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# New Technique for Online Measurement of Water-Soluble Fe(II) in Atmospheric Aerosols

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A prototype instrument has been developed for online analysis of water-soluble Fe(II) (WS\_Fe(II)) in atmospheric aerosols using a particle-into-liquid-sampler (PILS), which concentrates particles into a small flow of purified water, coupled with a liquid waveguide capillary cell (LWCC) and absorbance spectrophotometry to detect iron–ferrozine colored complexes. The analytical method is highly precise (<3% RSD), and the overall measurement uncertainty and limit of detection for the complete PILS–LWCC system are estimated at 12% and 4.6 ng m<sup>-3</sup>, respectively. The online measurements compared well with those of 24 h integrated filter samples collected at two different sampling sites ( $n = 27$ ,  $R^2 = 0.82$ , slope 0.90 ± 0.08, and intercept 3.08 ± 1.99 ng m<sup>-3</sup>). In urban Atlanta, fine particle WS\_Fe(II) concentrations measured every 12 min exhibited large variability, ranging from below the detection limit (4.6) to 370 ng m<sup>-3</sup> during a 24 day period in June 2008. This instrument provides new capabilities for investigating the sources and atmospheric processing of fine particle WS\_Fe(II) and may prove useful in studies ranging from effects of particle WS\_Fe(II) on human health to effects of particle WS\_Fe(II) on atmospheric chemistry and ocean biogeochemistry.

## 1. Introduction

There is growing interest in both anthropogenic and natural emissions of redox-active trace metals, such as iron, because of their role in redox-driven cycling of organic and inorganic compounds in particulate matter sources and receptors. This action catalyzes reactions that yield reactive radicals and can produce reactive oxygen species (ROS), such as the hydroxyl radical, superoxides, etc. (1). The most important reactions producing ROS are the Fenton and Haber–Weiss reactions in which the hydroxyl radical is formed by reduced iron and hydrogen peroxide. The hydroxyl radical can then transform amino acids and carbohydrates, initiate lipid peroxidation, and oxidize nucleobases and thereby affect human health (2). Similar production of free radicals (i.e.,

ROS) affects the oxidation capacity of the atmosphere. The ROS oxidizes the reduced form of trace substances such as sulfur, nitrogen, and carbon (H<sub>2</sub>S, dimethyl sulfide (DMS), SO<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>O, NO, CH<sub>4</sub>, CO, etc.) to their oxidized forms (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and CO<sub>2</sub>), which in turn are important atmospheric trace components in terms of climate change and human health (3). Furthermore, the availability of labile iron regulates the growth, biomass, and species composition of phytoplankton over large areas of the ocean surface and so affects the global carbon cycle via carbon sequestration by phytoplankton (4, 5).

Spectrophotometry can be applied to the measurement of trace levels of metals in solution via a suitable metal-specific ligand of high absorptivity. Stookey (6) developed a method for iron determination using ferrozine (3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine), which reacts with labile Fe(II) in solution to form a stable, highly water soluble magenta-colored complex. This approach has been widely used for the direct determination of iron in water (7–9). When used with a liquid waveguide capillary cell (LWCC) of sufficiently long path length (e.g., 1 m), iron and other trace metals can be detected in solutions at concentrations of less than 1 μg L<sup>-1</sup>. Zhang et al. (7) have reported a gas segmented online measurement of Fe(II) and Fe(III) at nanomolar levels in seawater using an LWCC.

Majestic et al. (9) demonstrated that LWCC–spectrophotometry can be used to measure water-soluble Fe(II) (hereafter, WS\_Fe(II)) and Fe(III) in ambient aerosols extracted from filters. Aerosols are typically collected on filters over integration periods of 12–24 h, making them unsuitable for investigating variations in atmospheric trace metal concentrations on shorter time scales. More highly time resolved data could provide unique insights into sources, atmospheric processing, and possible impacts on human health and atmospheric chemistry. Furthermore, there is concern that substantial changes in the redox state of metals may occur on the time scales of typical filter-based sampling approaches, and therefore, online systems may provide an improved measurement of ambient WS\_Fe(II) by minimizing the time between particle collection and analysis.

In this study, the online analytical method developed for WS\_Fe(II) in natural waters (7) is applied to the analysis of ambient atmospheric particles. The approach is to couple a particle-into-liquid sampler (PILS) (10, 11) to the analytical methods for measuring WS\_Fe(II) in natural waters (7, 9). In previous work, the PILS has been coupled to detectors for measuring a range of aerosol components, such as a dual channel ion chromatograph (PILS–IC) for aerosol ionic compounds, and a total organic carbon analyzer (PILS–TOC) to measure organic aerosol components (11, 12). Both systems have produced results comparable to those of integrated filters or other online measurement methods (13–15).

