Semicontinuous determination of anions, cations, and heavy metals in aerosols using PILS-IC-VA

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Metrohm

Summary

The collection of representative aerosol samples and the therewith associated analysis are still the most challenging parts in air monitoring. This poster presents an approach that couples a Particle-Into-Liquid-Sampler (PILS) to a dual-channel ion chromatograph (IC) for measurement of aerosol anions and cations and a voltammetric measuring stand (VA) to determine the heavy metals. Feasibility of the PILS-IC-VA online system was demonstrated by collecting aerosol samples in Herisau Switzerland, at defined time intervals; air pollution events were simulated by burning lead- and cadmium-coated sparklers.

The PILS-IC-VA setup is straightforward and allows semicontinuous measurements of water-soluble aerosol ionic components at 60 min intervals. PILS-IC-VA is an indispensable tool to monitor rapid changes in aerosol particle ionic composition, caused, for example, by brief smoke plume impacts, that would be impossible to detect with filter methods. PILS-IC-VA is an invaluable contribution for investigating the composition, transport, and evolution of atmospheric aerosols. The system is highly suited for long-term unattended field use in remote regions.

Instrumentation

➢ ADI 2081 Particle-Into-Liquid-Sampler (PILS)

➢ 940 Professional IC Vario TWO/SeS/PP für Anionen- und Kationenbestimmung

➢ 797 VA Computrace
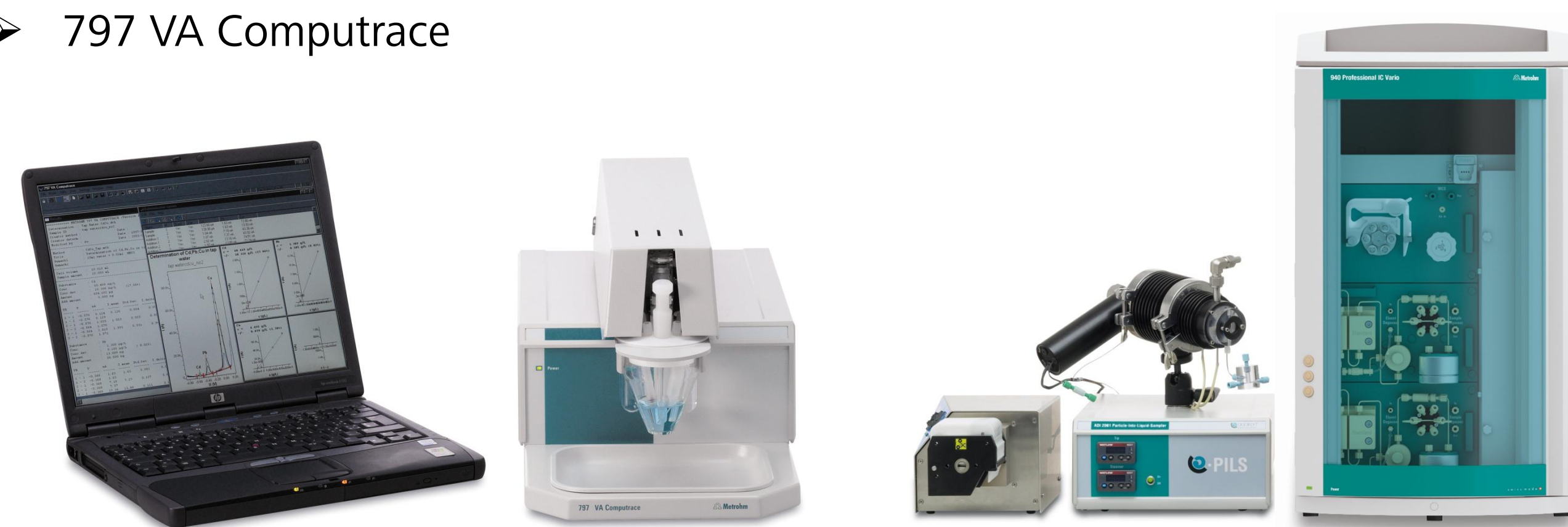
Introduction

Airborne particulate matter has strong impacts on public health and the climate. Although common filter-based measurements can provide daily particle contributions, they suffer from their poor temporal resolution and their labor-intensive offline character. Acute exposures that appear only for a very short time get lost in the long averaging times of the filter.

