Online Multi-elemental Monitoring of Environmental Atmospheric Gases with a Gas Exchange Device Coupled to the High Sensitivity Thermo Scientific iCAP Qs ICP-MS

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Key Words
Environmental gas monitoring, KED, Nuclear , Air, Pollution

Goal

To demonstrate real time multi-elemental analysis of environmental contaminants in air in using a gas exchange device coupled to the Thermo Scientific™ iCAP™ Qs ICP-MS.

Introduction

Environmental pollution is an immediate and growing concern. Environmental monitoring has become a key mechanism in determining how industrial activities and accidental contamination impact our water supplies, ecosystems and the air that we breathe. Strategic policies such as Clean Air for Europe (CAFE) and the United States Clean Air Act (CAA) for example, provide a framework of standards and objectives for the control of persistent pollutants that can damage health and the environment. Daughter directives within the CAFE program call for monitoring of nickel, arsenic, cadmium, mercury and lead. Of particular concern are fine particles with a diameter of less than 2.5 µm (PM2.5), which can penetrate deep into human bronchial tubes causing asthma and bronchitis. In China, where coal burning is still the biggest energy source and private car use is rapidly increasing, an estimated 70% of cities have PM2.5 levels above[1] the daily 75 µg PM2.5/m^3 Chinese National Air Quality Standard limit[2].

The Fukushima Daiichi nuclear power plant incident in 2011 demonstrated an immediate need for the monitoring of specific analytes in ambient air[3] in order to determine the distribution of radioactive materials in the environment, support remediation strategies and assess any possible subsequent threat to human health.

Current approaches for measuring radioactive contamination in the environment require the collection and preparation of soil and water samples and impingers or filtering for air sampling. These methods, however, cannot provide the real time results necessary for a meaningful assessment of current environmental conditions.

This application note evaluates the use of a gas exchange device (GED) coupled to the iCAP Qs ICP-MS for the direct analysis of atmospheric air (Figure 1). The GED overcomes problems in the direct analysis of air by ICP based techniques by exchanging atmospheric gases with argon which is compatible with the ICP ion source. Direct air sampling using the GED and on-line elemental analysis by high sensitivity ICP-MS therefore provides immediate information on airborne contamination.

The fast elemental scan speeds afforded by ICP-MS allow for the measurement of single particle events (SPE) that are seen as pulses in the signal intensity as they are processed by the ICP ion source. As air entrained elements are in particulate form, the ICP-MS based analysis of SPE can determine the number and even size of particles, therefore providing valuable information on elemental transport in the environment.

Gas Exchange Device

Figure 1. Gas Exchange Device coupled to the Thermo Scientific iCAP Qs

The GED (J-SCIENCE LAB Co. Ltd., Kyoto Japan) consists of 2 inner tubes of 0.07 µm porous glass that act as a membrane and an outer body made of (PYREX™) glass (Figure 2). The gas sample is introduced into the central inner tube of the GED device and argon is introduced into the outer tube at 2 L/min using the GED internal mass flow controller.

As the particulate supporting gas travels along the inner tube, atmospheric gases diffuse out of the inner tube (indicated by the blue arrows in Figure 2) and argon diffuses from the outer tube into the inner tube (indicated by the yellow arrows). Ultimately, before the sample enters the plasma, the atmospheric gases have been replaced by argon while particulate matter from the sample remains.

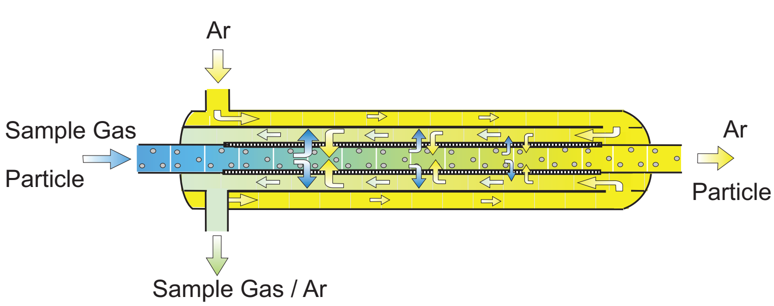

Figure 2. Principle of Gas Exchange Device

Instrument Configuration

A Thermo Scientific iCAP Qs ICP-MS was used for all measurements. The sample introduction kit consisted of a demountable quartz torch with a 2.0 mm ID sapphire injector. The spray chamber was removed and the exit line from the GED was attached directly to the injector using a PFA adapter. The instrument was operated in a single QCell mode, using kinetic energy discrimination (KED) with pure He as the collision gas. The use of pure He KED eliminates interferences, ensuring low backgrounds and maintains high sensitivity for the analytes measured.