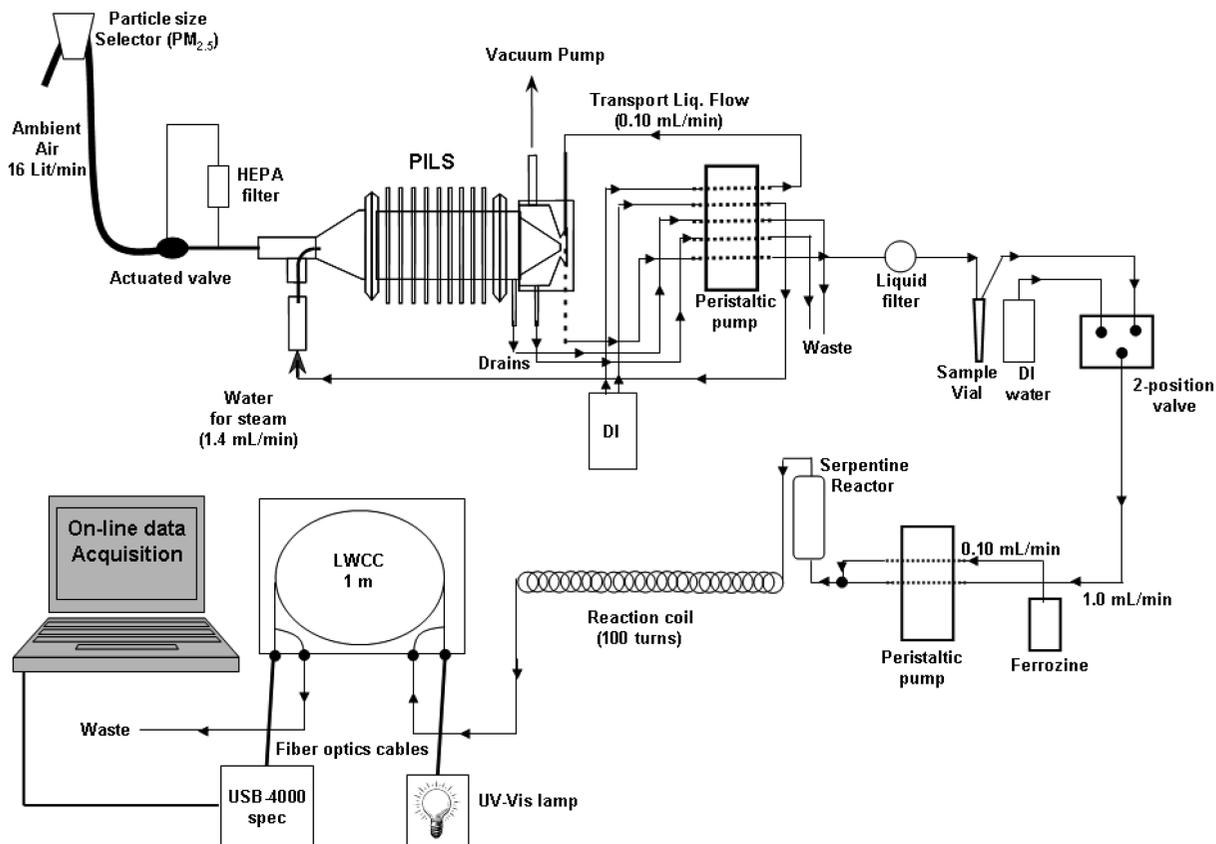
## 2. Experimental Section

**2.1. Reagents and Standards.** All volumetric flasks, bottles, vials, and other equipment (made up of only polypropylene or polyethylene) used in making standards and reagent solutions were thoroughly cleaned using 6 N hydrochloric acid followed by repeated rinsing with DI water (>18.0 MΩ resistivity). All acids used were trace metal grade (VWR). Working standards (range 0.50–40 μg L<sup>-1</sup>, i.e., 9–716 nM) were prepared by dilution of a 1000 mg L<sup>-1</sup> Fe(II) stock solution (acidified to pH 1 with HCl), prepared gravimetrically

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**FIGURE 1.** Schematic diagram of PILS–LWCC for online measurements of WS\_Fe(II). Note that the particle size selector is optional; larger particles could also be sampled. The figure is not to scale.

from ammonium iron(II) sulfate. The Fe(II) working standards were acidified to pH 2 by adding appropriate amounts of 6 N HCl.

