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Aerosol Electroanalysis by PILSNER: Particle-into-Liquid Sampling for Nanoliter Electrochemical Reactions

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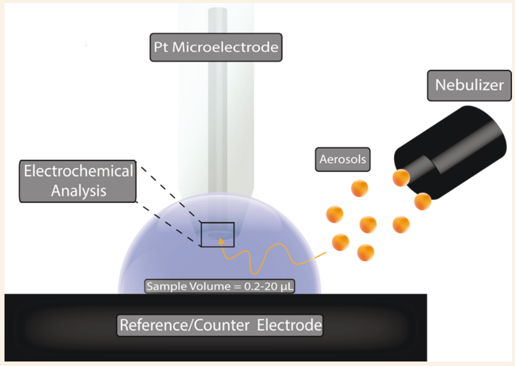

ABSTRACT: Particle-into-liquid sampling (PILS) has enabled robust quantification of analytes of interest in aerosol particles. In PILS, the limit of detection is limited by the factor of particle dilution into the liquid sampling volume. Thus, much lower limits of detection can be achieved by decreasing the sampling volume and increasing the surface area-to-volume ratio of the collection substrate. Unfortunately, few analytical techniques can realize this miniaturization. Here, we use an ultramicroelectrode in a microliter or smaller sampling volume to detect redox active species in aerosols to develop the technique of Particle-into-Liquid Sampling for Nanoliter Electrochemical Reactions (PILSNER). As a proof-of-concept to validate this technique, we demonstrate the detection of $K_4Fe(CN)_6$ in aerosol particles (diameter ~0.1−2 μm) and quantify the electrochemical response. To further explore the utility of the method to detect environmentally relevant redox molecules, we show PILSNER can detect 1 ng/m^3 airborne Pb in aerosols. We also demonstrate the feasibility of detecting perfluorooctanesulfonate (PFOS), a persistent environmental contaminant, using this technique. PILSNER is shown to represent a significant advancement toward simple and effective detection of a variety of emerging contaminants with an easily miniaturizable and tunable electroanalytical platform.

KEYWORDS: *Aerosol, Cyclic Voltammetry, Amperometry, Anodic Stripping Voltammetry, Online Sampling, Molecularly Imprinted Polymer, Electrochemistry, Atmospheric Chemistry*

■ INTRODUCTION

Aerosols, defined as suspensions of liquid or solid particles in a gas,[1] are ubiquitous in almost every environment. Aerosol chemistry and physics are accepted to play critical roles in important natural processes such as cloud formation,[2] ozone depletion,[3] and long-distance chemical transport.[4] Additionally, chronic exposure to high concentrations of aerosols of diameters less than 2.5 μm, often referred to as PM 2.5 in the literature, is linked to numerous health issues including respiratory and heart problems[5] and overall morbidity. Liquid aerosols and microdroplets have also been shown to have unique properties such as reaction rate acceleration[6,7] and spontaneous radical generation,[8] making them of particular analytical interest and relevance. As such, techniques for sampling and analyzing aerosols quickly and accurately are of great importance. While some sampling technology has been developed to meet this need,[9−11] the small size, high physical and chemical heterogeneity, and potential reactivity of aerosols continues to make accurate, inexpensive, and technically simple sampling very challenging.[12]

One commonly employed aerosol sampling technique is particle-into-liquid sampling (PILS). In this technique, particles are impacted onto a liquid interface and incorporated into the bulk solution (or sampling volume). Analytes in the aerosol are extracted by this sampling volume, and the resulting sample is analyzed by another technique, such as mass spectrometry[13] or fluorescence.[14] Despite its analytical power, PILS is limited by both the relatively large volume into which particles are usually sampled (usually on the order of mL, creating a large dilution factor for analytes) as well as its off-line nature. If techniques are developed to probe smaller sampling volumes, the limit of detection (LOD) of PILS can be driven down by orders of magnitude. To mitigate dilution limitations in PILS, we introduce here particle-into-liquid sampling for nanoliter electrochemical reactions (PILSNER).

