Hydrodynamic Electrochemistry in 20 μL Drops in the Rotating Sample System

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The Rotating Sample System (RSS) has been conceived in the authors' laboratory as a convection platform for microliter-sized solution volumes. Convection is achieved by rotating a small drop of sample on a stationary substrate by humidified gas jets directed tangentially at the drop base with the working electrode and a liquid junction embedded in it. Simplicity and portability of the device, and substrates complete with microfabricated electrode and junction made potentially disposable, are further competitive advantages with respect to competing, conventional analytical systems. In this work the RSS' performance with variation of system parameters such as the position and size of gas jets used for sample rotation, and position of the working electrode in the substrate are studied. Trace levels of Pb could be detected with this system and is reported here.

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Introduction

Conventional electrochemistry typically involves planar macro-electrodes and is diffusion limited. One dimensional diffusion in these systems leads to progressive depletion at the working electrode (WE), making the more desirable stationary techniques out of reach, and sensitivities often insufficient. Forced convection can be used to limit diffusive transport to within the immediate vicinity of the WE, resulting in higher sensitivities as well as steady state mass transport and thus, stationary voltammetry. Besides the obvious advantages in analytical applications, this renders also mechanistic studies of electrode processes as well as related homogeneous reactions, more efficient. To achieve the requisite conditions, different methodologies have been proposed such as rotating wires, streaming mercury electrodes, vibrating electrodes, and systems where there is forced flow past a stationary electrode such as conical, tubular, screen, packed-bed electrodes in fluid streams, channel electrodes, bubbling electrodes, and most prominently, the Rotating Disc Electrode (RDE) system.¹

The Rotating Sample System (RSS, Fig. 1) which has been conceived and developed in the authors' laboratory^{2,3} derives its inspiration from the RDE approach. The RSS cell generates convection by rotating a liquid microsample atop a stationary hydrophilic substrate with the working electrode and liquid junction embedded flush with it (Fig. 1) and surrounded by a hydrophobic ring to keep the sample in position. This in effect provides a very simple equivalent to the costly, complex, and much larger RDE system. Yet, the RSS approach does not involve any moving mechanical parts since rotation is achieved by employing a humidified gas (*e.g.*, air) jet or jets. The fact that the sample volume can be very small (in the order of ten to twenty microliters), and that the substrate can be microfabricated and disposable, renders the RSS system attractive for use in biomedical and environmental applications.

Its utility can be extended to monitoring and measuring contaminants in industrial samples, and for basic electrochemical studies.

The RSS approach has been shown to achieve diffusion layer thicknesses in the order of 10 μm and less, at comfortable gas flow rates (around 100 mL/min).² This performance is equivalent to a disc electrode rotated at about 3000 rpm, yet no signs of deformation of the sample drop are apparent to the eye: it remains semi-spherical which indicates the remarkable strength of surface tension at the boundaries of a miniature aqueous drop and air. Earlier findings² corroborated the expected trend that the diffusion layer thickness decreases with

Fig. 1 Schematic diagram of the Rotating Sample System as used in this work to explore flexible cell design. The position of the 150 μm Pt mini-disc working electrode (WE) is variable with respect to the axis of rotation by moving the hydrophobic silicone elastomer ring accordingly. Liquid junction is made of a hole, filled with agar gel, to connect the sample drop to an underlying reference compartment where an Ag|AgCl reference and a stainless steel counter electrode are housed, bathed in 0.1 M KNO_3 solution (not shown).

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Fig. 2 Schematic diagram (top view) of a microfabricated RSS cell, as used in exploring the effects of position of the air jet, its nozzle diameter, and gas flow velocity. The thick solid line (a) indicates the microfabricated Pt ring electrode and its connection to the contact pad (b). The connecting wire (c) is buried under the silicone elastomer (d) to ensure that a contiguous hydrophobic barrier surrounds the sample drop. The nozzle (e) was placed on top of the substrate; its horizontal position with respect to the vertical axis of rotation of the sample drop is defined by the x and y coordinates as shown in the top view. The liquid junction (f) and reference/counter electrode compartment are similar to the RSS cell with flexible geometry shown in Fig. 1.

increasing sample rotation rate. Also, considering that the results are very reproducible suggests that laminar flow conditions exist in the rotating drop.