On the basis of reaction kinetics of Fe(II) and ferrozine, Lin and Kester (16) reported that a ferrozine concentration of 80  $\mu\text{M}$  is sufficient for complete complexation with Fe(II) concentrations of up to 1  $\mu\text{M}$ . However, for online measurements of Fe(II) where complete mixing is difficult, either higher concentrations of ferrozine or longer reaction times are needed for complete complexation. Zhang et al. (7) used 10 mM; however, in an effort to reduce reagent consumption we found that 5 mM was possible when used in conjunction with a serpentine reactor (discussed below) to enhance mixing of sample and reagent solutions for the same reaction time. More efficient methods for mixing sample and ferrozine may, however, make possible even lower ferrozine concentrations.

Surfactants are commonly used in gas segmented continuous flow analysis to achieve a smooth flow with low baseline. Zhang et al. (7) compared Brij-35 with other surfactants such as Aerosol 22 and Dowfax and reported that Brij-35 was the best surfactant for iron analysis to minimize sample smearing within tubing between consecutive samples. For our application, a 1 mL aliquot of Brij-35 surfactant (polyoxyethylene(23) lauryl ether,  $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$ , Sigma) was mixed with 100 mL of the stock ferrozine solution and used as a daily working reagent solution. The consumption of this reagent solution was approximately 100 mL/day.

**2.2. PILS.** The particle-into-liquid sampler was used to capture ambient aerosol particles into a liquid stream for spectrophotometric analysis. Sample air is drawn at a flow rate of  $\sim 16 \text{ L min}^{-1}$  through a cyclone inlet (URG-2000-30EH, Chapel Hill, NC) to remove particles larger than 2.5  $\mu\text{m}$  aerodynamic diameter for measurement of PM<sub>2.5</sub>. The air is rapidly mixed with saturated water vapor near 100 °C, producing supersaturated water vapor that condenses on all ambient particles larger than approximately 10–30 nm. These

activated particles then grow to 3–5  $\mu\text{m}$  diameter and are then removed from the aerosol phase and collected on a surface with an inertial impactor. Purified water is pumped over the impaction plate ( $\sim 0.10 \text{ mL min}^{-1}$ ), flows around its perimeter, and merges with the liquid from the droplets (Figure 1). This process dilutes the constituents of ambient aerosols by roughly 6 orders of magnitude (assuming typical liquid water associated with PM<sub>2.5</sub> is on the order of 10  $\mu\text{g m}^{-3}$ ). The combined flow is extracted from the impactor and then analyzed for water-soluble components of interest. The details of PILS operation are reported elsewhere (10, 11).

The concentration of measured aerosol chemical components in the liquid sample is converted into a corresponding air concentration by

$$C_A = 1000 C_L F_L / F_A \quad (1)$$

where  $C_A$  is the ambient aerosol concentration ( $\text{ng m}^{-3}$ ) of Fe(II),  $C_L$  is the measured liquid sample concentration ( $\mu\text{g L}^{-1}$ ),  $F_L$  is the flow rate of liquid out of the PILS ( $\text{mL min}^{-1}$ ), and  $F_A$  is the sampled air flow rate ( $\text{L min}^{-1}$ ).

**2.3. LWCC.** A 100 cm LWCC (model LWCC-2100, World Precision Instrument, Inc., Sarasota, FL), with an internal volume of  $\sim 250 \mu\text{L}$ , was used to achieve high sensitivity with the ferrozine spectrophotometric method. In our application, light from a dual deuterium and tungsten halogen light source (DT-Mini-2, Ocean Optics, Inc., Dunedin, FL; spectral range (UV–VIS–NIR)  $\sim 200$ –1100 nm) is introduced into the LWCC through a fiber optic cable (QP400-2-SR, Ocean Optics, Inc.) (Figure 1) and, after passing through the LWCC, is collected and guided to the detector (USB4000 miniature fiber optics spectrometer, Ocean Optics, Inc.) with a second fiber optical cable. The concentration of WS\_Fe(II) is determined by measuring its absorbance in the LWCC, similar in most other respects to the approach used in standard single-beam UV–VIS spectrometers. Since this is a single-beam system,

sample absorbance must be referenced to system blanks and/or nonabsorbing wavelengths. In this study, absorbance is referenced to 700 nm (17), which was typically found to range between 0 and 0.1 absorbance unit.