In PILSNER, a small (200 nL to 20 μL) droplet of water or electrolyte solution serves as a "collector droplet" into which aerosol particles are deposited. In the current work, the aerosol is generated from analyte solutions using a jet nebulizer, but in principle, this technique would work with other natural or artificial aerosol sources. Particles are directed into striking the

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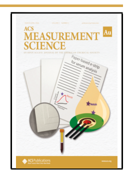

collector droplet, which itself is in contact with a conductive glassy carbon chip as well as the tip of an ultramicroelectrode (*i.e.*, a scanning electrochemical microscopy (SECM) tip). By using the glassy carbon chip as a counter and pseudoreference electrode, electrochemical techniques can be applied to the droplet to analyze its contents and the contents of the collected aerosol. This strategy for analyzing aerosols is thus both fast and has the potential for very low limits of detection given the inherent capabilities of electrochemical detection and the reduced degree of analyte dilution in small sampling volumes. Figure 1A,B serves to illustrate the experimental setup and the

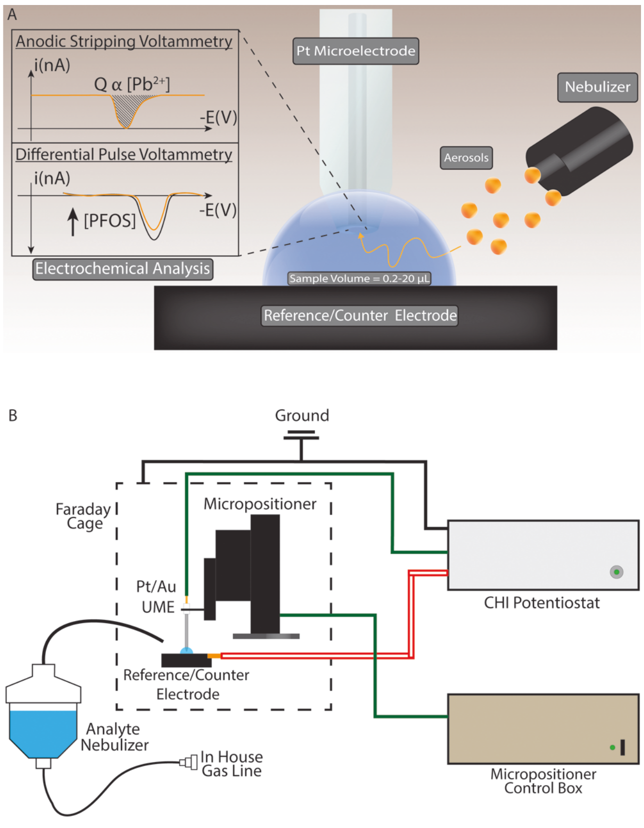

Figure 1. (A) Illustration of the PILSNER setup during the analysis of Pb aerosol via anodic stripping voltammetry and PFOS aerosol via differential pulse voltammetry. (B) Schematic of the PILSNER system. For PFOS analysis, the pseudoreference/counter electrode was modified with a well, as described below.

resulting electrochemical responses. In this work, the efficacy of the technique in analyzing the well-behaved redox analyte $K_4Fe(CN)_6$ in aerosol is shown using amperometry to track particle collection in real time. Cyclic voltammetry of the collected ferrocyanide was also performed to demonstrate that the system behaves as expected electrochemically (Figure S1). The potential applicability of the technique is demonstrated with the detection of aerosols containing low-ng/m^3 concentrations of Pb using anodic stripping voltammetry. The detection of aerosols generated from water solutions of perfluorooctanesulfonate (PFOS), a highly persistent environmental contaminant in rivers and soils,[15] using a molecularly imprinted polymer (MIP)-modified ultramicroelectrode is also shown. The efficacy of this type of MIP-modified ultramicroelectrode has been previously demonstrated,[16−19] and its effectiveness in conjunction with PILSNER demonstrates the potential for the combination of PILSNER with other electrochemical techniques. Broadly speaking, these data demonstrate the potential effectiveness of PILSNER in detecting emerging contaminants in environmental aerosols.