The automated Particle-into-Liquid-Sampler (PILS), however, offers enhanced time-resolved data by permanently collecting airborne particulate matter. It allows capturing the particles in an air flow and dissolving the soluble constituents in a steam jet for subsequent analysis. Whilst the hyphenation of PILS with an ion chromatograph (IC) allows the parallel determination of standard anions and cations, the coupling to a voltammetric measuring stand facilitates detection of heavy metals.

In this poster, the PILS-IC-VA system is evaluated with respect to its capacity to provide accurate high-resolution measurements of ambient aerosol samples.

Sample preparation

The captured air particles, which are sampled through a cyclone that controls the size of the entering particles applying a size threshold of 10 μm (PM_{10}), enter the condensation growth chamber, where they are mixed with injected supersaturated steam. Rapid adiabatic mixing allows the aerosol particles to grow into droplets large enough to be collected by an impactor. Afterwards, the solution with the diluted aerosol particles is split into three streams and analyzed by dual-channel ion chromatography and voltammetry. Since ambient air in Herisau was almost contaminant-free, sparklers, previously immersed in a 200 g/L lead nitrate and 1 g/L cadmium nitrate solution, were burned near the aspiration tube of the PILS.

Aerosol monitoring – single sample

The aerosol sample was collected on 6 February 2011 at 11 a.m.

