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Research Article

Analysis of Liquid Particles in Aerosols via Charge-Induction Amperometry (ALPACA) for Rapid Electrospray Droplet Charge Analysis

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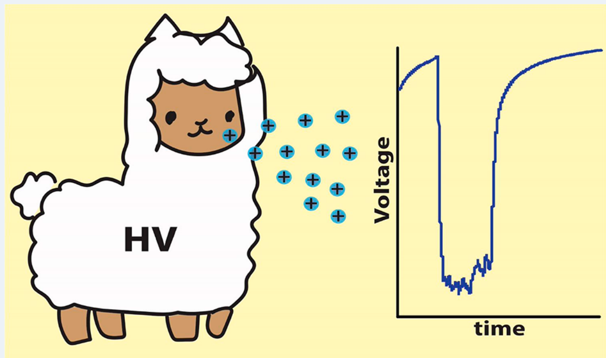
ABSTRACT: The rapid and on-line study of aerosols and their properties is technically demanding due to their small size (<10 μm diameter) and the resultant required scale of any such measurements. Most such techniques require the use of lasers (e.g., phase Doppler anemometry), condensation growth, or other complex hardware. To this end we introduce analysis of liquid particles in aerosols via charge-induction amperometry (ALPACA), an extremely simple potentiostat-based technique capable of on-line, rapid measurement of the aggregate charge of aerosol particles. This technique demonstrates high signal-to-noise responses, is not subject to chemical noise, and has the potential for significant future miniaturization. This technique is applied in this work for the detection of charges on electrosprayed droplets. The mechanism of detection of the technique is discussed using both amperometry and open circuit potential (OCP) to measure droplet charge properties. ALPACA represents a significant advancement toward simple, inexpensive aerosol charge detection.



■ INTRODUCTION

Aerosols, often defined as solid or liquid particles of diameters of less than 10 μm suspended in a gas,[1] have a wide variety of physical properties and behaviors which make them challenging to study. This study remains important, however, as many aspects of the effects of aerosols on the environment, climate, and human health are not fully understood. For example, meteorological models rely on an understanding of cloud formation, which is a liquid aerosol growth process.[2] Many phenomena including breaking ocean waves,[3] forest fires,[4] and volcanic eruptions[5] release aerosol particles of various sizes, numbers, and compositions into the air. The immediate and long-term effects of these aerosols in the environment and on human health are not fully understood. For example, the chronic inhalation of high concentrations of PM 2.5 (particulate matter, or aerosols, of <2.5 μm diameter) is directly correlated to a wide variety of serious illnesses including inflammation, reduced lung function, and cardiovascular diseases including heart failure.[6]

A variety of techniques, both on-line and off-line, exist to measure aerosol particles, but few focus on measuring the charge properties of such aerosols. Indeed, varying aerosol charge properties are detrimental to some types of analyses such as differential mobility, and such techniques actively neutralize aerosols before analysis, and/or attempt to prevent aerosols from changing in size-to-charge ratio during analysis to avoid skewing measurements.[7] However, the charge of an aerosol particle or droplet can often be an important property to measure. For example, a recent study has found that the charge properties of exhaled aerosols affect how well they are captured by different face mask materials.[8] The purpose of this work is to introduce a new simple, inexpensive, and miniaturizable technique for measuring charge properties of aerosols, as discussed below. This technique was tested using droplets generated by electrospray ionization (ESI), commonly used as an ion-generation technique in mass spectrometry and for electrocoating applications. This technique, analysis of liquid particles in aerosols via charge-induction amperometry (ALPACA), has allowed for the direct measurement of charge on electrosprayed droplets with an extremely simple probe combined with a commercial potentiostat.

Electrosprayed droplets are aerosols, as in most flow regimes, they typically have diameters of less than 10 μm and are suspended in air.[1] Droplets generated by ESI rapidly fission and evaporate, rendering off-line techniques for aerosol measurement ineffective. Most on-line aerosol measurement techniques make chemical measurements and are by their very

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design unsuitable for aerosol charge analysis. Previous studies have demonstrated the detection and quantification of ESI droplets with printed circuit board electrodes,[9] and indirect measurements of positive charges in ESI droplets have been made using pH-sensitive dyes.[10] However, these techniques are technically complex, and the need for simple and widely applicable aerosol charge measurement techniques persists.

Here, we detail a new analytical technique for making such determinations. ALPACA utilizes a platinum wire loop as a detector onto which charged droplets adsorb, inducing a charge. This charge can then be interpreted, via the transduction of charges measured as a current in the detector wire, using a commercial potentiostat. The basic setup for ALPACA for analyzing electrosprayed droplets is shown and described in Figure 1. In this work, ALPACA has been applied to the detection of electrosprayed droplets using open-circuit potential (OCP) and amperometric measurements. These interpretations of the charge deposited by ESI droplets represent new techniques by which the properties of electrosprayed droplets may be explored.