■ MATERIALS AND METHODS

Chemicals and Materials

Potassium hexacyanoferrate (II) trihydrate (≥99.95% trace metals basis), ferrocenemethanol (97%), *o*-phenylenediamine (*o*-PD, ≥98.0%), and heptadecafluorooctanesulfonic acid potassium salt (PFOS, ≥98.0%) were purchased from Sigma-Aldrich. Lead(II) nitrate (99+%) was purchased from Acros Organics. Potassium chloride (≥99.0%, heavy metals ≤5 ppm) was purchased from Thermo Fisher Scientific. The acetate buffer was made from acetic acid (Sigma-Aldrich, ≥99.95% trace metals basis) and sodium acetate from MCB Reagents (ACS grade). Dulbecco's phosphate buffered saline (PBS, 1×) was obtained from Gibco. The platinum scanning electrochemical microscopy tip (10 μm diameter, $R/G \sim 25$) and the gold scanning electrochemical microscopy tip (12.5 μm diameter) were obtained from CH Instruments (Austin, Texas). All voltammetry and amperometry was performed on the CHI model 601D or 6012D potentiostat. The glassy carbon pseudoreference/counter electrode was obtained from Alfa Aesar. Solutions and water droplets were prepared with ultrapure water (Millipore Milli-Q, 18.2 MΩ·cm). Aerosols were generated by flowing in-house air through a Hudson RCI 1724 nebulizer filled with solution. The flow rate was regulated by an Amvex Medical Flowmeter to 5 L/min. Electrochemical measurements were taken within a well-grounded Faraday cage. Images and videos were captured using a Park Systems CoolingTech Digital Microscope focused and positioned ∼2.5 cm from the electrodes.

Detection of Ferrocyanide

For the detection of ferrocyanide in aerosols, a 0.2−10 μL nano- or microdroplet of ultrapure water was placed onto the glassy carbon chip using a micropipette. The ultramicroelectrode was inserted into the collector droplet via a micropositioner (Model ROE-200, Sutter Instruments) approaching from above the droplet. The ultramicroelectrode tip was positioned approximately in the center of the droplet. Initial contact with the droplet could be observed by the deformation of the droplet into a semiconical shape about the ultramicroelectrode tip. The tip of the nebulizer was positioned ∼1.6 cm away from the droplet. An amperometric $i-t$ curve was used to monitor the spraying and collection of aerosol particles. The measurement was started before spraying, continued while the aerosol was sprayed into the droplet, and ended a short time after the aerosol spraying was stopped. The amperometric $i-t$ curve was performed at +0.6 V versus the glassy carbon pseudoreference electrode with a sample interval of 0.1 s and no quiet time. The voltage used was based on a cyclic voltammogram of a 10 μL potassium hexacyanoferrate droplet obtained with the same setup. Due to the communication between the electrodes and the unique setup of PILSNER, offset currents were baseline subtracted. It should be noted that only amperometry experiments involving ferrocyanide detection were exposed to aerosol and gas flow during the measurement. All other following experiments (anodic stripping, CVs, and DPVs) were performed with no gas flow or aerosol exposure during the electrochemical measurement. We also note that the use of the carbon quasi-reference electrode may induce drift. We generally observed up to 100 mV of drift from experiment to experiment. However, because we are interested most in current magnitude, we used the potential window of the droplet (water oxidation and water/oxygen reduction) to gauge variations in reference electrode between experiments.

Detection of Lead

Anodic stripping voltammetry (ASV) was used to detect Pb in aerosols. Similar to before, a 2 μL droplet of ultrapure water was placed onto the carbon chip. After inserting the ultramicroelectrode into the droplet and adjusting the nebulizer, the solution (100 μM −

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10 mM) of $Pb(NO_3)_2$ was sprayed at the droplet from a distance of 1.6 cm. The Pb aerosol was sprayed for 60 s before starting the voltammetry. The following settings were used for ASV: a preconcentration time of 240 s, a potential range from −2.0 to 2.0 V, a scan rate of 200 mV/s, and a sample interval of 1 mV.