#### 2.4. PILS–LWCC System for WS<sub>Fe(II)</sub> Measurement.

The analytical method for continuous flow analysis of water-soluble iron in seawater of Zhang et al. (7) was adopted and modified for our specific requirements. The PILS–LWCC system consisted of a PILS, two multihead peristaltic pumps (ISMATEC), one two-position valve (Alltech, Inc.), one self-made serpentine reactor, a 100-turn reaction coil, an LWCC, a UV–VIS light source, and a USB-4000 spectrophotometer (Figure 1). Five channels on one peristaltic pump using Tygon tubing (Cole-Parmer) were connected to the PILS. These included two drains (arbitrary flow rates), a water supply channel for vapor generation ( $\sim 1.4 \text{ mL min}^{-1}$  liquid flow rate), a pure DI water flow introduced over the top of the impactor ( $0.1 \text{ mL min}^{-1}$ ), and a channel extracting liquid sample from the impactor base (Figure 1). The nominal liquid flow rate of this channel was  $0.12 \text{ mL min}^{-1}$ ; however, larger i.d. pump tubing was chosen to ensure that all liquid was extracted, resulting in a two-phase flow of water and air. Following the peristaltic pump, the sample stream was forced through a  $0.45 \mu\text{m}$  polypropylene syringe filter (Alltech, Inc.) to remove insoluble particles that can block the LWCC and then collected in a loosely sealed polyethylene vial. The syringe filter was typically changed once in 2 days, but periodically once a day under more polluted conditions, indicated by a darker appearance.

A batch-analysis system using a collection vial versus a continuous flow approach was chosen to maximize sensitivity while minimizing the potential for interferences from small gas bubbles in the LWCC. A computer-controlled procedure was used for the analysis of liquid sample in the vial. The automated two-position valve alternately directed sample through the analysis system either from the sample vial or from a separate vessel containing DI water. Analysis of samples collected in the vial was segmented by a large air slug and DI water blanks to minimize carryover between samples. The total volume of tubing (made up of either PEEK or FEP Teflon) from the inlet of the peristaltic pump to the outlet of the LWCC was approximately 4 mL, significantly larger than that of the liquid sample being analyzed ( $\sim 1.4 \text{ mL}$ ). The air slug and water followed the sample and filled the rest of the system during each analysis cycle. The air slug was introduced by pumping out liquid from the collection vial for a time longer (2 min) than required (1.5 min) to completely empty. Both the two-position valve and the second peristaltic pump were computer-controlled. Once the vial was emptied and an air slug introduced, the two-position valve was turned to DI water, and the sample vial then began to fill with PILS sample that was analyzed in the next cycle.

The second peristaltic pump (Figure 1) was computer controlled, withdrew sample or DI water at  $1 \text{ mL min}^{-1}$  and ferrozine at  $0.1 \text{ mL min}^{-1}$ , and combined them after the pump using a simple T-junction. These flows were then mixed in a self-made serpentine reactor consisting of 0.75 mm i.d. PEEK tubing 270 cm long with approximately 48 knots. Once the slug of mixed solution had completely entered the 100-turn reaction coil (600 cm long, 0.75 mm i.d. PEEK tubing coiled around a rigid  $\sim 1.6 \text{ cm}$  diameter pipe), the flow was stopped for 4 min to allow WS<sub>Fe(II)</sub>–ferrozine complexation. Experiments with standards showed that, for our setup, 4 min was the optimal time required for complete complexation; at shorter times lower WS<sub>Fe(II)</sub> concentrations were observed, whereas little change in concentration was observed for longer times. The sample was then pumped through the LWCC, stopped again well before the trailing air slug entered, and held there for 2 min to acquire the sample absorbances

at 562 nm (Fe(II)–ferrozine complex) relative to 700 nm (background). The difference in absorbance units ( $\text{AU}_{562} - \text{AU}_{700}$ ) is used to quantify the WS<sub>Fe(II)</sub> concentration in the liquid sample and thus in ambient aerosols.

The process of mixing the sample and ferrozine, forming the complex, analysis in the LWCC, and flushing the complete system (except for the sample collection vial) with a mixture of ferrozine and DI water takes approximately 12 min. During this time, the next sample is collecting in the vial for the subsequent analysis cycle, resulting in a sample integration time of 12 min. With a PILS nominal sample output flow rate of  $0.12 \text{ mL min}^{-1}$ , and 12 min integration time,  $\sim 1.44 \text{ mL}$  of liquid is collected in the sample vial per cycle. This volume is sufficient to flush the LWCC (internal volume  $\sim 250 \mu\text{L}$ ) several times and fill it completely for analysis.