Table 1. Instrument operating parameters

Parameter	Value
Sample gas	0.68 L/min
Air sampling rate	0.235 L/min
Auxiliary gas	0.8 L/min
Cool gas	14 L/min
Forward power	1550 W
Collision cell gas	He at 4.5 mL/min
KED barrier	3 V

Tuning, Sampling and Data Acquisition

The combined GED-ICP-MS system was optimized using a gas mixture of volatile ^{52}Cr, ^{95}Mo, and ^{184}W species generated by an Element Standards Gas Generator (ESGG) (J-SCIENCE LAB). The ESGG produces a continuous stream of elemental vapor in an argon gas flow that is introduced into the GED.

Ambient air was sampled via a TYGON® R3603 tube (i.d. 3.2mm, o.d. 6.4mm), approximately 15 m long. One end of the tube was connected directly to the GED; the other end was fed through an outside window, 10 m above ground. The argon sample gas flow of 0.68 L/min entrained the outside air through the tube and into the GED at a flow rate of 0.235 L/min. Sampling conditions are shown in Table 2.

Table 2. Sampling Conditions

Parameter	Value
Location	Bremen, Germany
Date, Time	18 Dec 2012, 9:30 am to 13:30 pm
Weather Conditions	Overcast, 6 °C, Wind: ENE 14 km/h

To determine optimal dwell times for the analysis of atmospheric particles, time resolved analyses of the target isotopes (^{66}Zn, ^{118}Sn, ^{121}Sb, ^{141}Pr, ^{205}Tl, $^{206, 207, 208}$Pb, ^{209}Bi and ^{238}U) were made using dwell times of 0.5, 1, 10 and 100 ms over a period of 300 s. In a subsequent 4 hour measurement of the outside air, a 10 ms dwell time was used for all isotopes.

Result and discussion

Ambient air was self-aspirated into the GED-ICP-MS and the target isotopes were analyzed at different dwell times as described. For analyses that intend to evaluate particle information, dwell times should be carefully optimized to favor the analysis of full SPEs. Dwell times that are too short, will measure sections of the SPE and dwell times that are too long will tend to measure multiple particle events in one scan.

Figure 3 (100 ms dwell) and Figure 4 (10 ms dwell) show time resolved scans for both an N_2 gas blank and an air sample. When comparing Figures 3 and 4, it is clear that 10 ms dwell time (higher scan frequency) provides improved discrimination between particle events and that individual events have a higher signal to noise ratio. At 100 ms dwell time, multiple events are captured together and averaged so that particle event information such as the number and intensity of events is lost.

Even shorter dwell times should further improve time resolution and dwell times of 0.5 and 1 ms were also evaluated. It was observed however, that shorter dwell times captured partial particle events and did not provide additional information compared to the 10 ms dwell time scans.