Using the Rotating Sample platform with a microfabricated platinum ring electrode (Fig. 2), determination of mercury² in aqueous samples has been shown to be feasible using anodic stripping voltammetry. Copper detection capability in an acid pre-treated and filtered (to remove serum proteins) serum matrix has been demonstrated in our laboratory.³ In addition, the RSS' utility in detection of other metal ions has also been explored.⁴ Given the potential for useful applications, a better understanding of the RSS' performance *vis-à-vis* its system parameters is warranted.

While similarities can be drawn between the RSS and the RDE,⁵ differences exist in specific details. The unique aspect of the RSS is that sample drop integrity is maintained during rotation due to surface tension. Also, since a gas jet (or jets) is used to achieve sample rotation instead of directly rotating a "rigidly" coupled electrode as in the RDE approach, a "soft" mechanical coupling of the gas jet and the surface of the liquid sample is to be considered. In this work these aspects, unique to the Rotating Sample System, are explored experimentally. Dependence on the number, and placement of gas jet(s) relative to the sample to examine coupling of the air jet(s) with the sample, and the effects of gas flow rate and nozzle diameter on the ultimate electrochemical properties of the RSS, are also investigated.

Trace analysis of Pb in 20 μL samples is also reported here. Pb in blood is considered to have several deleterious effects on human health.⁶ The RSS here could provide with an alternative to the expensive, bulky and labor intensive current state-of-the-art AAS⁷ and ICP-MS⁸ techniques. Several electrochemical approaches to Pb detection such as the RDE,⁹ sonoelectroanalysis,¹⁰ flow injection¹¹ and stirred systems¹² have also been explored. The RSS operates with much smaller sample volume than is required in the aforementioned methodologies. Moreover, the RSS can be modified to employ

different electrode materials such as carbon,^{9,12} boron doped diamond electrodes^{10,13} and mercury^{11,14,15} for Pb detection purposes.

Experimental

Materials

All chemicals were from Sigma (St Louis, MO, USA); solutions were made with Milli-Q water (18.2 M Ω cm Milli-QUV plus from Millipore, Billerica, MA, USA). For trace Pb analysis the water was distilled using a quartz distiller to obtain ultra-pure water. Also, polypropylene flasks (Nalge Nunc International, Rochester, NY, USA) were used for storing Pb solutions to preempt any contamination due to storage in glass containers.¹⁶ The two RSS setups used in this work (Figs. 1 and 2) were characterized using 1.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ with 0.1 M KNO_3 as supporting electrolyte. Capillary tubes (0.025 mm wall thickness; A. H. Thomas Co., Philadelphia, PA, USA) of 0.5 mm inner diameter (i.d.) were used to rotate the drops in experiments with flexible cell geometry (Fig. 1). Capillaries of different i.d. values were used in the experiments involving the microfabricated RSS cell (Fig. 2). In order to visualize flow patterns within a rotating drop, Evans Blue dye was inserted into a rotating drop using a pulled glass capillary.

Apparatus

To evaluate system performance by changing the position of the air jet and the diameter of the air-nozzle used for sample rotation, a microfabricated RSS cell was used with a Pt ring WE, deposited symmetrically around the junction hole (Fig. 2). Fabrication of this device has been described earlier.^{2,3} The nozzle of the humidified air jet was mounted on a three axis manipulator (WPI, Sarasota, FL, USA). The nozzle positions were recorded by taking a top view image of the RSS setup using a CCD camera (CV-S3200 from JAI, Copenhagen, Denmark).

To evaluate system performance for different positions of the WE in the substrate with respect to the sample drop, another system with a Pt mini-disc electrode and flexible geometry was adopted. The corresponding electrochemical cell (Fig. 1) was fabricated using a part of a microscope glass slide (7.5 cm $\times$ 2.5 cm and 0.1 cm thick, from Fisher Scientific, Pittsburgh, PA, USA) as substrate. The WE was made from 150 μm diameter platinum wire (Alfa Aesar, Ward Hill, MA, USA). Silicone elastomer (DOW Corning, Midland, MI, USA) was applied to form the hydrophobic ring that confines the sample drop into a semi-sphere. Epoxy resin (ITW Performance Polymers, Riviera Beach, FL, USA) was used for gluing purposes. Similar setup was also used for trace Pb analyses.