Fabrication of the MIP-Modified Ultramicroelectrode

The MIP-modified ultramicroelectrode was prepared on a CHI Au SECM tip ($r = 6.25$ μm) via cyclic voltammetry in a 2:1 (v/v) acetate buffer (pH = 5.8):methanol solution containing 1 mM PFOS and 10 mM *o*-PD. A glassy carbon rod and Ag/AgCl electrode (stored in 1 M KCl) were used as the counter and reference, respectively. The cyclic voltammetry was performed with a scan rate of 0.2 V/s and potential window of 0 to 1 V vs Ag/AgCl for 10 cycles. Following polymerization, the MIP-modified ultramicroelectrode was incubated in a 50:50 water:methanol solution for 20 min, under mild stirring, in order to extract the template molecules. The ultramicroelectrode was then rinsed with Millipore Milli-Q 18.2 MΩ·cm water before being placed in the sample solution.

Differential Pulse Voltammetry for PFOS Detection

To investigate the performance of the MIP-modified ultramicroelectrode for use in the PILSNER system, control calibration curves monitoring the ultramicroelectrode's response to increasing concentrations of PFOS via differential pulse voltammetry (DPV) were first constructed in droplets. The MIP-modified Au ultramicroelectrode was used as the working electrode and a glassy carbon chip was used as both the counter and the pseudoreference electrode as described previously. Prior to obtaining each differential pulse voltammogram, the MIP-modified ultramicroelectrode was incubated in a 20 μL droplet of 1× PBS containing 2 mM ferrocene methanol and an appropriate concentration of PFOS for 3 min. The peak height (nA) was recorded from each differential pulse voltammogram, and the blank-subtracted current response ($i - i_o$) was used as the response vs increasing concentrations of PFOS. The following parameters were used to perform the differential pulse voltammetry experiments (all potentials are vs the glassy carbon quasi reference electrode): an initial potential of −0.2 V, final potential of 0.5 V, increment of 0.001 V, amplitude of 0.02 V, pulse width of 0.025 s, sample width of 0.0125 s, and pulse period of 0.075 s.

The PILSNER setup itself was slightly modified for the detection of PFOS aerosols. A small section of a pipet tip was cut off and hot-glued to the carbon pseudoreference electrode to produce a small well (diameter of ∼0.5 cm) into which the sample droplet could be placed. This well reduced the evaporation rate of the droplet. It also helped keep the droplet shape by preventing it from spreading across the glassy carbon chip surface, as spraying PFOS into the droplet significantly reduces its surface tension. The collector droplet was a 20 μL droplet of 2 mM ferrocenemethanol in phosphate-buffered saline (PBS). One millimolar PFOS in PBS was then aerosolized into the well at a distance of ∼1.6 cm for 1 or 2 min periods. A DPV measurement was taken after an incubation time of 3 min.

Aerosol Particle Sizing

Aerosol particle sizes were measured with a VPC3000 Counter (Extech Measurement Solutions). The nebulizer tip was positioned perpendicular to the counter inlet and sprayed with 400 mM ferrocyanide for 1 min in cumulative measurement mode. All particle size measurements were repeated in triplicate.