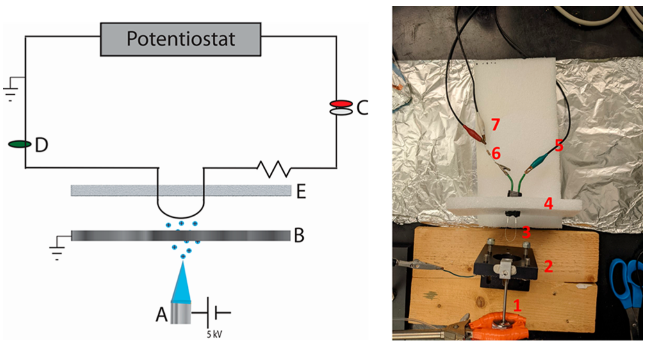

Figure 1. Simplified diagram (left) and image (right) of ALPACA-ESI configured for use with amperometry. Electrospray is achieved by spraying solution from a capillary (A/1) against a 70% transparent steel mesh (B/2) by applying a high (5 kV) voltage difference. C/7 and D/7 correspond to counter/reference electrode (red/gray) leads, and D/5 corresponds to the working electrode (green) lead, respectively. A Pt wire loop isolated by a foam divider (E/4) serves as the detector. A variable resistor (6) is added in series with the wire detector to prevent current overflow (discussed further in the main text). A grounded Faraday cage (not shown) was placed over this setup during measurements.

MATERIALS AND METHODS

Materials. ESI experiments utilized a 50:50 mixture of ultrapure water and methanol (Fisher Scientific, Optima grade) to mimic a typical solvent system used in ESI applications. Adventitious ions in solution were found to be sufficient to produce stable electrospray, and no additional solution additives (such as acid) were necessary. All experiments were performed within a grounded Faraday cage. The ESI emitter used was a Bruker AP1 stainless steel emitter with a 100 μm inner capillary diameter, with air as the nebulizing gas supplied at 5 PSI. Voltage during ESI experiments was supplied to the emitter tip with a Spellman model CZE1000R power supply at 5 kV. The emitter was electrically isolated using electrical tape and a slate ring stand base.

Analysis of Liquid Particles in Aerosols via Charge-Induction Amperometry (ALPACA). The probe used for ALPACA consisted of a 3 cm length 0.25 mm diameter platinum wire connected in a loop and soldered to two high-voltage antidischarge copper wires. A platinum wire was chosen as the charge collector for its simplicity, ease of integration into the ALPACA circuitry, potential miniaturizability, and its demonstrated ability to collect and detect appropriate numbers of charged droplets while not producing excess noise. The connecting wires were spaced 1 cm apart with insulating plastic spacers and electrical tape. The exposed leads of the copper wire were sealed using insulating shrink wrap to ensure that all droplets landed only on the platinum "detector" loop. For amperometry experiments, one copper wire lead was connected directly to the working electrode, and the other lead was connected jointly to the counter and reference electrode leads. An initial applied voltage of 0 V was used except where stated. Between the potentiostat and the counter/reference leads, a variable resistor (100 kΩ to 22 MΩ) was wired in series to simulate a dummy cell and to prevent excessive current from flowing from the counter electrode. Except where stated, a resistor value of 10 MΩ was used. For OCP experiments, the counter reference electrode lead was disconnected, as it serves no function in OCP for the circuit type used. The resistor between the potentiostat and the reference electrode was also moved and placed between the grounded working electrode and the detector loop. ESI was performed as described previously using 50:50 methanol/water, an applied voltage of ±5 kV, and the steel mesh aperture from an aperture-to-detector wire distance of 5 cm. The ALPACA probe sans the detector wire was insulated from ESI droplets by embedding it through a plastic foam block. Images of the probe setup are shown in Figures 1 and Figure S1. Further justification for the use of this configuration is discussed in the results section.