The Ag|AgCl reference (BAS, West Lafayette, IN, USA) and stainless steel counter electrodes (Alfa Aesar) were placed under the substrate in 0.1 M KNO_3 , connected to the sample side by a liquid junction filled with 1 wt% agar gel (Sigma). Humidified air jets driven by an aquarium pump (Wollinger Bros., Oakland, NJ, USA) were directed toward the sample from 0.5 mm i.d. glass capillaries. Air flow rates were measured with volumetric flow meters (Cole-Parmer Instrument Co., Niles, IL, USA). For trace Pb analysis, humidified nitrogen gas jet was used instead of air jet.

Electrochemical measurements for testing effects of the position of gas jets were performed using BAS 100 W potentiostat (BAS, West Lafayette, IN, USA) with microfabricated sensors (Fig. 2).² For all other studies a CH100 electrochemical workstation (CH Instruments, Austin, TX,

USA) was used. Images of the rotated sample drop were acquired using a CCD camera (see above).

All calculations were done using Matlab 6.0 (Math Works, Natick, MA, USA).

Procedures

Fabrication of the electrochemical cell with flexible geometry (Fig. 1). Two holes 1 mm in diameter were drilled through the glass slide. Glass of the same material was heat melted around the tip of the platinum wire with 150 μm diameter so as to cover the tip completely with a glass bead, a little larger than the drilled hole. This end of the wire was inserted in one of the holes so that it fits in snugly. The bead was then glued onto the substrate using epoxy resin. The substrate surface was then polished to leave a flush platinum mini-disc exposed to form the WE. The other hole is for the liquid junction. Silicone elastomer was printed to form a hydrophobic ring to keep the sample in position; internal diameter of this ring is calculated as 4.2 mm for a 20 μL drop to ideally form a perfect hemisphere. Different positions of the electrode were realized by simply re-applying the elastomer in different positions by shifting the relative position of the circular hole in the elastomer. This way the axis of rotation of the sample *vis-à-vis* the electrode position could be shifted while ensuring similar electrode surface conditions; therefore an exact comparison in the responses is possible. This arrangement also allowed the investigation of system characteristics with the working electrode positioned at the center of the sample drop.

It is noted that the presence of an electrical contact line between the electrode and the contact pad of the substrate may have an averaging effect along the radius of the drop. This was minimized by fabricating a contact line very thin with respect to the ring electrode in the cell shown in Fig. 2. In the setup shown in Fig. 1, electrical contact is made on the other side of the glass slide which eliminates this problem altogether. Also, mechanical polishing of the WE is possible in contrast to earlier microfabricated electrodes^{2,3} (Fig. 2) since this is in comparison a mechanically more robust electrode.

Two anti-parallel humidified air jets were employed in this device for more axis-symmetric rotation of the sample. Humidified air-jets ensure that loss of sample volume due to evaporation is minimal.² The position of the electrode *vis-à-vis* these jets was kept such that the electrode-junction hole line was parallel to the axes of the jets in all experiments (Fig. 1).

Determination of the effective surface area at, and edge current of, the working electrode and the diffusion layer thickness. Electrode area was determined by chronoamperometry where the transient current response for a microdisk electrode is given by Cottrell's equation, *i.e.*, the first term in Eq. (1):¹

$$i(t) = nFDC \left(\frac{A}{(\pi Dt)^{1/2}} + 4r_e \right) \quad (1)$$

where r_e is WE disc radius, A (cm^2) the active surface area, 1 mM concentration C (mol/cm^3) of potassium ferricyanide with diffusion coefficient D ($D = 7.3 \times 10^{-6} \text{ cm}^2/\text{s}$). Thus, the slope of a linear fit to the current *versus* inverse square root of time plot also has information regarding active electrode surface area. The obtained electrode area was also verified by using cyclic voltammetry at different scan rates¹.

The bias of the linear fit from the chronoamperometry experiment gives the edge current (the second, "microelectrode", term in Eq. (1), i_{edge}). Edge currents are negligible in the case of macro-electrodes; however it is no longer negligible for a mini-disc electrode such as the one used

here (150 μm diameter).