■ RESULTS AND DISCUSSION

Ferrocyanide Detection and Voltammetry

To understand the underlying physical and chemical mechanisms of PILSNER, aerosol produced by a jet nebulizer from 400 mM ferrocyanide in water was analyzed using a sampling volume of ultrapure water. Amperometric i−t curves of experiments repeated with different collector droplet sizes are shown in Figure 2. A clear increase in current magnitude corresponding to the collection and subsequent oxidation of analyte is observed in each experiment. As the sampling volume gets larger, the magnitude of the current change also gets larger. The decrease in current magnitude after the jet nebulizer is turned off at 60 s is likely due to decreased convection in the sampling volume, lowering the limiting current value. The limiting current (i_{lim}) on an ultramicroelectrode is directly related to the concentration of redox active species by $i_{lim} = 4nFDCa$, where n is the stoichiometric number of electrons, F is Faraday's constant (96 485 C·mol^{-1}), D is the diffusion coefficient of redox species (∼7×10^{-10} m^2·s^{-1}), C is the concentration (the value we calculate from this analysis), and a is the radius of the ultramicroelectrode (5 μm). For reference, the calculated concentrations of ferrocyanide in the collector droplet for the 0.2, 0.5, and 2 μL collector droplet traces were 6.1, 17.6, and 24.7 mM, respectively. It should be noted that these concentrations are not the same as the concentration in the sample aerosol; the difficulty in determining the "true" analyte concentration in the aerosol is discussed below. Cyclic voltammograms of the sampling volume in the absence of impacting aerosol particles containing captured ferrocyanide were used to further validate the collection of aerosol particles (Figure S1). The distance between the ultramicroelectrode and the reference/counter electrode is on the order of a millimeter. Considering the Einstein diffusion equation (Eqn. S2), the amount of time it would take species to diffuse between electrodes is ∼100 *s*. Thus, we expect no feedback effect[20] in our analyses. This will become a consideration for much smaller droplets.

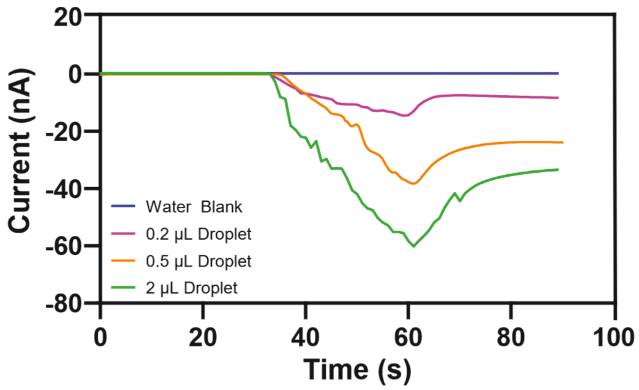

Figure 2. PILSNER i−t curves of various sample volumes exposed to 400 mM ferrocyanide aerosol. The sample volume was exposed to aerosol from t = 30 s to t = 60 s. Baseline adjusted.

The magnitude of the drop in limiting current in the amperometry experiments was used to estimate, based on average aerosol particle size and concentration measurements (Figure S2), that approximately 10^7 particles were collected during each of the 30 s experiment windows (Eqn. S1). Because liquid aerosols rapidly evaporate under most conditions due to their high surface area,[21] which concentrates their contents, this estimate represents an upper bound. It is likely that the number of aerosols captured is much smaller, as the original count estimate assumes that there is no particle evaporation and the final ferrocyanide concentration in the aerosol is still 400 mM (where it likely is higher). This is further corroborated by the fact that the number of aerosol particles collected, calculated in Eqn. S1 from the electrochemical data, seemingly exceeds the total particle count measured by the Extech counter. This places the theoretical electrochemical upper limit of detection for captured particles, based on the volume of delivered aerosol, at roughly 10^3 particles/mL concentrations. It is worth noting, however, that only a fraction of the total particles are captured, and a measurement of the exact collection efficiency of particles cannot be determined without a more accurate and technically demanding determination of aerosol particle sizes post-evaporation (as a function of distance from the collector volume, time, and aerosol composition). Improving this collection efficiency with improved geometry and aerosol introduction would reduce the LOD further. Reducing the size of the collector also improves the LOD by reducing the factor by which captured particles are diluted, in accordance with Equation S1. The size of the sampling volume is perhaps the most critical parameter influencing performance in PILSNER. As has been presented, a predominantly water-containing collector droplet evaporates slowly over time. This evaporation rate is dependent on the humidity, which is a limitation that will be studied and mitigated in future work using ionic liquids as the collector droplet material. The effect of collector droplet evaporation for a 2 μL droplet is included in Figure S6. For the sampling of natural aerosols, the velocity of ambient aerosol particles will also likely be of concern during collection. For such sampling, we propose the use of a pump to accelerate particles toward the collector droplet at similar volumetric rates to what is used in this work (5 L/min). There is significant precedent for using pumps for the purpose of aerosol sampling up to high flow rates (>20 L/min).[22,23]