One drawback with this batch-analysis approach is that ferrozine is wasted since it is mixed with the pure water during the flushing cycle and mixed with all the sample in the vial, only a portion of which is analyzed. More effective use of ferrozine is possible with a continuous flow system; however, we found that a gas segmented continuous flow system operates best at liquid flow rates of  $\sim 1 \text{ mL min}^{-1}$ , similar to that used by Zhang et al. (7) and what we used in the analysis portion of our system. At lower flow rates any small gas bubbles that inadvertently enter the LWCC are difficult to remove. Although the PILS could be operated to deliver a sample at  $\sim 1 \text{ mL min}^{-1}$  by increasing the flow of DI water added to the top of the impaction plate, this would result in an approximate order of magnitude increase in dilution and loss in sensitivity compared to the batch system described here with a sample flow rate of  $0.12 \text{ mL min}^{-1}$ .

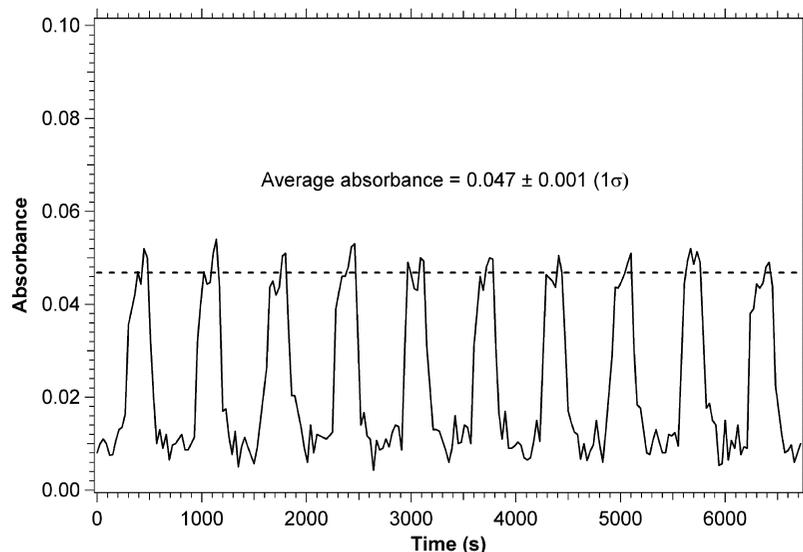
Studies have reported that the Fe(II)–ferrozine complex forms completely in aqueous solutions of pH between 4 and 9 and once formed remains stable for pH 0–7.5 (6, 16). The pH of PILS liquid samples has been found to always remain close to 5.6 due to dissolution of atmospheric CO<sub>2</sub> in the DI water flowing over the impaction plate. Therefore, no buffer solution was added in our analysis system, as done in other methods to maintain a solution pH of  $\sim 5.5$  (7).

Finally, as part of the ambient aerosol sampling procedure, dynamic blanks were performed to correct for any other interferences by directing ambient sample air through an HEPA filter prior to entering the PILS (Figure 1). A timer-actuated valve was nominally set to make a dynamic blank measurement once a day for a duration of 1.5 h, although different times during the day were often used on different days.

**2.5. Daily Field Maintenance Procedures.** Day-to-day operational requirements of the PILS–LWCC system included maintaining the supply of ferrozine reagent and DI water and running a calibration standard once every 1 or 2 days to verify that the complete analytical system was functioning within acceptable limits and to provide data for assessing analytical precision throughout a study. All tubing lines (except the peristaltic pump tubing) and the LWCC were cleaned daily with triethanolamine, methanol, and 2 N HCl (as suggested by the LWCC vendor) to minimize shifts in baseline over time. Peristaltic pump tubing was cleaned with triethanolamine and 2 N HCl. Liquid and sampler air flow rates were checked approximately once a week.

**2.6. Interference.** Artifacts or interferences stemming from both the particle collection and analysis methods are possible. Biases were investigated by use of dynamic blanks and comparison with samples extracted from colocated filters, as discussed in the Results and Discussion.

There is the potential for redox changes of WS<sub>Fe(II)</sub> in the PILS aerosol scavenging/collection process, which involves the use of steam condensation. Liquid drops in the PILS containing WS<sub>Fe(II)</sub> are, at least initially, near 100 °C, but cool rapidly in the system's condenser. Below, com-



**FIGURE 2.** A low standard ( $1 \mu\text{g L}^{-1}$ ) in the PILS–LWCC collection vial run as a sample for  $\sim 2$  h ( $n = 10$ ). The pattern is due to the automated analysis procedure that involves analysis from the sample vial, separated by analysis of DI water (see Figure 1). The relative standard deviation for these data is below 3%.

parisons with integrated filter samples are used to address this possible artifact. Redox changes may also result from the high degree of dilution involved in this water-based sampling and analysis approach. This cannot be addressed by comparison with filter samples since similar levels of dilution are employed in both methods.