Plateau currents of stationary CV plots, obtained when the sample was efficiently rotated in the RS system, have been used earlier² to estimate the diffusion layer thickness (δ),^{2,3} correcting here also for edge currents:

$$\delta_{\text{corrected}} = \frac{nFADC}{i_{\text{plateau}} - i_{\text{edge}}} \quad (2)$$

Trace Pb analysis. Pb measurement with the RSS in the 160–1600 parts-per-billion (ppb) range was first performed using differential pulse stripping voltammetry. Mercury was pre-deposited onto the electrode from a 1.5 mM HgCl_2 solution containing 5% HCl for 250 s. This is done to prevent hydrogen evolution, which would mask the Pb stripping current on a bare platinum electrode.^{11,14,15} After pre-concentration of Pb on the WE during rotation of the sample for 30 s, a 30 s quiet time was applied with the air jets were switched off. The potential at the WE was clamped at deposition potential during all this time to avoid any oxidation of Pb that might otherwise occur due to corrosion processes. Blank runs (with samples containing no Pb), simulating identical experimental conditions were interspersed between subsequent Pb tests so that the system self-cleans itself and ensures no residual Pb contributed to the stripping current.

Two 0.5 mm i.d. glass capillaries were glued to the glass substrate to preempt any variation in diffusion layer thickness which may have been caused due to slight variation in nozzle positions. Thus for each individual sample, RSS system parameters such as electrode position, nozzle position and gas flow rate (180 mL/min) were fixed.

Pb solutions were prepared by serial dilutions of a Pb standard solution for atomic absorption spectrometry. A solution with 0.1 M KNO_3 was used as background at pH 2.3, acidified with trace-select HNO_3 . Three sets of calibrations (increasing followed by decreasing followed by increasing concentration of Pb: 'up-down-up') were performed. A background solution with no Pb was also used as a blank. A 300 μm diameter Pt mini-disc electrode with its center positioned 1.8 mm from the axis of rotation was used.

To test for reproducibility and to confine enhanced sensitivity by using RSS parameters tuned for lower Pb concentrations, measurements were also performed for 16 ppb samples ($n = 5$). Hg pre-deposited, Pt mini-disc electrode with 100 μm diameter, whose center was positioned 1.8 mm from the axis of rotation was used in this case for a 750 s pre-concentration time for Pb.

Results and Discussion

Air-nozzle study

To optimize the air jet-drop mechanical coupling, the relative jet-drop position as well as the nozzle inner diameter for air jet were systematically varied with the same volumetric gas flow rate. The experiments were conducted with a single gas jet and using the microfabricated version of the RSS cell incorporating a Pt ring electrode (Fig. 2). Plateau current of cyclic voltammetry (CV) was used to determine the diffusion layer thickness (Eq. (3)); the active electrode area was obtained from chronoamperometry.

The narrower the nozzle the thinner the diffusion layer, *i.e.*, the better is the electrochemical performance of the system (Table 1). Thus, the same volumetric gas flow rate that translates to higher linear gas velocities in narrower tubing apparently induces higher rotation rate of the drop. This

Table 1 Diffusion layer thickness as a function of the position and the inner diameter of nozzle for a single air jet

		Nozzle inner diameter (mm)								
		0.5			1.0			2.0		
					Mean linear air velocity at nozzle (m/s)					
		12			3			0.7		
		x/mm	y/mm	$\delta/\mu\text{m}$	x/mm	y/mm	$\delta/\mu\text{m}$	x/mm	y/mm	$\delta/\mu\text{m}$
-0.24	0.53	8.85	0.14	0.35	11.0	0.60	0.97	20.5
		-1.63	0.53	8.90	-1.63	0.35	11.0	-2.37	0.97	21.0
		-3.26	0.53	9.70	-3.08	0.35	11.0	-4.09	0.97	22.0
		0.41	0.53	8.3	-0.39	0.74	12.0	-4.09	0.97	19.5
		0.41	0.79	14.5	-0.39	1.18	18.0	-4.09	1.39	19.5
		0.41	1.03	28.05	-0.39	1.62	34.0	-4.09	2.16	45.0

Nozzle position is defined by the horizontal coordinates of the capillary outlet (nozzle) at the axis (x and y , in mm, see Fig. 2); δ is diffusion layer thickness as obtained from the plateau current of cyclic voltammetry of 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ at the microfabricated Pt ring electrode (Fig. 2). The volumetric gas flow rate was kept 140 mL/min throughout for all air jets. With the nozzle placed on top of the substrate, the height of the axis of the air jet is at half its inner diameter plus 0.025 mm (due to tubing wall) above the base.