ALPACA with OCP and Amperometry. OCP measurements were performed with a maximum run time of 600 s, a sample interval of 0.005 s (the minimum sampling time achievable with the device), and voltage thresholds of ±1.5 V. Measurements were performed on the CHI model 6012D potentiostat. ESI sample solutions of 50:50 methanol/water were introduced at 200 μL/h using a Cole-Parmer 74800-05 syringe pump and Hamilton gastight model 750N 500 μL syringe and PEEK fittings. ESI was performed using a potential of 5 kV at a distance of ~1 cm against a grounded stainless-steel mesh (Figure 1) directly in front of the collector wire at a distance of ~5 cm. The steel mesh (6.3 wires/cm, 0.5 mm diameter wire; transparency of ~70%) was used to provide a ground against which to perform ESI. The high transparency allowed for transmission of a large enough fraction of electrosprayed droplets for detection. ESI experiments were performed with the nebulizing gas and voltage on throughout (to make any potential background noise consistent), with the syringe pump cycling on or off manually to begin and end each ESI on/off cycle. Amperometry experiments were run with a constant voltage of 0 V based on a control CV of the collector droplet with a sampling rate of 2 kHz (the maximum sampling rate achievable with the device). Notably, in ALPACA, this initial applied voltage is simply an applied difference between the connected leads of the probe and sets the background current via Ohm's law.

RESULTS AND DISCUSSION

Analysis of Liquid Particles in Aerosols via Charge-Induction Amperometry (ALPACA). Circuit diagrams for the use of ALPACA for amperometry and OCP measurements

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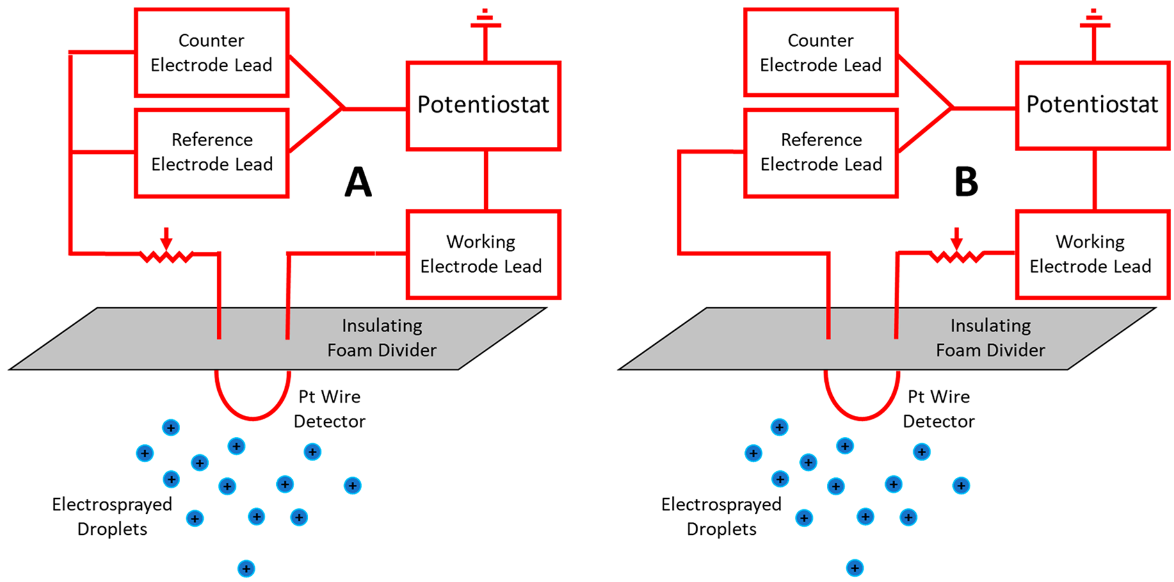

Figure 2. Simplified circuit diagrams of ALPACA used with amperometry (A, left) and OCP (B, right). A variable resistor is used in series with the Pt detector loop to prevent excessive current flow from the counter electrode during amperometry. This resistor is instead wired in series between the working electrode and the wire detector loop during OCP measurements. The counter electrode lead is disconnected during OCP experiments, as this lead performs no function during this type of analysis. The foam divider is included to ensure that droplets exclusively land on the Pt detector wire. Further explanation of this setup is included in the main text.

are shown in Figure 2, and labeled images of the ALPACA probe setup are shown in Figure 1 and Figure S1. A platinum wire loop is connected on one end to the potentiostat's working electrode lead, and the counter and reference electrode leads are connected to the other end of the loop. Charged ESI droplets land on the wire and induce a current/voltage response. A resistor is placed in series with the counter/reference leads during amperometry to prevent excessive current from flowing from the counter electrode, causing an overflow. During OCP measurements, this resistor is instead connected between the working electrode lead and the detector loop, and the counter electrode lead is disconnected. The rationale for the use of these configurations is discussed below.