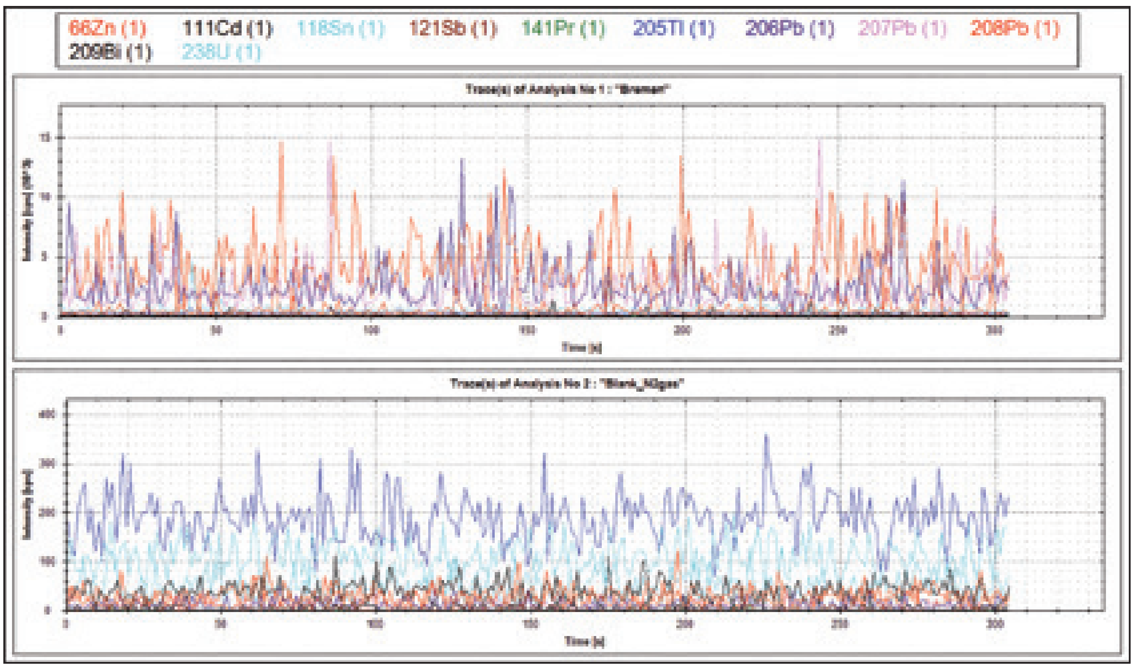

Figure 3. Time resolved scans for ambient air and an N_2 gas blank using a 100 ms dwell time. Please note the different (vertical) intensity scales on the two scans

Figure 4. Time resolved scans for outside air and an N_2 gas blank using a 10 ms dwell time. Please note the different (vertical) intensity scales on the two scans

A 10 ms dwell time was chosen for a longer term measurement of over 4 hours. Figure 5 shows a 30 minute section of the 4 hour monitoring period. Particle events for Zn, Pb and Bi are clearly shown.

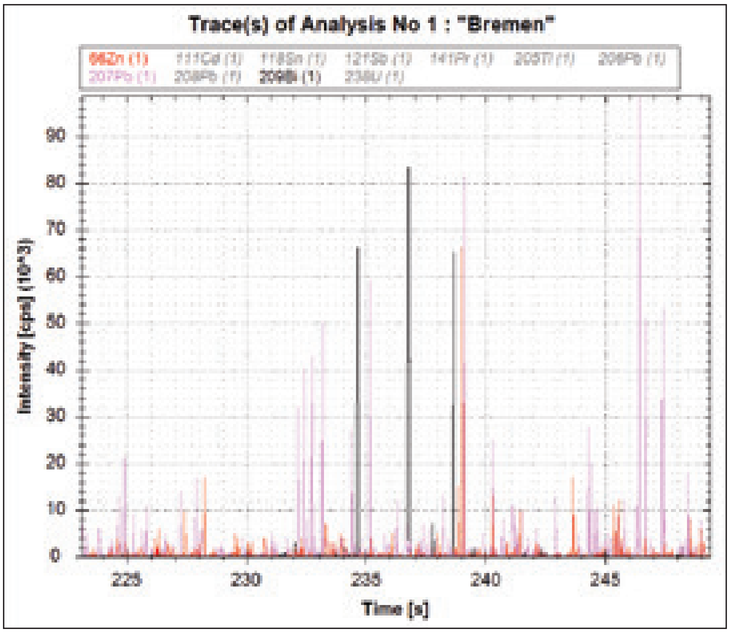

Figure 5. 30 minute section of the 4 hour air monitoring period

The environmental source of the particles observed in these analyses is practically impossible to determine as the particle trajectory travel distance is unknown. In this application, lead particles can be seen at regular intervals throughout the 4 hour period. The cycling and transport of lead in particulate matter is well documented, therefore lead particles are likely to occur in industrial and urban areas. For a more accurate evaluation of particle sources in air, further sampling points and baseline data regarding the geochemical cycling, potential sources and detailed environmental conditions at the time of sampling are required.

Conclusion

The Thermo Scientific iCAP Qs ICP-MS has demonstrated the high sensitivity and freedom from background interferences required for the measurement of particles in ambient air. The iCAP Qs ICP-MS has flexible scan times with a data buffer system capable of handling the large amounts of data acquired during long term *in-situ* analyses. QCell technology eliminates interferences whilst ensuring high sensitivity even for the lower mass isotopes thanks to its high transmission efficiency. A single mode KED approach could thus be employed for a number of isotopes across the mass range.

The use of a Gas Exchange Device coupled to the iCAP Qs ICP-MS is not limited to monitoring environmental air. Additional applications include monitoring a large range of gas samples such as specialty gases, semiconductor gases in the workplace, tobacco smoke and the presence of radionuclides.

Acknowledgement:

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