a) Ion chromatography

Column:	Metrosep A Supp 5 - 150/4.0
Column temp.:	30 ℃
Eluent:	3.2 mmol/L sodium carbonate
	1.0 mmol/L sodium hydrogen carbonate
Flow:	0.7 mL/min
Loop:	250 μL
PILS air flow:	16.7 L/min (= 1 m³/h)
Flow$_{sample\ stream}$:	0.23 mL/min
V$_{sample\ stream}$:	1.94 mL
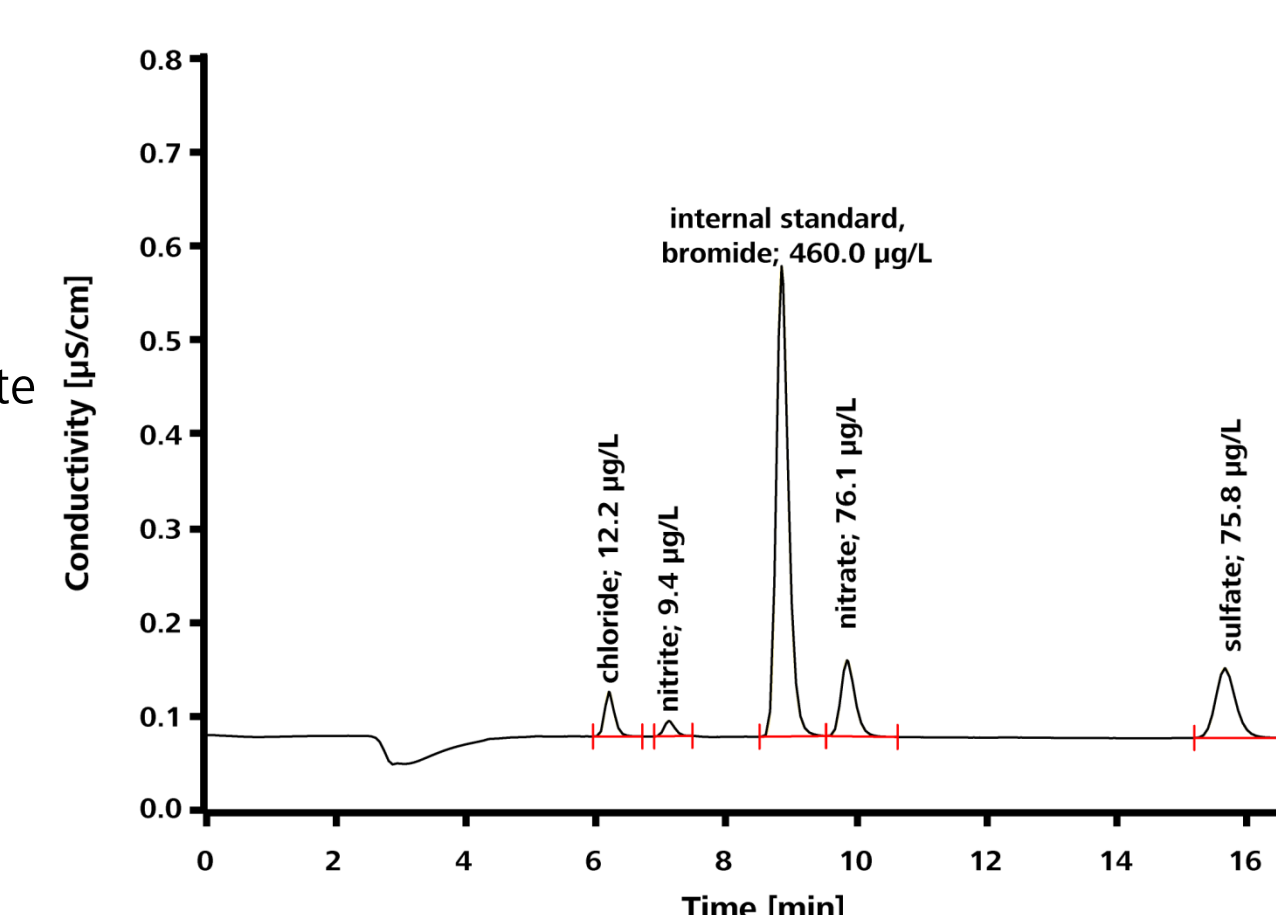