Examples of amperometric responses using ALPACA to detect droplets produced by positive mode ESI (ESI+) and negative mode ESI (ESI−) are shown in Figure 3. These amperograms are interpreted as a sum of many current transients induced by ESI droplets depositing on the detector wire. As charge continuously deposits onto the wire loop, a limiting current is reached when the rate of charge deposition matches the rate of dissipation caused by donation (or extraction) of electrons through the working electrode lead to ground.

In CH Instruments 600 series potentiostats, including the model 6012D used in this work, the working electrode is grounded, and the counter electrode applies the voltage to the cell.[11] Thus, when the counter and reference electrodes are directly connected, the reference electrode reports back the exact same voltage that the counter electrode is applying with essentially no resistive drop. As a result of this lack of feedback, the working electrode, which is controlled by an operational amplifier, does not vary the applied voltage (in a typical electrochemical cell, this voltage is varied to account for resistive solution or boundary potential drop). This creates a very stable baseline current in ALPACA which is dependent only on the resistance of the load resistor (and on the applied

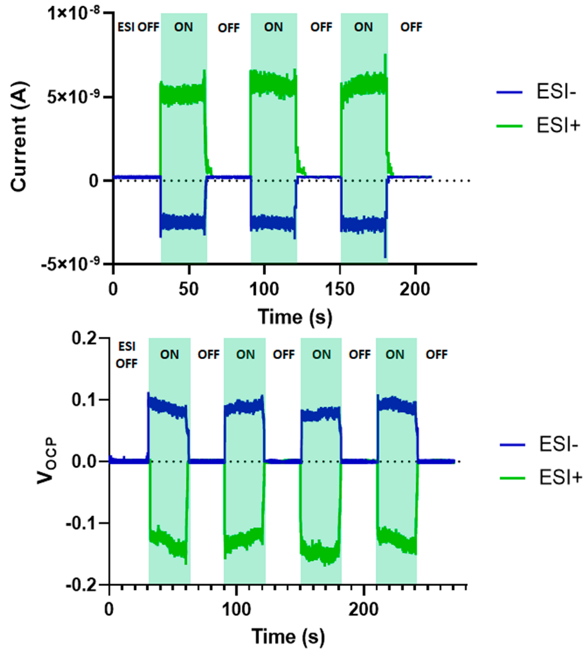

Figure 3. Top: Example ALPACA amperograms from ESI+ (green trace) and ESI− (blue trace) of 50:50 MeOH/water spray exposures with an applied voltage of 0 V. The electrode and resistor configurations for this measurement were based on Figure 2, left. Bottom: Example ALPACA-OCP responses to ESI+ and ESI− exposures. The electrode and resistor configurations for this measurement were based on Figure 2, right.

voltage in amperometry). This baseline stability, caused by the removal of all chemical noise from the electrochemical "cell", greatly increases signal-to-noise and aids in the detection of faint signals. When electrosprayed droplets land on the detector wire during amperometry experiments, a current is induced in the wire. This current follows the path of least resistance through the working electrode to ground where it is detected by a transimpedance amplifier. The counter and reference electrodes are connected in this configuration to complete the measurement circuit, and any voltage applied (or bias between the electrode leads) at the counter electrode creates a baseline current based on Ohm's law and the applied voltage magnitude. Except where stated, an applied voltage of 0 V was used for amperometry experiments, as there is no analytical value to applying a voltage to increase the magnitude of the background current. Data demonstrating the effect of varying the applied voltage during amperometry are shown in Figure 4.

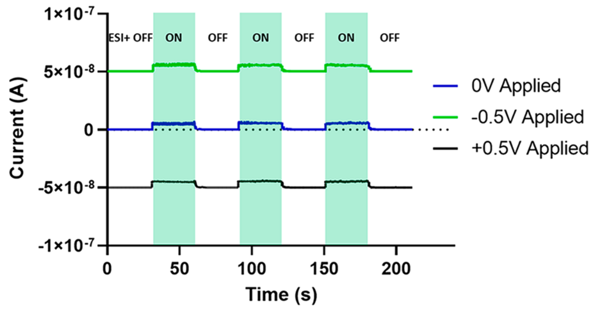

Figure 4. Varying ALPACA current response to exposure to ESI+ droplets as a function of changing the applied amperometric voltage with a 10 MΩ load resistor. Note that the change in current magnitude of ~50 nA follows Ohm's law [$0.5\ V = (50 \times 10^{-9}\ A) \times (10 \times 10^{6}\ \Omega)$]. Note also that there is little change in the magnitude of the current response during the ESI+ exposures, as the induced charges deposit between the grounded working electrode and the resistor and thus experience little resistive drop.

