 mM potassium ferrocyanide (Certified ACS grade, Fischer), 5 mM potassium ferricyanide (Certified ACS grade, Fischer), 5 mM ruthenium (III) hexamine chloride (highest purity available, Alfa Aesar), and 5 mM dopamine HCl (99%, Alfa Aesar) were obtained and used as received. All except the dopamine were prepared in 0.1 M KCl (ACS grade, J. T. Baker) as their supporting electrolyte. Dopamine (5 mM) was prepared in 0.1 M phosphate buffer at pH 7.2, using mono and dibasic forms of sodium phosphate (Aldrich).

Experimental parameters.—The potentials applied to the generating and collecting electrodes were determined from cyclic voltammograms (CV) of the Red/Ox analytes. CVs were taken over potential ranges for the analytes in question, using a three electrode system; the working electrodes were members of the array, a SCE as the reference, and platinum flag as the counter electrode. The potential window of −0.4 V to 0.4 V vs SCE was used for ferricyanide, ferrocyanide and ruthenium (III) hexamine; −0.1 V to 0.55 V for dopamine. Potentials applied to the generator and the collectors were such that diffusion limited anodic and cathodic currents were achieved at these electrodes. The ETOF parameters were as follows: for ferrocyanide: the generator was pulsed to −0.2 V, while the collectors were held at 0.4 V in a solution of 5 mM ferricyanide; for ferricyanide: the generator pulsed to 0.4 V and the collectors held at −0.1 V vs SCE in 5 mM ferrocyanide in 0.1 M KCl; for ruthenium (II) hexamine: the generator was pulsed to −0.4 V, while holding the collectors at 0.1 V in 5 mM ruthenium

Figure 4. The circuit diagram of the generation electrode controller (GEC). The relay trigger, the start trigger, and the flip-flop restart connect the GEC to the NI 9403 Digital I/O module. The 750a start scan connects the GEC to the cell control port on the CHI 750a. J3 is the second working electrode lead connecting through the relay, and +5V and the ground at the lower right is from the power source for the system.
Pulsing the potential at the generator produces a transient-peak seen in the amperometric display at the collector, Figure 2. Using this peak-shape, it is much easier to determine the time of flight, and the brief duration of the pulse does not generate enough material to allow feedback. Pulse widths for the generator were selected after consulting a paper by Amatore, so that the potential pulse applied to the generator would be less than the shortest time, $t_{\text{min}}$, (Equation 5) for the molecule to diffuse between the two electrodes (otherwise redox cycling could occur).

$$t_{\text{min}} = \frac{g^2}{4D}$$

In this equation $g$ is the gap between the two electrodes and $D$ is the diffusion coefficient. According to Equation 5, the generator pulse was set to 15 ms.

**ETOPO data analysis.**—Pulse generation provides a peak in the collection current, allowing for easy determination of the $t_{\text{min}}$. Figure 2 shows the transient current seen at the collector as a result of a potential pulse at the generator, and the time of maximum collection. The distance traveled has previously been measured in one of two ways: measuring from the edge of the generator electrode to the edge of the collector electrode, or from the center of the generator to the edge of the collector. We found that both methods gave comparable results, but used the edge to edge determination for $d$. The starting point, $t_{\text{min}} = 0$, also has options: the rising edge of the generator pulse, the falling edge of the generator pulse, or the mid-point of the generator pulse. Any of these three options are valid as long as the defined start time is consistent throughout the experiment. For the case here, the time for maximum collection was measured from an artifact seen in the collector current, appearing as a spike the instant the generator is turned on. The current spike is caused by uncompensated resistance between the two electrodes.

The artifact eliminates the reliance on the temporal resolution of the second working electrode (2 ms), and allows time to be measured with the primary working electrode, which has a higher temporal resolution (1 ms). This was also useful, as it provides a point-in-time for synchronization, allowing the signal averaging of hundreds of repeat experiments, and provides a zero for the measurement of $t_{\text{min}}$.

**Functionality of hardware and software.**—To prove the functionality of the hardware and software, we chose an ETOPO experiment from the literature where the diffusional distance, $d$, is varied by addressing three sets of flanking collectors in the array, each pair a larger distance from the generator. Band electrodes in the array were 4 μm wide, 2 μm long, with 4 μm separation. A solution of ferricyanide was used and the $t_{\text{min}}$ for the ferrocyanide generated measured at the three distances. Figure 6, left, shows an overlay of the collector currents at increasing distances from the generator. As the distance increases, more of the generated species is lost to the bulk solution resulting in decreased collection current. Because of the overall broadening of the peak, time of maximum collection is difficult to determine at larger distances, and the signal to noise decreases. Noise has not been recorded as a problem before, as larger band electrodes up to 2.0 cm long with micrometer separation provided larger currents.

