Online determination of element composition and mass of single airborne particles by ICP-MS

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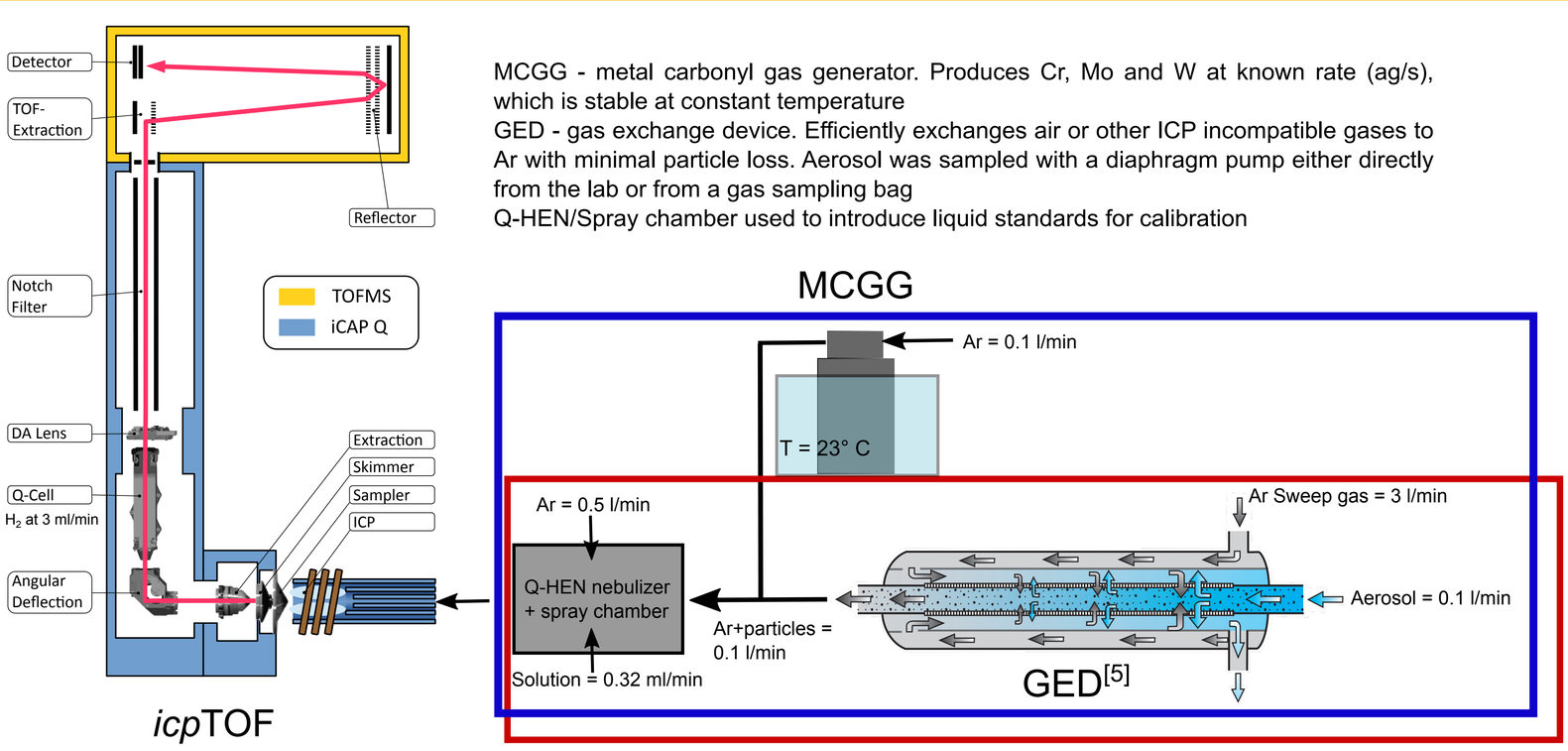
► The analysis of metals in APM is commonly realized by collecting aerosols on a filter, digesting it and measuring by, for example, inductively coupled plasma mass spectrometry (ICP-MS). This approach is time consuming and prone to contamination.

► Real-time multi-element monitoring of APM in ambient air by ICP-MS is possible with proper interfaces, such as differential mobility analyzer or gas exchange device (GED) [1,2].

► In comparison to bulk analysis, single particle detection with ICP-MS improves signal/noise and provides information about particle mass and particle number concentration [3].

► In contrast to other ICP-MS, the new *icp*TOF measures also elemental composition of single particles, which makes it unique for complex aerosols [4].