The experiments in Figure 2 do not show an increase in current magnitude with decreasing collector droplet size despite the reduction in particle dilution. This observation may be due to mechanical differences in aerosol collection not directly related to the volume of the collector droplet; specifically, it is possible that the higher curvature of smaller droplets is less conducive to aerosol collection. The effect of convection is also evident in observations regarding the speed of signal onset during PILSNER. Collector droplet size affects the maximum time required for complete diffusional mixing of aerosol analytes in the collector. For a 1 μL droplet, the time for signal onset caused purely by diffusion is calculated to be about 1 min using the Einstein relation (Eqn. S2). However, video recordings of aerosol collection (Figure S3) in PILSNER indicate that mixing is nearly immediate, with current increases occurring within <1 s of aerosol introduction. This further suggests that convective mixing caused by the aerosol and gas impacting the collector droplet is the dominant mechanism of droplet homogenization while the nebulizer is turned on. The effect of convective mixing within the collector droplet, as well as the effect of reducing droplet sizes to even smaller nanoliter volumes, will be the subject of future study.

Lead Detection via Anodic Stripping Voltammetry

The analysis of Pb in aerosol was also performed to demonstrate the applicability of PILSNER for the detection of environmentally relevant contaminants. Aerosolized particles containing Pb are an EPA-monitored health concern, generated largely by industrial processes such as mining or smelting, or as combustion byproducts.[24] Figure 3 shows an anodic stripping voltammogram of two experiments using aerosol generated from 100 μM lead(II) nitrate and water. The oxidation peak around −1 V represents the stripping of Pb deposited on the ultramicroelectrode. Figure S4 shows the anodic stripping voltammograms of several experiments using aerosol generated from either water or lead(II) nitrate. These experiments demonstrate that the LOD of PILSNER for detecting aerosolized Pb is at least 100 μM (2 ppm in the aerosol). This concentration corresponds to a total airborne Pb concentration of 1 ng/m^3 of aerosol-containing gas based on the flow rate of supply gas and estimated particle counts (Eqn. S3). For comparison, exposure to Pb aerosol may be as high as tens to hundreds of μg/m^3 in high-exposure workplaces such as manufacturing sites,[25] and the EPA three-month average exposure limit for suspended airborne Pb is 150 ng/m^3.[26] This LOD suggests PILSNER may be well suited for analyzing Pb aerosol exposure. This LOD represents a lower bound, as the concentration calculation assumes that no evaporation of the aerosol has occurred prior to size measurement. However, even given a hypothetical situation where 99% of the water in the aerosol has evaporated, the estimate of the PILSNER Pb LOD would still be around 100 ng/m^3, which is still appropriately sensitive for sampling natural aerosols. These LODs compare favorably with typical LODs and background species detection limits for traditional bulk PILS, which vary with the target aerosol but have been reported to be in the roughly 50−200 ng/m^3 range.[27,28] We hypothesize this LOD may still be improved by aforementioned optimization steps. For example, the LOD of PILSNER is dependent in part on the LOD of the anodic stripping voltammetry being applied, which itself is based in large part on the preconcentration time applied to the collector. Preconcentration time in PILSNER is then in turn limited by the evaporation rate of the collector, the mitigation of which will be a separate avenue of future experimentation. Electrode fouling, especially for ultramicroelectrode, may also occur in lead and gasoline-containing aerosols with high organic content. The extent and mitigation of this effect would warrant further investigation for the application of PILSNER to this particular type of measurement.