The equation relating distance and time is given by Equation 3. This relationship, and the $t_{\text{min}}$ data from Figure 6, left, was used to construct Figure 7, left. From the slope of the line ($K/D$), and a known diffusion coefficient for ferrocyanide, was used to determine $K$, 2.13 ± 0.08 (n = 15), which is a unitless parameter, for the array geometry used. This number was slightly larger (5%) than expected based on the theoretical work done by Amatore, indicating that the range for $K$ should not exceed a value of 1, with array dimensions used here.

We have not found ETOPO experiments using similar array geometries to ours, but we can say that our experimental $K$ is very close to the theoretically predicted range.

In the previous experiment, the diffusive travel of ferrocyanide was used to determine $K$. With the geometric constant, $K$, known,
it is then possible to determine the diffusion coefficients of Red/Ox species by simply measuring t_{mc}. As such, a second experiment was done to determine the diffusion coefficient for ferricyanide. A solution of ferricyanide was used, and the t_{mc} of the ferricyanide generated was measured at the three distances shown in Figure 6, right. The diffusion coefficient for ferricyanide was determined to be 7.3 ± 0.7 × 10^{-6} cm^2/s (n = 15) using the slope of the line in Figure 7, right, and the previously determined K for the electrode geometry. This value is within 2% of the literature value of diffusion coefficient for ferricyanide. These results convinced us that our instrumentation was working correctly, and we proceeded with the development of using electrode arrays to determine diffusion coefficients.

**Proving K constant for multiple Red/Ox species.**—K has been shown to be a constant when using a single redox species with a known D. The Wrighton group determined K for individual redox probe molecules in the early 1990s using the ETOF method with model compounds: in bulk solution with ruthenium (II) hexamine, in gels with ferrocene derivatives, and in solid polymers with silver ions that were stripped off of the generator electrode. Varga mathematically derived K, in a version of Equation 3 for a unique geometry describing glucose diffusion from a micropipette to an electrode, to determine glucose diffusion in solutions and gels. Slowinska heavily modified the ETOF technique to study the capacitance of membranes on potentiometric sensors. The empirical data for hydrogen and silver ions was used to match computational models that were used to determine K using Equation 3 for a unique geometry for the electrode geometry using the same probe molecule through solutions of various glucose concentrations, effectively increasing the viscosity; the work was still limited to a single analyte. Liu devised a method for the determination of diffusion coefficients using ETOF with cyclic voltammetry instead of the more traditional chronoamperometric methods; this was done by first modelling the cyclic voltammograms of ruthenium (II) hexamine and then verifying the resultant K with empirical data.

By only focusing on a single Red/Ox analyte, others did not challenge whether the K determined for one electrode geometry was applicable to other analytes using the same geometry. While other groups have focused on theory, no experimental data has been collected proving whether K is constant for multiple analytes.

The elegance of Equation 4 is in what is not found in the equation. There is no reliance of solution viscosity, number of electrons transferred, electron transfer kinetics, electrode rotation rate, nor solution conductivity. What follows is evidence that diffusion coefficients for multiple Red/Ox species can be determined quickly by using Equation 3, and that K is a constant for multiple Red/Ox species, in solutions of various viscosity. The line is constructed in Figure 8 by measuring t_{mc} for Red/Ox species with known diffusion coefficients in a particular buffer system/solution, according to Equation 4. The analytes chosen were ferricyanide, ferrocyanide, and dopamine o-quinone (assumed to have the same diffusion coefficient as dopamine) to make the “calibration curve” for the array. The curve in Figure 8 can be approximated by a linear fit (γ = 0.0027x − 0.2949), with a slope that is equal to d/K. The distance between the electrodes is constant (d) suggesting that the K is solely based on geometric parameters instead of being influenced by properties of the electrolyte solution, and it appears to be constant for multiple Red/Ox analytes. The y-intercept is meaningless but is a consequence of the fact that there must be an x-intercept. This is important because it means that at a given separation between the two electrodes, d, as the rate at which a species diffuses increases, t_{mc} must necessarily decrease. Eventually t_{mc} will
reach such a small value such that $t_{\text{misc}}$ cannot be resolved from $t_{\text{misc}} = 0$ s, given the temporal resolution of the data collection system. For the electrode separation used here, the x-intercept predicts that species diffusing faster than approximately $1 \times 10^{-4}$ cm$^2$/s cannot be determined. Most species in solution diffuse slower than this, so the technique is generally applicable for redox species in solution.

