CONTINUOUS ANALYSIS OF ATMOSPHERIC AEROSOLS USING MICROCHIP ELECTROPHORESIS

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ABSTRACT

Atmospheric aerosols represent the most significant unknown for predicting the impact of human activity on the atmosphere. To understand their impact, we must also understand their composition. Here, we have developed a miniaturized total analysis system to collect aerosol particles and analyze their components by microchip capillary electrophoresis. The microchip reservoirs are interconnected via air ducts to compensate for a sampling-induced pressure drop. Conductivity detection is performed in a novel bubble cell zone that improves compatibility with high separation fields. The coupled system allows for semi-continuous measurements of common aerosol components with one minute time resolution.

KEYWORDS: Aerosol, Sampling Interface, Environmental Monitoring

INTRODUCTION

Atmospheric aerosol monitoring has steadily gained interest due to effects of particulates on both weather and health [1]. Aerosols exhibit high temporal and spatial variability, making extended, routine analyses across broad geographic regions a necessity [1]. Current composition monitoring techniques include filter extraction analyzed offline with ion chromatography (IC) or gas chromatography (GC), the particle-into-liquid-system (PILS) coupled directly to IC, and the aerosol mass spectrometer (AMS) [1, 2]. None of these techniques possess the attributes needed for routine, widespread monitoring – inexpensive instrumentation, rapid analysis, and the ability to monitor many species simultaneously. The water condensation particle counter (WCPC) has potential for providing an inexpensive aerosol collector [3]. Furthermore, microfluidics has already been established for providing rapid and inexpensive chemical analyzers [4]. Combined, these two methods yield a new instrument that meets the demands for routine aerosol composition monitoring.

Our work has focused on interfacing the WCPC to microchip capillary electrophoresis (MCE) to provide a device capable of routine aerosol monitoring. The WCPC condenses water onto aerosols, increasing particle size and allowing for inertial impaction into the microchip sample reservoir (Figure 1). This approach places the sample reservoir 3-4 torr below atmospheric pressure. To compensate for the pressure differential and avoid unwanted liquid hydrodynamic flow, the sample and buffer reservoirs are connected via a network of air ducts. By sealing the buffer reservoirs, isobaric operation is thus achieved. Contact conductivity detection is performed using a novel bubble cell detection zone that lowers the local separation

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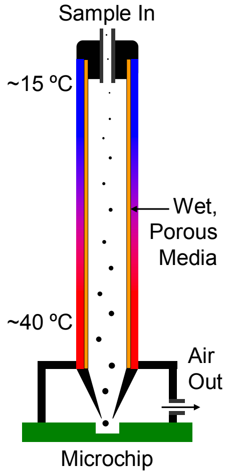

Figure 1. Schematic of WCPC impaction onto the microchip.

field, reduces the voltage drop between electrodes, and minimizes unwanted electrochemical reactions.

EXPERIMENTAL

Fabrication of poly(dimethylsiloxane) (PDMS) microchips was performed as reported previously [5]. Separation channel width was 50 µm and increased to 200 µm in the detection zone. Detection electrodes were 15 µm gold-plated tungsten and were spaced 100 µm center-to-center. These electrodes were connected to a Dionex CD20 conductivity detector and output was monitored with National Instruments LabView software and a USB-6210 DAQ. Collection was performed at 20 kHz and boxcar averaged for an effective collection rate of 10 Hz.

The WCPC was provided by Aerosol Dynamics [3]. The inlet and exit temperatures were maintained at 15 °C and 40 °C, respectively. The WCPC sampled air at 0.4 L/min and deposited aerosols via inertial impaction into the sample reservoir. Headspace pressure in the reservoirs was equalized using an additional PDMS layer containing air ducts that connected the buffer reservoirs while closing them to the atmosphere. To allow for extended analyses, a sample flushing system was installed by inserting 1/16” tubing into channels connected to the sample reservoir. These tubes allowed syringe pumps to flush the reservoir by repeating a fill/evacuate sequence.

RESULTS AND DISCUSSION

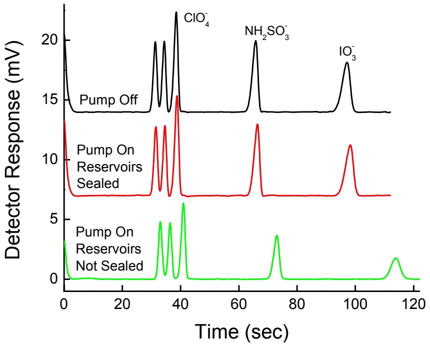

Figure 2. Comparison of separations with (top) no sampling pump, (middle) pump on with reservoirs sealed, and (bottom) pump active with no reservoir sealing.

The integrated system was tested by comparing separations of a standard mixture in a variety of operating conditions. Figure 2 shows electropherograms of perchlorate, sulfamate, and iodate with (a) the sampling pump off, (b) the pump on with buffer reservoirs sealed from the atmosphere, and (c) the pump active but the buffer reservoirs at atmospheric pressure. Without reservoir sealing, activating the sampling pump resulted in a pressure difference that caused hydrodynamic flow and yielded respective analyte peak area decreases of 26%, 37%, and 50% as well as an increase in migration times. With the reservoirs sealed, peak areas differed by 2% or less, indicating a lack of hydrodynamic flow.

Separations were developed for common inorganic cations and anions in aerosols (Figure 3). After optimization, analysis time was ~1 min at 250 V/cm. Use of the bubble cell allowed operation at over 500 V/cm, resulting in 30 s analyses. Concentration limits of detection (LOD) were less than 1 µM for all analytes tested. Using oxalate as a model ion (LOD = 300 nM) and a typical reservoir volume of 10 µL, the calculated aerosol detection limit is 0.7 µg min m^{-3}. For a 3 hr sampling time, a detection limit of 4 ng m^{-3} can be achieved, similar to offline filter measurements.

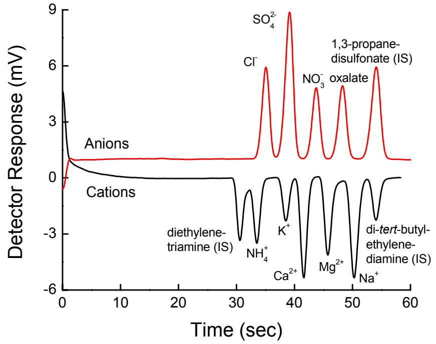

Figure 3. Example separations of aerosol cations and anions. Anion separation was at -250 V/cm and cation separation used 200 V/cm. IS = Internal Standard.

Although Figure 3 shows electropherograms obtained separately, simultaneous analysis of anions and cations on the same microchip has been reported [6]. We intend to develop a microchip for simultaneous monitoring of multiple analyte classes from a single sample, further increasing the flexibility and cost effectiveness of the WCPC-MCE system.

CONCLUSIONS

A WCPC aerosol collector was interfaced to MCE to provide a system capable of routine aerosol analysis for a variety of chemical components. Compatibility between the WCPC and MCE devices was obtained with pressure-equilibrating air ducts, and a bubble cell detection zone was used to allow high separation fields with contact conductivity detection. The integrated analyzer may find widespread applicability in aerosol monitoring due to its short analysis time and low cost and extend the use of miniaturized total analysis systems to routine environmental monitoring.

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