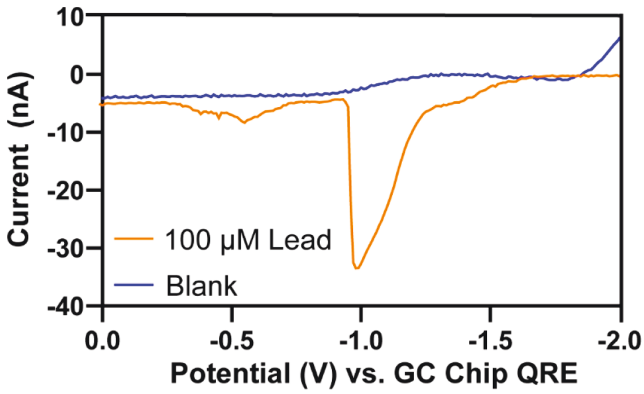

Figure 3. PILSNER-anodic stripping voltammogram of water and lead(II) nitrate aerosols. Listed concentrations indicate concentrations in the aerosol particles. Baseline adjusted.

PFOS Detection via Differential Pulse Voltammetry

The use of DPV to detect PFOS in PBS buffer was performed to demonstrate the potential of hybridizing PILSNER with other established electrochemical techniques in order to expand its applicability. The performance of the MIP-modified ultramicroelectrodes in collector droplets containing known concentrations of PFOS (sans aerosol exposure) is demonstrated in Figure 4, showing high linearity (R^2 > 0.90). This expected voltammetric behavior with respect to the decreasing current response observed with increasing PFOS concentrations occurs as a result of PFOS molecules occluding the

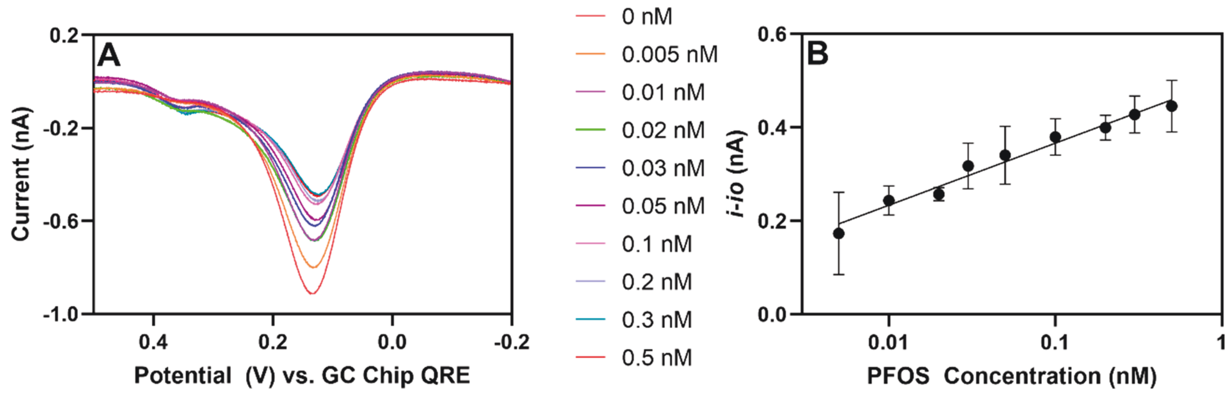

Figure 4. (A) DPV response in 20 μL droplets of 1× PBS with 2 mM ferrocene methanol and increasing concentrations of PFOS using a MIP-modified Au ultramicroelectrode, and the same glassy carbon chip quasi-reference electrode and counter used throughout this work. All DPVs were normalized such that the starting current was 0 nA. (B) The resulting calibration curve from the DPVs in panel A, illustrating the dependence of the blank subtracted current response ($i - i_o$), on the natural log of PFOS concentration, with the x-axis on a logarithmic scale. The equation of best fit was $y = 0.06(\pm0.01)\ \ln(x) + 0.50(\pm0.04)$ and the R^2 value was 0.93 (±0.04). All points were statistically different according to a one-way ANOVA test ($n = 3$). The LOD of PFOS detection in the collector droplet was determined to be 0.3 pM based on the sensitivity of the calibration curve and an assessment of that slope against 3 times the noise of the blank (0 nM) peak current measurement.