|	
Column:	Metrosep C 4 - 150/4.0
Column temp.:	30 ℃
Eluent:	2.0 mmol/L nitric acid
	0.7 mmol/L dipicolinic acid
Flow:	0.9 mL/min
Loop:	250 μL
PILS air flow:	16.7 L/min (= 1 m³/h)
Flow$_{sample\ stream}$:	0.23 mL/min
V$_{sample\ stream}$:	1.94 mL
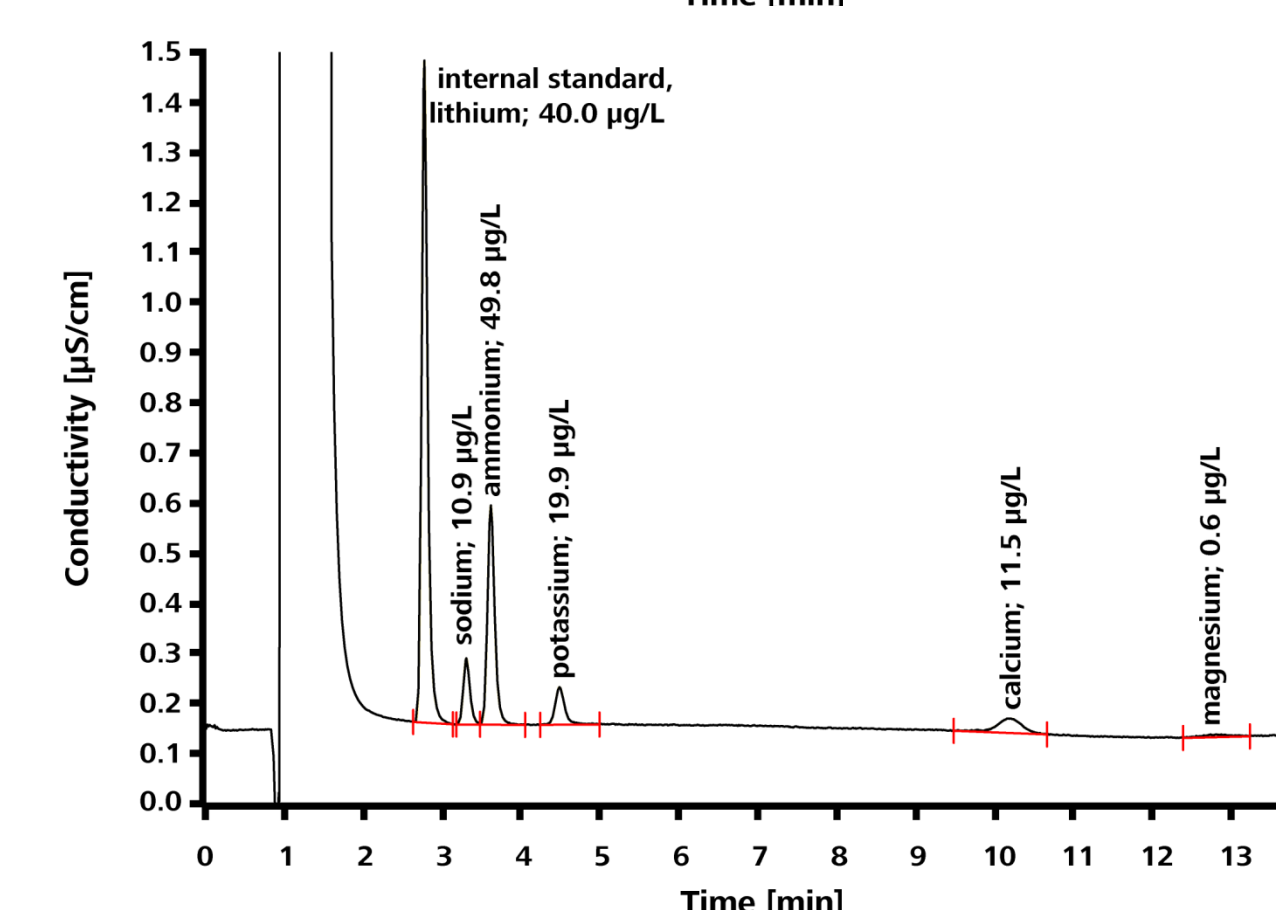
b) Voltammetry