The use of ferrozine to quantify WS\_Fe(II) is also subject to possible measurement biases. Murray and Gill (18) observed that ferrozine added to an Fe(III) solution will show a slow increase of color with time, possibly due to reduction of Fe(III) to Fe(II) by ferrozine. Hong and Kester (19) investigated this effect and observed that the extent of Fe(III) reduction was on the order of 10% after a 10 min reaction period and approached a limiting value on the order of 25% for prolonged reaction times. Since the reaction time in our system is approximately 5 min, interference from Fe(III) conversion is likely not significant, but is potentially a more significant issue when doing offline filter analysis, where sample processing times may be longer. Among the transition metals, only Co(II) and Cu(I) form color complexes with ferrozine under the reaction conditions (6). Co(II)/Fe(II) ratios up to 8.0 and Cu(I)/Fe(II) ratios up to 5.0 (in solution) cause  $\leq +5\%$  and  $\leq +15\%$  deviation, respectively. These interferences are expected to be minimal since much lower ratios of these metals are expected in the ambient aerosol (1).

### 3. Results and Discussion

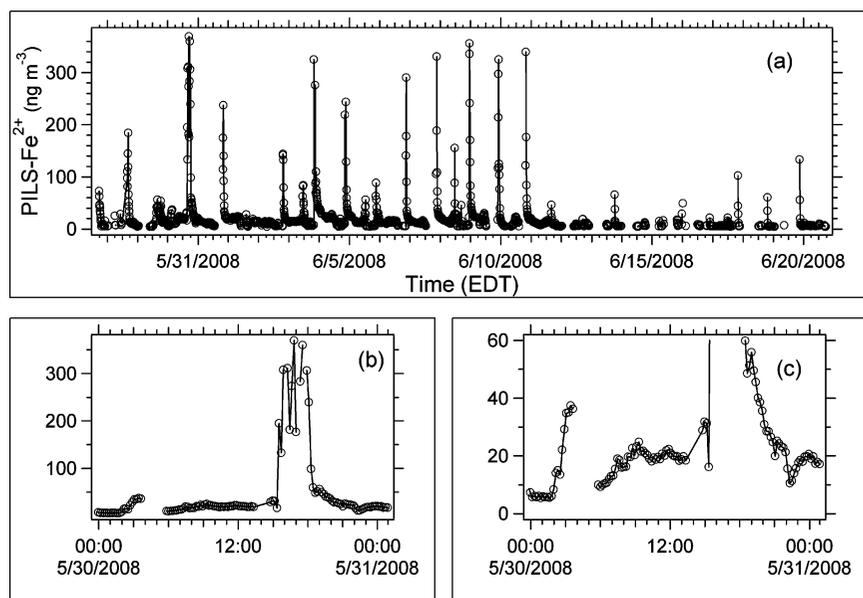
**3.1. Calibration.** The Fe analytical portion of the PILS–LWCC system was calibrated by running Fe(II) standards in a manner identical to that of authentic samples (see Figure 1). Approximately 1.5 mL of standard solution was placed into a series of PILS sample collection vials, and the automated analysis sequence used for ambient samples was run. A linear regression on absorbance versus Fe(II) resulted in  $R^2 = 0.9999$ , slope  $0.0446 \pm 0.0003$  ( $1/\text{ng mL}^{-1}$ ) ( $\pm 1\sigma$ ), and intercept  $0.0097 \pm 0.004$  (arbitrary units) ( $\pm 1\sigma$ ). The longer term precision/stability of the calibration was also investigated. Slopes of several calibrations performed on different days in the laboratory and during different ambient field studies ranged from 0.0423 to 0.0462 ( $1/\text{ng mL}^{-1}$ ), with an average of  $0.0448 \pm 0.0015$  ( $1/\text{ng mL}^{-1}$ ) ( $\pm 1\sigma$ ); see the Supporting Information, Table 1. The relative standard deviation for Fe(II) determination using the LWCC Fe analytical system was estimated to be  $<3\%$  on the basis of the replicate measurements ( $n = 10$ ) of a  $1.0 \mu\text{g L}^{-1}$  standard solution (Figure 2). These results

indicate good short- and long-term precision and the robustness of this method for quantifying Fe(II).