Instrumentation and methods



MCGG - metal carbonyl gas generator. Produces Cr, Mo and W at known rate (ag/s), which is stable at constant temperature

GED - gas exchange device. Efficiently exchanges air or other ICP incompatible gases to Ar with minimal particle loss. Aerosol was sampled with a diaphragm pump either directly from the lab or from a gas sampling bag

Q-HEN/Spray chamber used to introduce liquid standards for calibration

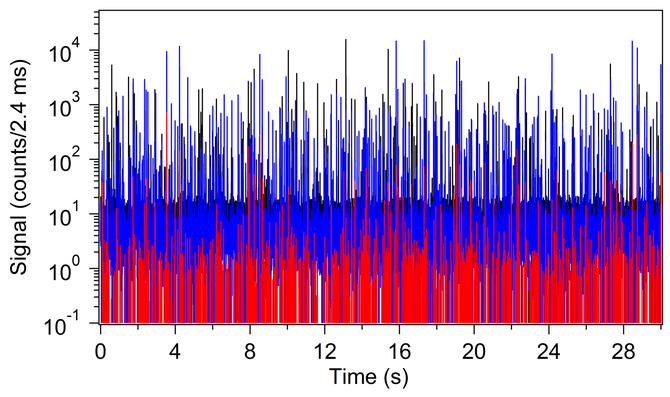
Calibration method 1

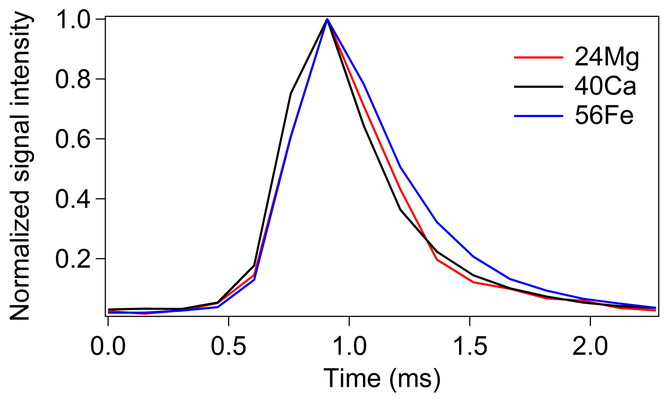
1. Measure signal intensity of Cr, Mo, W from MCGG
2. Establish calibration curve for Cr, Mo, W with standard solutions
3. Measure uptake rate of Q-HEN
4. Calculate from 1,2,3 the effective mass of liquid entering the ICP
5. Measure sensitivity of all elements with multi-element solutions and convert it into (g/s) using effective mass from 4

Calibration method 2

1. Measure Au nanoparticles of known mass from NIST
2. Establish calibration curve for Au with Au standard solutions
3. Measure uptake rate of Q-HEN
4. Calculate from 1,2,3 the effective mass of liquid entering the ICP [3]
5. Measure sensitivity of all elements with multi-element solutions and convert it into (g/s) using effective mass from 4

Method validation with NIST standard





Transport efficiency	%
Determined with Method 1	1.47
Determined with Method 2	1.46

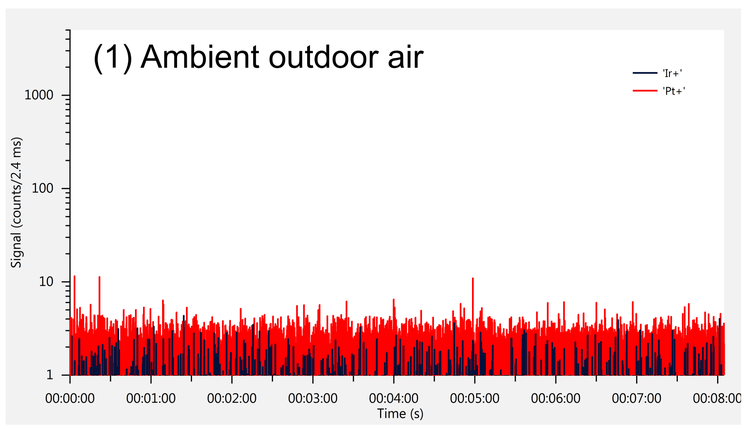
LOD for Au (fg)	0.02
LOD for Au (nm)	13

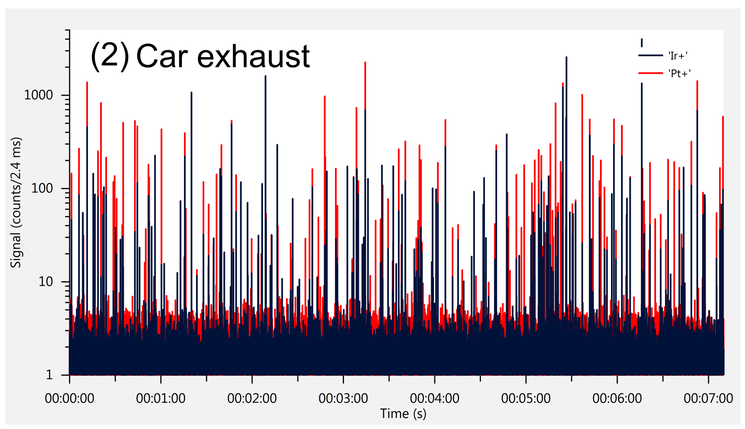
Element	Mg	Al	K	Ca	Fe
Mass determined with Method 2 (fg)	6.48	19.77	19.01	22.48	22.14
Mass determined with Method 1(fg)	6.50	19.85	19.08	22.56	22.22
Element/Al certified (bulk)	0.24	--	0.31	1.70	1.14
Element/Al determined	0.3±1.2	--	0.4±1.4	1.1±3.4	1.1±3.5
Ratio recovery (%)	137.60	--	134.49	66.83	96.32
LOD (fg)	0.47	0.26	6.20	0.19	0.07