Zinc, cadmium, lead, and copper are determined using anodic stripping voltammetry (ASV). The metals first undergo cathodic enrichment at the electrode and are then anodically stripped during the detection phase. Since the oxidation of the four metals occur at different potentials, they are determined in a single run.

Sample loop	1.94 mL
Electrolyte	2.0 mol/L acetic acid
	1 mol/L ammonium hydroxide, pH = 4.6
Working electrode	Hanging Mercury Drop Electrode (HMDE)
Reference electrode	Ag/AgCl/KCl (3 mol/L)
Auxiliary electrode	Platinum
Mode	Differential pulse
Deposition potential	−1.15 V
Deposition time	90 s
Start potential	−1.15 mV
End potential	0.15 mV
Sweep rate	0.06 V/s
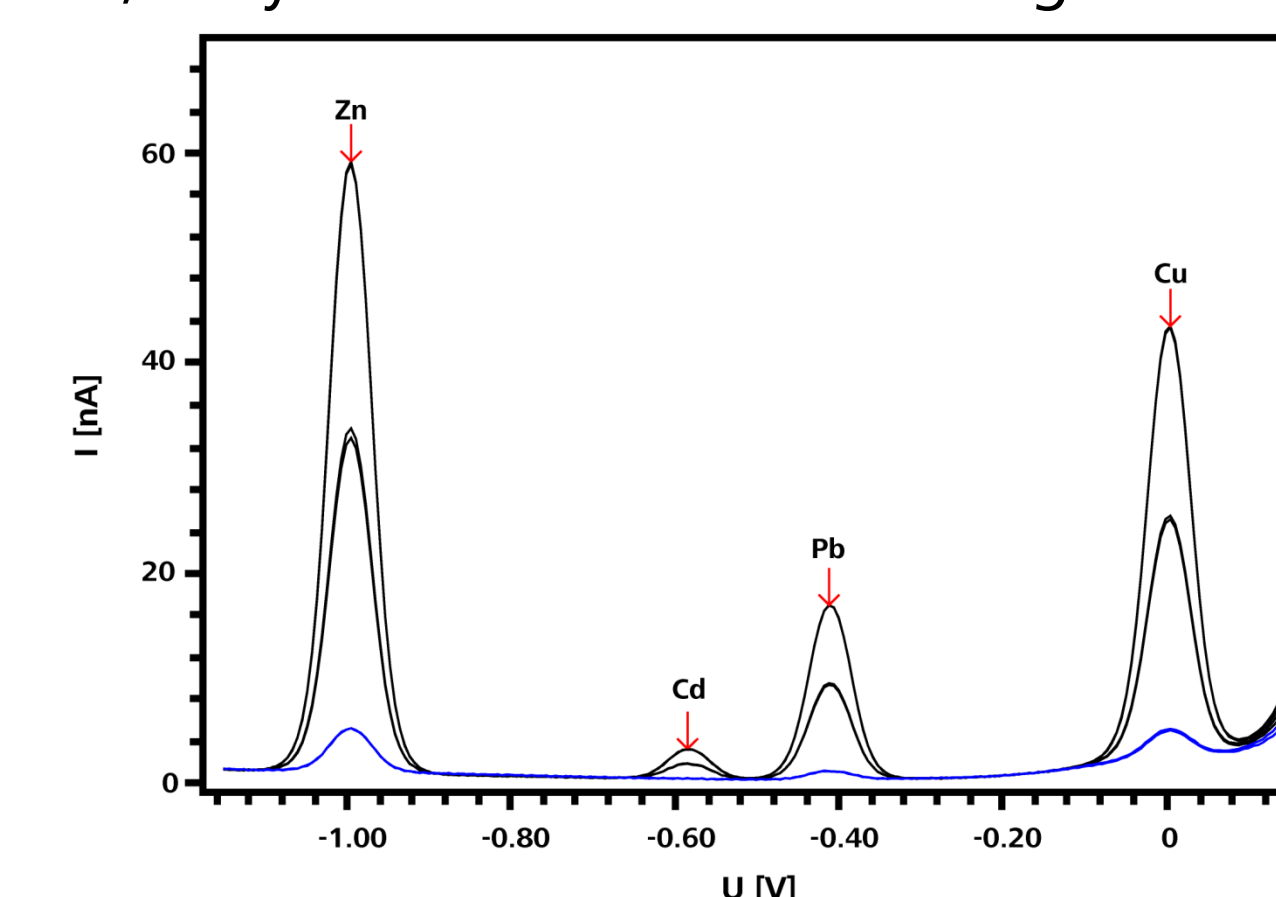
Semicontinuous aerosol monitoring