Fig. 3 Cyclic voltammograms (CV) in a 20 μL sample drop containing 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ with 0.1 M KNO_3 as background electrolyte for the Pt mini-disc electrode positioned at the axis of rotation on the substrate with various air jet flow rates (a = 0 mL/min, b = 20 mL/min, c = 39 mL/min, d = 63 mL/min, e = 98 mL/min, f = 140 mL/min, g = 140 mL/min). Initial potential 350 mV, scan rate = 100 mV/s. Two anti-parallel air jets were used, except for the highest air flow rate (g) where CV was also obtained with one air jet.

observation indicates that deterioration of the soft mechanical coupling between jet and drop due to decreasing contact area with reduced nozzle inner diameter is less pronounced than the simultaneous positive effect of increasing air jet velocity.

It is noted that average air jet velocity is inversely proportional to the square of nozzle inner diameter while the contact area is proportional to the diameter. Thus, their mutual effects could, in principle, compensate each other for the same volumetric gas flow. The fact that this is not the case suggests that divergence of the air jet upon exit from the nozzle is quite significant, even over the short distance from nozzle to drop. The contact area therefore decreases to a lesser extent than the cross sectional area of the nozzle. Air jet velocity therefore increases faster than the contact area decreases, which explains the findings.

The effect of variation of air jet-drop relative position is more sensitive in the direction perpendicular to the air jet (y direction) than in the direction tangential to the drop (x direction). The

Fig. 4 Images showing flow patterns in a rotating drop by injection of Evans dye at the apex of the drop. Pictures of the drop rotated by 39 mL/min gas jet were taken.

best hydrodynamic effect, *i.e.*, the thinnest diffusion layer, for the same nozzle inner diameter is ensured when the axis of the air jet is nearly tangential to the drop (lowest value of y in Fig. 2, see Table 1) and closest to it (highest x value). This position with the narrowest nozzle used can ensure a diffusion layer in the order of 8 μm thick with this simple system and using just a single gas jet for sample rotation.

Variation in diffusion layer thickness with WE position along the drop radius

The RSS with flexible geometry (Fig. 1) was used to compare system performance for various positions of the working electrode. Two anti-parallel, tangential air jets were employed.

The active surface area of the Pt mini-disc electrode of this cell was determined using a chronoamperometry experiment. The values for electrode area were also validated using cyclic voltammetry experiments using different scan rates. The thus obtained area compared well with each other as well as with the nominal area (wire cross-section), the latter being always somewhat larger (not shown).

Relative contribution of the edge current to total current becomes more significant at lower gas flow rates and/or shorter electrode distances from the axis of rotation, (Table 2). This results in a decrease in total current, and hence an increase in

Table 2 Plateau and edge currents at various air flow rates for different positions of the Pt mini-disc electrode, using two anti-parallel air jets for sample rotation

Air flow rate (mL/min)	Electrode position from axis of drop rotation (mm)				
	0.82	1.44	1.53	1.89	
					Plateau current (nA)
140	107	160	166	268	
98	97	139	142	193	
63	84	118	118	163	
39	72	96	100	132	
Edge current to be subtracted	19	17	16	18	Mean 17.5 ± 1.2 nA
% of total plateau current	17.7 – 26.3	10.6 – 17.7	9.6 – 16.0	6.7 – 13.6	

Electrode position is measured from axis of rotation of the sample drop. Edge current in each case was calculated using chronoamperometry. The system in Fig. 1 was used in these experiments.

diffusion layer thickness. The edge current is about 26% of the total current at a gas flow of 39 mL/min and in the closest position of the WE to the center, 0.82 mm. It makes up, however, only about 7% total current in more hydrodynamically efficient settings, *i.e.*, at 140 mL/min flow rate and $r = 1.89$ mm.

The diffusion layer thickness was evaluated according to Eq. (2) at different positions of the electrode at different air flow rates (Table 2). For the working electrode positioned at the axis of rotation of the drop, as the rotation rate is increased, the current slightly increases indicating increasing hydrodynamic flow at the surface of the electrode, but peaks in the cyclic voltammograms are still discernable (Fig. 3a–f) as opposed to the plateau current which was observed for electrode positions away from the axis of rotating drop (not shown). This indicates that while some convection effects are noticeable with slightly increased peak heights, quiescent conditions exist close to the axis of rotation. Diffusion here is in between semi-infinite and diffusion layer limited regimes.