The line constructed from Equation 4 can also be used to determine the diffusion coefficients for Red/Ox analytes by simply measuring $t_{\text{misc}}$. The $t_{\text{misc}}$ for ruthenium (II) hexamine chloride was measured, 0.405 s, and using the calibration curve from Figure 7, the diffusion coefficient for ruthenium (II) hexamine was determined to be $8.4 \pm 0.5 \times 10^{-6}$ cm$^2$/s. This is because ruthenium (II) hexamine was generated from the ruthenium (III) hexamine in solution, and this method determines the diffusion coefficient of the diffusing species between the two electrodes. This determined diffusion coefficient was found to lie within 7% of the literature value and the null hypothesis could not be rejected at the 95% confidence interval, so it can be said that the value determined was equal to that found in the literature.\(^{33}\)

**Determination of diffusion coefficients in viscous solutions.—** These results show that this kind of data treatment/calibration curve can be used for the rapid determination of the diffusion coefficients of multiple Red/Ox species in solutions of varying composition, for example our alternative data analysis of the ETOF experiment for dopamine was performed in 0.1 M phosphate buffer, while the others used 0.1 M KCl as their supporting electrolyte. We examined viscosity effects by performing additional experiments in solutions of 20% v/v ethylene glycol as the solvent for the supporting electrolyte. The time of maximum collection for ruthenium (II) hexamine, ferricyanide, ferrocyanide, and dopamine shifted to 0.70 s, 0.835 s, 0.993 s, and 0.998 s respectively. The calibration curve in Figure 8 was used in Figure 9 to determine diffusion coefficients of each in the more viscous solutions (the green points in Figure 8). The diffusion coefficients determined for ferri/ferro cyanide, dopamine, and ruthenium hexamine in the more viscous solution were determined from Figure 8 and are shown in Table I.

As expected the diffusion coefficient for each of the Red/Ox analytes has decreased by approximately 30% in the more viscous solution. Because there are no literature values for the diffusion coefficients in the more viscous solutions, we made estimates using the Stokes-Einstein equation: \(^{30}\)

$$D = \frac{T k_b}{6 \pi \eta r}$$

Where $D$ is the diffusion coefficient, $T$ is the temperature, $k_b$ is Boltzmann’s Constant, $r$ is the radius of the spherical particle, and $\eta$ is the viscosity of the solution. Predicted values for the diffusion coefficients in the more viscous solutions are shown in the table, assuming that the change in solvent only affects the viscosity. Other than the Stokes-Einstein equation there has been little theoretical work predicting how diffusion coefficients should change with changes in viscosity. It has been shown that relative errors between experimental and the theoretical prediction from Stokes-Einstein range between 12 and 35% with more extreme errors possible based on the non-spherical nature of the particles that diffuse.\(^{30}\) Dopamine o-quinone and ferrocyanide in Figure 8 appear to have the same diffusion coefficients in the 20% v/v ethylene glycol solution. Ferrocyanide has the expected slower diffusion coefficient in the more viscous solution, dopamine o-quinone however has a faster than expected diffusion coefficient. This could be because of unexpected solvent effects between the dopamine and the 20% v/v ethylene glycol solution altering the hydrated radius to smaller value. The determined diffusion coefficient for dopamine o-quinone is still in the low end of the expected range of disagreement (12–35%) with the Stokes-Einstein estimation.

**Conclusions**

This alternative treatment of ETOF data can quickly determine diffusion coefficients for Red/Ox species from a single experiment. The method outlined here can be used to determine the diffusion coefficients, as viscosity increases, empirically and swiftly. This method can also be used to determine if diffusion coefficients predicted using the Stokes-Einstein equation make empirical sense. The percent error between the diffusion coefficients estimated with Stokes-Einstein and the diffusion coefficients determined empirically using our alternative method of ETOF was in the range of 11–17% error of the predicted values, and the acceptable range of percent errors is from 12–35%.\(^{44}\) These values fall within the acceptable range, and were determined without expensive modeling software or time consuming experiments.

Future applications could include determining diffusion coefficients through membranes. Since diffusion coefficients through membranes set the sensitivity of amperometric sensors, we envision, this research could be used to recalibrate implanted electrochemical sensors in biological applications, as well as a variety of other applications. There are as yet other possible applications that have not been considered because ETOF lacks the visibility needed for people to begin working on these important applications.

**Table I.** Estimation of diffusion coefficients using micro electrode arrays.

| Species, generated | D, Literature, cm$^2$/sec $\times 10^6$, Aqueous | D, cm$^2$/sec $\times 10^6$, 20% v/v ethylene glycol | D estimate, Stokes-Einstein, cm$^2$/sec $\times 10^6$, 20% V/V ethylene glycol | % Difference |
|-------------------|-----------------------------------------------|-------------------------------------------------|-------------------------------------------------|--------------|
| ferricyanide      | 7.20                                          | 5.1 $\pm$ 0.4                                   | 4.45                                            | 13           |
| ferrocyanide      | 6.40                                          | 4.5 $\pm$ 0.1                                   | 4.01                                            | 11           |
| ruthenium(II) hexamine | 7.86                                          | 5.8 $\pm$ 0.2                                   | 4.82                                            | 17           |
| dopamine-orthoquinone | 6.00                                          | 4.4 $\pm$ 0.1                                   | 3.70                                            | 17           |

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