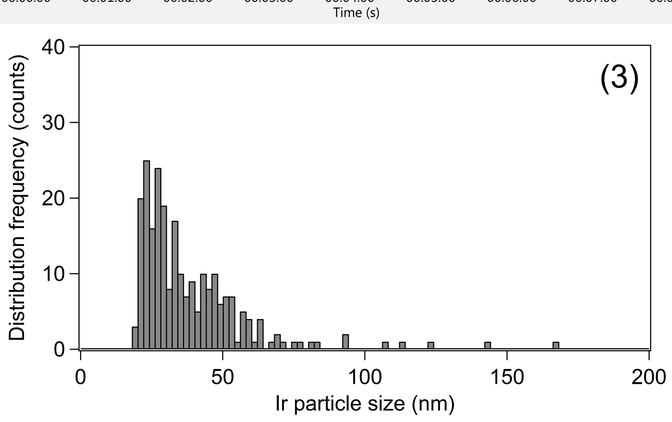
Standard reference material urban particulate matter NIST 1648 was suspended in a gas sampling bag with nitrogen and sampled with the diaphragm pump. **Left**-time traces of selected isotopes recorded with 2.4 ms integration time and using hydrogen in the Q-cell to improve the detection of Fe, Ca and K. **Right**-average transient signal of 330 single particles containing Mg, Al, K, Ca, and Fe.

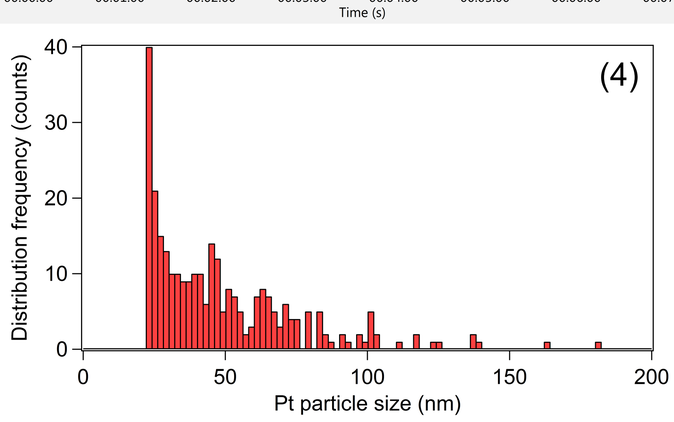
Element mass and element ratios of single particles determined with two methods. Only the elements present in the SRM at wt% concentration were evaluated. 330 particle signals with the intensity of all Mg, Al, K, Ca, and Fe being above the threshold were evaluated. Element-specific thresholds were calculated from blank – air sampled through a particle filter inserted at the inlet.

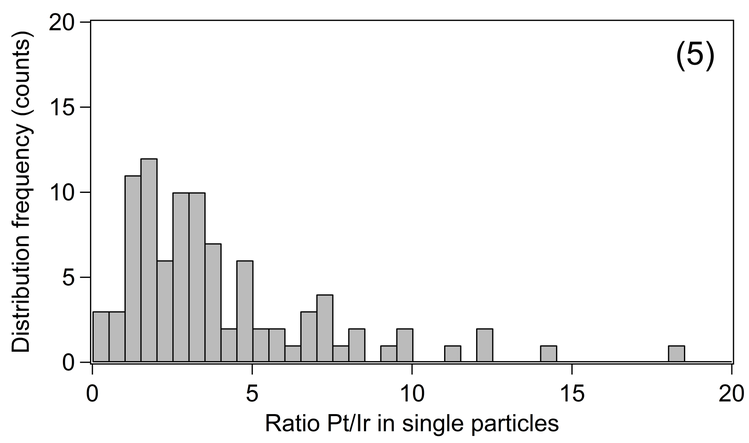
Measurement of particles from car exhaust











1-2 - Signals of Ir and Pt from ambient outdoor air and car exhaust recorded with 2.4 ms integration time. Car exhaust was sampled outdoor into the gas sampling bag and measured 10 minutes after sampling. Ir and Pt particles are most likely produced in the catalytic converter.

3-4 – Ir and Pt particle size distributions. Particle sizes were calculated using Method 2 and assuming particles are pure metallic (composed of either Ir or Pt), spherical, and with the density of bulk material.

5 – Pt/Ir ratio distribution in single particles. 18% of detected particles contained both Ir and Pt. Pt/Ir mass ratio in single particles varied significantly with the average around 2.5.

Summary

► Element mass and element composition of single aerosol particles can be determined online with the new combination of the GED and the *icp*TOF. These properties can be used for fundamental aerosol studies and identification of emission sources.

► Both calibration methods gave very similar results for the NIST standard with recoveries in the range of 67-140%.

► Ir and Pt particles detected from the car exhaust and quantified using Method 2 were in the nano-size range with the ratio of Pt/Ir varying from 0-10.

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