To capture the short-term impacts of air pollution, near real-time determination of the aerosol composition is necessary. After burning a sparkler, time series of aerosol water-soluble ionic components such as anions, cations, and heavy metals were determined at a 60 min time resolution during one week.
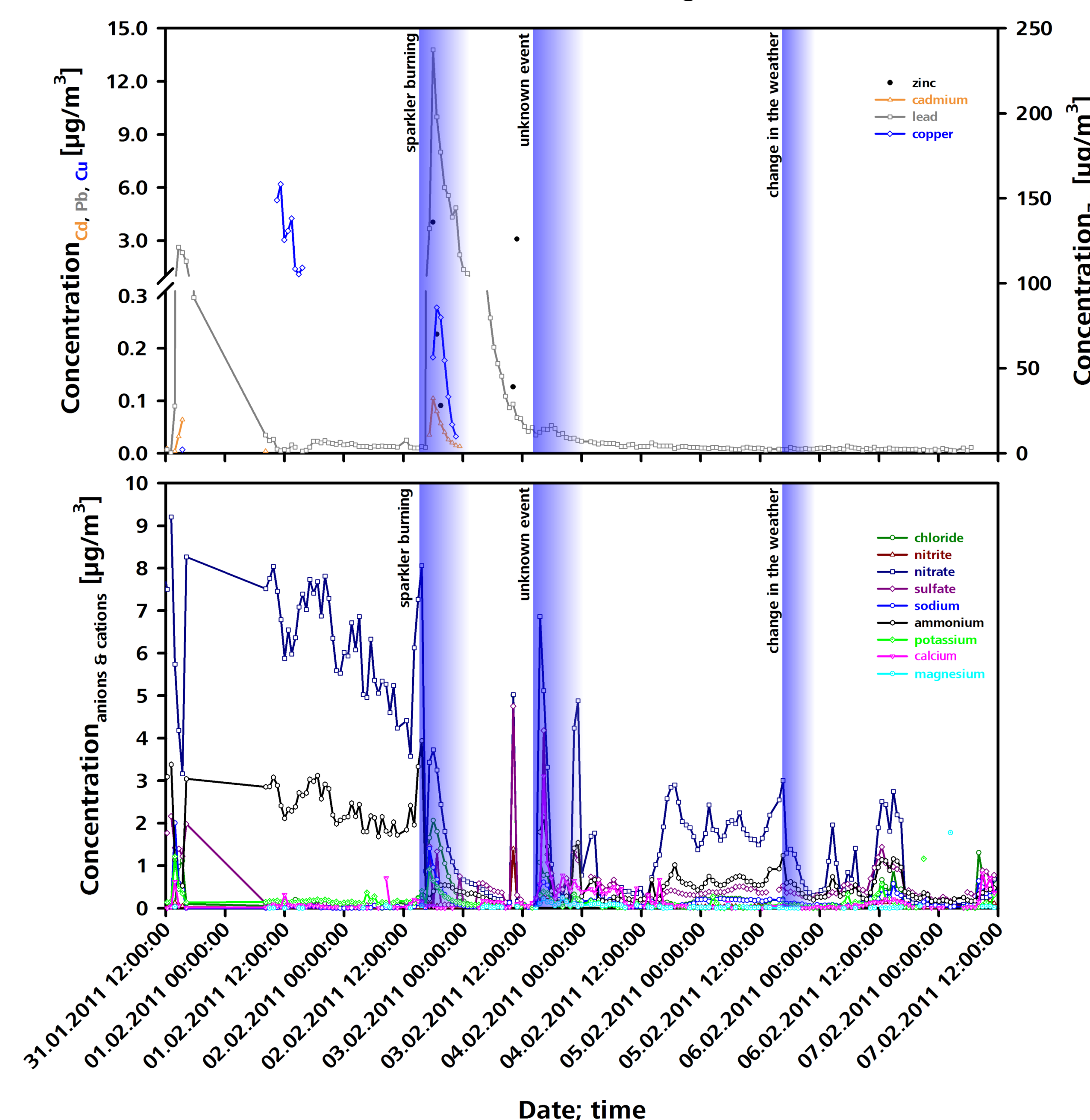
The time series of the major ionic species determined by PILS-IC-VA clearly show the impact from sparkler burning and highlight the extraordinary responsiveness of the analytical unit. The highest spikes belong to nitrate, ammonium, and lead. Chloride, sulfate, sodium, and potassium still show distinct spikes, while nitrite, calcium, and magnesium as well as the heavy metals, copper and cadmium, were found at concentrations below 0.3 μg/m³. PILS-IC-VA offers heavy metal detection limits in the ng/m³ range and thus copes with the specifications stipulated in the EU directive 2004/107/EG.

References

(1) R.J. Weber, D.A. Orsini, Y. Daun, Y.-N. Lee, P.J. Klotz, and F. Brechtel, A Particle-Into-Liquid Collector for rapid measurement of aerosol bulk chemical composition, Aerosol Sci. Technol. **35**, 718-727 (2001).

(2) C. Emmenegger, R. Jansen, and M. Laeubli, Determination of anions and cations in aerosols, Pittcon 2008, http://www.metrohm.com/com/Applications (search for 8.000.6014EN).

(3) J. Gandhi and P. Jones, Analysis of airborne particulate matter by PILC-IC, Pittcon 2010, http://www.metrohm.com/com/Applications (search for 8.000.6058EN).

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