Notably, the signal response in ALPACA amperometry is unidirectional and shows a steady-state current of positive or negative current in ESI+ and ESI−, respectively (see Figure 3, top). This is observed in spite of the fact that both positive and negative droplets are expected to be formed simultaneously during normal ESI.[12] The unidirectional signal in ALPACA is likely a consequence of parasitic capacitance between the leads of the op-amp in the transimpedance amplifier used at the potentiostat's working electrode. Nonideality in an op-amp with one lead connected to ground, as is the case with the potentiostat working electrode, will have a nonzero capacitance between the op-amp leads, usually on the order of a few picofarads.[13] Given that the potentiostat's transimpedance amplifier measures the current in this circuit between the resistor and capacitive element, the consequence of a 10 MΩ resistor being in series with a picofarad capacitance leading to ground is the creation of a passive integrator circuit with a calculated cutoff frequency of about 16 kHz, which is well below the expected droplet detection rate. This means that signals observed in ALPACA with amperometry are most accurately interpreted as integrals of deposited charge. This phenomenon, and the interpretation and consequences of this type of integration, are discussed in Calculation S1.

The use of ALPACA with OCP was also demonstrated using the circuit configuration shown in Figure 2B. It was found empirically that droplets landing on the collector wire had insufficient charge to induce a measurable voltage when ALPACA was configured as in Figure 2A. This is hypothesized to be due to the way that the potentiostat takes V_{OCP} measurements.

In amperometry, the quantity being measured is the current through the working electrode. However, during OCP, the current across the reference electrode is used to measure V_{OCP}. The resistor in the potentiostat that is in series with the reference electrode has an extremely high resistance (on the order of teraohms[11]), so the current passed through it is considered electrochemically negligible. However, in the ALPACA configuration in Figure 2A, a far lower impedance path to pseudoground is available to deposited charge through the working electrode, which is connected to an op-amp with its noninverting input at chassis ground. Thus, no V_{OCP} can be measured, as no measurable current is passed through the reference electrode due to the availability of a far more favorable ground path through the working electrode. The addition of a large (44 MΩ) resistor in series with the working electrode (Figure 2B) instead creates a current divider with the internal resistance of the reference electrode, allowing for a portion of the OCP current to be measured as V_{OCP}. ALPACA-OCP data are shown in Figure 3, bottom, for ESI+ and ESI− measurements. The simplified model of ALPACA as a current divider for charge deposited on the collector wire is shown in Figure S2. This model is supported by data in Figure 5 showing that increasing the MΩ series resistance in 100 MΩ increments increases the measured V_{OCP} by diverting more current through the reference electrode.

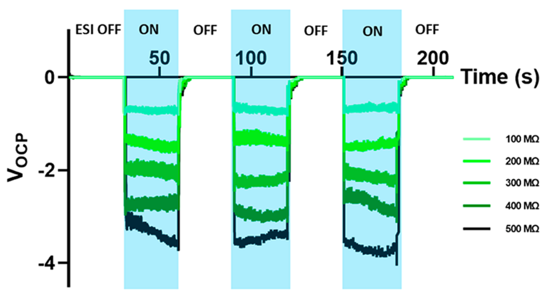

Figure 5. ALPACA-OCP responses to ESI+ exposures with various resistor values wired in series with the working electrode, as described in Figure 2 and Figure S2. VOCP magnitude increased with increasing resistance, as more current was diverted to pass through the reference electrode.

CONCLUSION

A new droplet charge detection method, analysis of liquid particles in aerosols via charge-induction amperometry (ALPACA), is introduced and characterized. This technique measures aerosol charges directly with a platinum wire, which can be detected and interpreted with a standard potentiostat. This technique is shown to be capable of direct detection of charged species produced by the electrospray process using a simple two-electrode system. It was found that charge detection occurs as a result of droplet charges inducing measurable currents in the detector wire, as opposed to traditional mixed-potential theory or Nernstian interpretation of electrochemically induced voltages or currents. ALPACA thus represents a potential low-cost, simple sensor for the detection of electrosprayed droplets. ALPACA may have applications in the field-detection of other types of charged aerosols. Many ambient aerosols have a small net charge due to triboelectric or other forces before or after particle generation.[14] These net charges can be important for understanding particle collection and deposition dynamics.

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For example, recent work has found that the charge of exhaled breath aerosol has an effect on filtration efficiency of those particles when drawn through various mask materials.[8] More sophisticated experiments to determine whether ALPACA-amperometry or ALPACA-OCP responses can be expanded for the detection of naturally occurring aerosol particles will be the focus of future work.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jasms.2c00227.

Photograph and circuit diagram of ALPACA as well as a calculation discussion (PDF)

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Notes

The authors declare no competing financial interest.

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