**3.2. System Background and Detection Limit.** Dynamic blanks were run during a number of field experiments to assess the overall system background, or influence of contamination, and to provide estimates of the limits of detection. The blank measurements ( $n = 48$ ) were performed for 1–2 h on different days and at different times. The mean value (and standard deviation) of the dynamic blanks was found to be  $4.4 \pm 1.5 \text{ ng m}^{-3}$ . All reported ambient concentration data ( $\text{ng m}^{-3}$ ) are blank subtracted using this average system blank value and are at ambient temperature and pressure. The limit of detection (LOD) was estimated as 3 times the standard deviation of the blank measurements, which resulted in an LOD of  $4.6 \text{ ng m}^{-3}$ . Thus, the blank uncorrected LOD is  $\sim 9 \text{ ng m}^{-3}$ . In our instrument, this corresponds to a liquid concentration of  $\sim 1.2 \mu\text{g L}^{-1}$ , approximately an order of magnitude larger than the detection limit of the analytical system alone, which is less than  $0.1 \mu\text{g L}^{-1}$ . Luo et al. (20) has suggested the expected concentration of soluble WS\_Fe(II) over several regions of the world to be significantly higher than this LOD. Overall method uncertainty of the WS\_Fe(II) measurements was estimated to be 12% on the basis of the combined uncertainties associated with PILS liquid (10%) and sample air (5%) flow rates and analytical precision of the LWCC–spectrophotometer (3%). Side-by-side measurements involving identical instruments would provide a more complete indication of overall measurement precision, but that has not been attempted.

**3.3. Field Deployment of the PILS–LWCC System.** The PILS–LWCC system for measurement of WS\_Fe(II) in fine aerosol particles (PM<sub>2.5</sub>) has been deployed at four different field sites (Detroit MI, two sites in Atlanta GA, and a rural site in Georgia); here results are presented from measurements made at one urban site in Atlanta during May to June 2008 and the rural site in Georgia. The sampling site (referred to as Fire Station 8) was located within the city next to a major roadway with significant diesel truck and automobile traffic. A large railway switching yard was located roughly 100 m from the site.

Temporal trends in aerosol WS\_Fe(II) concentration during the study period are depicted in Figure 3a. WS\_Fe(II) was found to range from below the detection limit (4.6) to  $370 \text{ ng m}^{-3}$  (mean 22.1, median 13.1, SD ( $1\sigma$ ) 38.9). This was

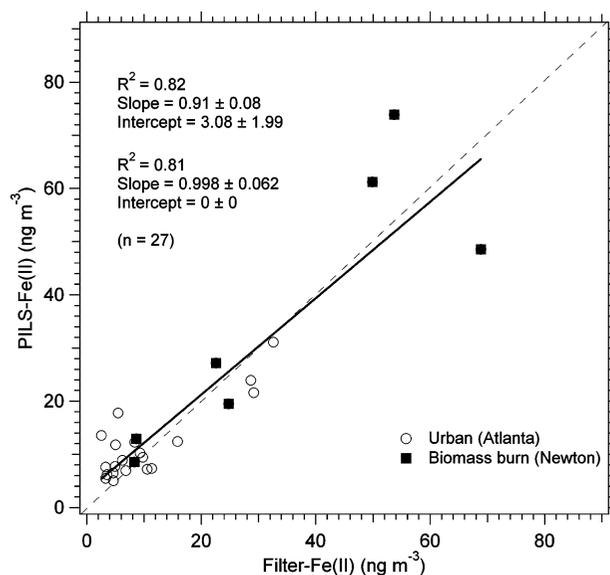


**FIGURE 3.** Temporal variability in fine ( $PM_{2.5}$ ) aerosol  $WS\_Fe(II)$  concentration measured in urban Atlanta using the PILS–LWCC: (a) during the whole study, (b) on a particular day, (c) same as (b) with expanded y-axis.

a period in which the high variability in aerosol  $WS\_Fe(II)$  concentration was mainly the result of large transient events typically observed in the evening (Figure 3b), superimposed on a relatively clean ( $10\text{--}20\text{ ng m}^{-3}$ ) background concentration (Figure 3c). The short duration of these events and consistency in timing suggest a local source due to some regular process or event. The transient events highlight the responsiveness of the instrument under rapidly changing concentrations and the utility of the instrument for capturing low-frequency, short-term events. Parallel to  $WS\_Fe(II)$  measurements with PILS–LWCC, supporting data were also collected to assist with sources and temporal variability reconciliation. These results will be presented in a future paper (Oakes et al., manuscript in preparation).

The PILS–LWCC was also deployed for a short time at a rural forested site in a region of prescribed burning aimed at removing forest underbrush and duff as a part of the combustion atmospheric dynamics research experiment conducted by the Joseph W. Jones Ecological Research Center at Ichauway, Newton, GA, during March 2008. These measurements were performed within the burning region along with online measurements of water-soluble potassium (PILS coupled to a  $K^+$  ion sensitive electrode). A significant correlation ( $R^2 = 0.88$ , slope  $0.0155 \pm 0.00163\text{ g/g}$ , intercept  $0.0027 \pm 0.0031\text{ }\mu\text{g m}^{-3}$ , figure not shown) was observed between  $WS\_Fe(II)$  and  $K^+$ , showing that biomass burning can be a significant source of  $WS\_Fe(II)$  in  $PM_{2.5}$ .