molecularly imprinted cavities on the surface of the modified ultramicroelectrode. A slight shift in the voltage corresponding to each peak current in each trace toward more positive voltages was observed with increasing PFOS concentrations. This effect is not exclusive to MIPs used with PILNSER and is discussed by Glasscott et al.[19] This shift is hypothesized to be the result of mass or charge transfer effects arising from the interaction of analyte with the surface structure of the modified ultramicroelectrode.

To demonstrate the compatibility of PILSNER with the MIP-modified ultramicroelectrode, Figure 5 shows data from

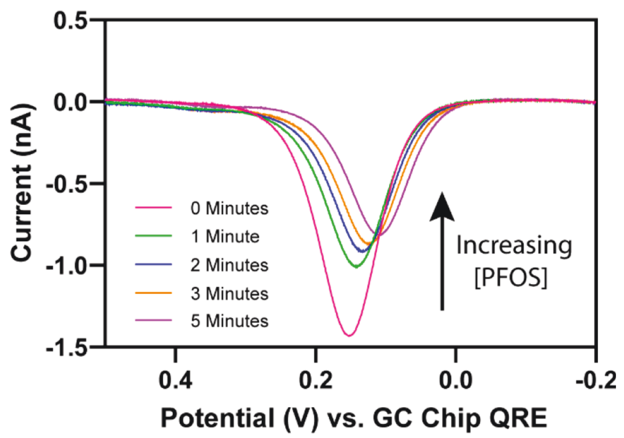

Figure 5. DPV responses in a 20 μL droplet of 1× PBS with 2 mM ferrocene methanol exposed to 1 mM PFOS aerosol for 1, 2, 3, and 5 min compared to a precollection pulse. All DPVs were normalized such that the starting current was 0 nA.

DPV measurements taken on a PBS droplet exposed to 1 mM PFOS aerosol for an increasing duration. Similar to the control MIP ultramicroelectrode experiment, a progressive decrease in voltammetric response is observed as the concentration of PFOS in the droplet increases over the duration of the aerosol exposure. This hybrid technique thus has the potential for real-time quantification of PFOS in natural aerosol particles. Considering that most persistent PFOS contamination is found in water sources such as streams and rivers given that it is a legacy compound,[29] PILSNER-DPV may also represent an alternative technique by which such samples may be analyzed with little to no sample preparation other than the need for nebulization.

CONCLUSION

The ability of a new technique, particle-into-liquid sampling for nanoliter electrochemical reactions (PILSNER) to detect liquid aerosol containing electrochemically active species has been demonstrated. Analysis of ferrocyanide aerosol using amperometry has shown that this technique effectively captures particles, and once deposited, analytes in the PILSNER collector can be analyzed electrochemically. The analysis of Pb aerosol using anodic stripping voltammetry and of PFOS aerosol by differential pulse voltammetry also shows that this technique has the potential for sensitive detection of heavy metal contaminants and other pollutants. Our results indicate PILSNER is an effective means by which ultramicroelectrodes can be used for ultrasensitive aerosol electroanalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmeasuresciau.1c00024.

Video of PILSNER collection (ZIP)

Calculations of aerosol counts, diffusion times, and aerosol volumes; ferrocyanide cyclic voltammograms; aerosol histograms; overlaid anodic stripping voltammograms; images of collector droplet; humidity-based amperometric response curve; statistical analyses; PFOS DPV initial currents; non-normalized PFOS DPV response; and amperometric controls (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

PILS, particle-into-liquid sampling; PILSNER, particle-into-liquid sampling for nanoliter electrochemical reactions; PFOS, perfluorooctanesulfonate; CV, cyclic voltammogram; MIP, molecularly imprinted polymer; SECM, scanning electrochemical microscopy; DPV, differential pulse voltammetry; ASV, anodic stripping voltammetry

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