To explain this effect, a very small amount of Evans Blue dye solution was introduced at the apex of a rotating drop from a pulled capillary tip for the observation of hydrodynamic flow pattern. It was found that the trajectory pattern visualized by the applied dye solution indicates a spiral path down towards the base of the drop along the surface; the trace then re-appeared at the axis of rotation beginning to move up before dilution of the dye (Fig. 4). This observation indicates that in addition to the primary motion of rotation, secondary flow patterns exist in the bulk of the drop. Close to the axis of rotation of the drop the dye trace indicates an upward flow exists. This leads to quiescent conditions there as evidenced from the cyclic voltammetry experiments.

When one of the air jets was switched off in this experiment, however, the peak in the center position disappeared and a plateau current became apparent with a significantly increased current level (Fig. 3g). The reason for this anomalous behavior is that the system in this case becomes asymmetric and the axis of rotation is therefore shifted away from the geometrical axis where the electrode is located; dye-insertion provided with a visual proof of the same. Thus, a system having two air jets provides for more axis-symmetric, *i.e.*, more ideal rotation patterns since the jets themselves are in this case axis-symmetric.

An analysis of data obtained at the WE positioned away from the center when only one air jet is used for rotation results in somewhat thicker diffusion layers (not shown) than those obtained with double jets at the respective positions. The increase in thickness of the diffusion layer (and the

Fig. 5 Up-down-up calibrations for anodic stripping analysis of trace Pb in 20 µl aqueous drops. Linear regression is shown for peak differential currents of samples containing 160, 400, 800, 1200 and 1600 ppb Pb. Pre-concentration potential of -750 mV was used as measured against Ag/AgCl reference electrode with junction (3M KCl) with a pre-concentration time of 30 s. In stripping step differential pulse voltammetry (DPV), the following parameters were used: 25 mV of amplitude, 4 mV of voltage step, 0.05 s of pulse width, 0.012 s of sampling period, 0.1 s of pulse period. Nitrogen gas jets for the sample rotation were switched off 30 s before the stripping step; the potential was clamped at -750 mV during this period (quiet time). A Hg pre-deposited, Pt mini-disc with 300 µm diameter was used as WE. Stripping voltammograms for samples containing 16 ppb Pb ($n = 5$). Pre-concentration time used here was 750 s for a 100 µm Hg layer pre-deposited onto the Pt mini-disc electrode. DPV parameters were the same as those used for up-down-up calibrations.

corresponding decrease in current) is, however, no greater than 10% at the studied WE positions. This corroborates the earlier observation that the actual jet linear flow velocity is more important in hydrodynamic efficiency than the contact area between drop and air jet(s).

Trace Pb analysis

Three sets of “up-down-up” calibration experiments were carried out with samples containing various concentrations of

Pb (Fig. 5) using differential pulse stripping voltammetry. Each set of calibration was performed with increasing Pb concentrations, followed by decreasing concentrations and then followed by the same concentrations in increasing order. Excellent linearity of calibration was obtained in each set with a unified regression coefficient of 0.9927 (Fig. 5). Using 3σ ,^{10,17} these settings yielded a detection limit of 14 ppb Pb level.

The amount of Pb, N , deposited during time t , is the difference between the initial amount in the sample and the decreased amount at the end of the deposition step. Diffusion limited depletion being proportional to concentration in the sample, deposition flux decreases exponentially with time:²

$$N = VC_0 \left(1 - e^{-\frac{AD}{Vd}t} \right) \quad (3)$$

where V is the volume of the sample (20 μL), C_0 is the initial concentration of Pb in the drop, A is the area of the electrode, D is diffusion coefficient of Pb^{2+} in aqueous solution, and δ is the diffusion layer thickness. The amount deposited can be obtained experimentally by integration of the stripping current. Equation (3) suggests that exhaustive deposition of the analyte requires long deposition times and/or a large electrode area. Since the electrode size used here is small and the deposition times are moderate, the deposited amount can be estimated with a linear approximation of Eq. (3) that is valid for short time period. The diffusion layer thickness (δ) for Pb stripping analysis is therefore estimated using

$$\delta = \frac{C_0 ADt}{N} \quad (4)$$

The estimated diffusion layer thickness was $10.2 \pm 1.6 \mu\text{m}$ obtained for set of experiment of decreasing Pb concentrations.