**3.4. Comparison to Integrated Filters.** Parallel to the online, semicontinuous measurement of aerosol  $WS\_Fe(II)$  at the two study sites discussed above (Atlanta and Newton, GA), nominally 24 h integrated aerosol samples ( $n = 27$ ) were also collected on Teflon filters (Zefluor,  $2\text{ }\mu\text{m}$  pore size, 47 mm diameter) using the same type of  $2.5\text{ }\mu\text{m}$  cyclone inlet and nominally same sample air flow rate ( $16.3\text{ L min}^{-1}$ ) as the PILS–LWCC system. These filters were placed in dry amber polypropylene bottles after collection and refrigerated at  $4\text{ }^\circ\text{C}$  until analysis, usually performed within 2–4 days. Longer delay between collection and analysis of aerosol samples could cause significant oxidation of Fe(II). Filters were extracted with sonication for 30 min with 30 mL of DI water. Extracts were filtered with a  $0.45\text{ }\mu\text{m}$  syringe filter (polypropylene, 25 mm diameter, Whatman) and then manually analyzed with a similar LWCC–spectrophotometer system in our laboratory. The time between filter extraction and sample analysis was approximately 60 min.



**FIGURE 4.** Comparison of aerosol  $WS\_Fe(II)$  measured online with PILS–LWCC (PILS-Fe(II)) to nominally 24 h integrated filter samples (filter-Fe(II)) for data collected at an urban site (Atlanta) and a biomass burning site (Newton). PILS-Fe(II) data were averaged to the filter integration time. The dotted line represents the 1:1 line. Deming linear regression results are also shown.

A comparison of the concentration of  $WS\_Fe(II)$  determined from the online system (PILS-Fe(II)), averaged over the filter collection time, to that of the integrated filter samples (filter-Fe(II)) is shown in Figure 4. A Deming regression analysis, a documented better way of comparing different methods (21), was used for linear regression analysis between PILS-Fe(II) and filter-Fe(II) because it considers errors in both variables, unlike standard linear regression analysis. The regression results were  $R^2 = 0.82$ , slope  $0.90 \pm 0.08$ , intercept  $3.08 \pm 1.99\text{ ng m}^{-3}$ , and  $R^2 = 0.81$ , slope  $0.998 \pm 0.062$  when the intercept was forced through zero (all uncertainties are  $\pm 1\sigma$ ). Though an association is clearly indicated (Figure 4), some scatter is apparent, which may be the result of several factors. This includes possible alteration of the  $WS\_Fe(II)$  within the PILS. Oxidation of Fe(II) to Fe(III) in the aqueous extracts may decrease the Fe(II) concentration

(8); however, reduction of Fe(III) to Fe(II) after addition of ferrozine could have the opposite effect, increasing Fe(II) concentrations (18, 19). These processes are less likely to affect the online PILS-Fe(II) measurement due to the shorter time (~12 min) between aerosol extraction and measurement and ferrozine/sample mixing and measurement. Conversion of Fe(II) to Fe(III) prior to filter analysis or within the PILS may account for the positive intercept shown in Figure 4. Differences between the online and 24 h integrated filter measurements may also be influenced by the age of the Fe(II) emissions. In contrast to Fe(II) in a chemically well aged air mass, fresher Fe(II) deposited on the filter may be more likely to be altered to another form during the longer filter integration times. Overall, there is significantly more scatter between PILS/filter comparisons for WS\_Fe(II) than what has been observed when measuring other compounds. For example, Orsini et al. (11) report a slope (and  $R^2$ ) for comparison between a PILS-IC and integrated filters of 1.03 ( $R^2 = 0.96$ ) for  $\text{SO}_4^{2-}$  and 0.93 ( $R^2 = 0.88$ ) for  $\text{NH}_4^+$ . These results reflect major progress in measuring the trace levels of WS\_Fe(II) in ambient particles, but also illustrate that challenges still remain. Finally, it is noted that this PILS-LWCC method could also be expanded to include measurements of water-soluble Fe(III) (7) or other water-soluble trace metals, such as copper and manganese (22, 23).

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### Supporting Information Available

Table depicting linear regression parameters for the calibration curve of WS\_Fe(II) on different days and during different field studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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