Repeatability and sensitivity for trace Pb detection using the RSS in the lower tens of ppb range was then tested. A Hg pre-deposited, platinum mini-disc electrode with 100 μm diameter was used for detection of 16 ppb Pb. Improved signal to noise ratio was achieved in this case by increasing the deposition time to 750 s (inset, Fig. 5). The measurement was repeated five times to test for reproducibility. The coefficient of variation for stripping peak heights and peak areas were 1.8% and 1.4% respectively. The diffusion layer thickness estimated from the five measurements was $9.2 \pm 0.1 \mu\text{m}$. With improved signal-to-noise ratio, this setup and protocol yielded a detection limit of 240 ppt (parts-per-trillion) Pb level based on 3σ .^{10,17}

Conclusions

The Rotating Sample System is based on the idea that for very small aqueous samples, effective hydrodynamic electrochemistry can be realized by turning the Rotating Electrode System upside down and keeping the electrode steady while rotating the sample drop on top *via* soft mechanical coupling with tangential air jets. At such small volume of the sample, surface tension ensures that drop integrity is maintained during rotation.

Increasing the number of air jets with the same air velocity each does not necessarily increase rotation very much, but provides for more axis-symmetric rotation of the drop. At least two air jets would be required for axis-symmetric rotation of the sample.

Secondary bulk flow patterns exist in addition to the primary rotation of the sample. This secondary flow within the drop

bulk modulates the diffusion layer thickness. These secondary flow patterns also contribute to the mixing effect in the sample. Minor variations of diffusion layer thickness are hence manifest with varying the distance of the working electrode from the axis of rotation. At the center of the sample, quiescent condition exists and offers an ideal location for the reference junction to be positioned.

Currents can be increased, and in stripping detection, deposition times shortened by positioning the electrode as close to the drop edge as possible since the diffusion layer is the thinnest here. This position is empirically the most optimal position for trace metal analysis. At the expense of increased pre-concentration time, improved signal-to-noise ratio can be obtained by decreasing the electrode size. Larger electrodes reduce the deposition time, but their detection level is limited by the background that forms the baseline. Therefore, for lower concentration ranges, as the results show, using a smaller electrode will enhance sensitivity significantly.

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References

1. A. J. Bard and L. R. Faulkner, "*Electrochemical Methods*", **2001**, John Wiley, New York, New York.
2. A. Cserey and M. Gratzl, *Anal. Chem.*, **1997**, 69, 3687.
3. A. Cserey, "*Novel Electrochemical Sensing Scheme for Cost-effective Diagnostics and On-line Monitoring of Nitric Oxide*", **2001**, Ph. D. Theses, CWRU, Cleveland, Ohio.
4. A. Cserey, G. N. Shetty, and M. Gratzl, unpublished results, CWRU, 2001 – 2003.
5. V. J. Levich, "*Physico-Chemical Hydrodynamics*", **1952**, Press of the Academy of Sciences of the Soviet Union: Moscow.
6. H. Needleman, *Ann. Rev. Med.*, **2004**, 55, 209.
7. D. Baralkiewicz, P. Niedzielski, and J. Siepak, *Ekologia i Technika*, **1996**, 4, 27.
8. E. H. Hansen and J. Wang, *Dansk Kemi*, **2002**, 83, 49.
9. C. Brihaye, G. Gillian, and G. Duyckaerts, *Anal. Chim. Acta*, **1983**, 148, 51.
10. C. Banks, J. Kruusma, and M. Hyde, *Anal. Bioanal. Chem.*, **2004**, 379, 277.
11. S. Jaenicke and H. Ginasingham, *Talanta*, **1998**, 45, 703.
12. P. N. Bartlett, G. Denualt, and M. F. B. Sousa, *Analyst*, **2000**, 125, 1135.
13. Y. Maeda, T. Hashimoto, K. Satoh, D. A. Tryk, and A. Fujishima, *J. Sur. Fin. Soc. Jpn.*, **2003**, 54, 64.
14. Y. Tekutskaia, L. Sofyina, L. Bender, and N. Onishchenko, *Gigiena i sanitariia, Hygiene et service sanitaire*, **1999**, 4, 72.
15. J. Duinker and C. Kramer, *Mar. Chem.*, **1977**, 5, 207.
16. E. Prichard and G. M. MacKay, "*Trace Analysis: A Structured Approach to Obtaining Reliable Results*", **1996**, The Royal Society of Chemistry, Cambridge.
17. Analytical Methods Committee, *Analyst*, **1987**, 112, 199.