Determination of anions and cations in aerosols by ion chromatography

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Metrohm Ion analysis

Ion Chromatography

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Summary

The study of adverse effects of air pollution requires semi-continuous, rapid and accurate measurements of inorganic species in aerosols and their gas phase components in ambient air. The most promising instruments, often referred to as steam collecting devices, are the Particle-Into-Liquid-Sampler (PILS) coupled to wet-chemical analyzers such as a cation and/or anion chromatograph (IC) and the Monitoring instrument for AeRosols and GAses (MARGA) with two integrated ICs. Both instruments comprise gas denuders, a condensation particle growth sampler as well as pump and control devices. While PILS uses two consecutive fixed denuders and a downstream growth chamber, the MARGA system is composed of a Wet Rotating Denuder (WRD) and a Steam-Jet Aerosol Collector (SJAC).

Although the aerosol samplers of PILS and MARGA use different assemblies, both apply the technique of growing aerosol particles into droplets in a supersaturated water vapor environment. Previously mixed with carrier water, the collected droplets are continuously fed into sample loops or preconcentration columns for on-line IC analysis. While PILS has been designed to sample aerosols only, MARGA additionally determines water-soluble gases. Compared to the classical denuders, which remove gases from the air sample upstream of the growth chamber, MARGA collects the gaseous species in a WRD for on-line analysis. In contrast to the gases, aerosols have low diffusion speeds and thus neither dissolve in the PILS denuders nor in the WRD.

Proper selection of the ion chromatographic conditions of PILS-IC allows for a precise determination, within 4 to 5 minutes, of seven major inorganic species (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-}) in fine aerosol particles. With longer analysis times (10-15 minutes) even airborne low-molecular-weight organic acids, such as acetate, formate and oxalate can be analyzed. MARGA additionally facilitates the simultaneous determination of HCl, HNO_3, HNO_2, SO_2 and NH_3.

PILS and MARGA provide semi-continuous, long-term stand-alone measurements (1 week) and can measure particulate pollutants in the ng/m³ range.

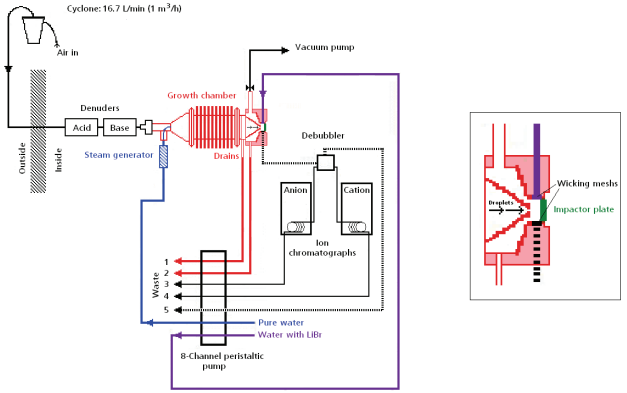
Introduction

The determination of anions and cations in atmospheric aerosols yields essential information concerning transport and atmospheric transformation processes as well as emission sources. Up to now these determinations have been carried out using filters that collect the aerosol particles over a long period of time, usually 24 hours. Prior to ion chromatographic analysis, the particles are removed from the filters and dissolved in water. However, this batch method only allows to determine averages over a time span of 24 hours or more. Additionally, this method is very labor-intensive, temporal resolution is poor and semi-continuous on-line measurements are not possible. On top of this, the results can be falsified by desorption processes and chemical transformations. The reliability of the results thus obtained is therefore questionable.

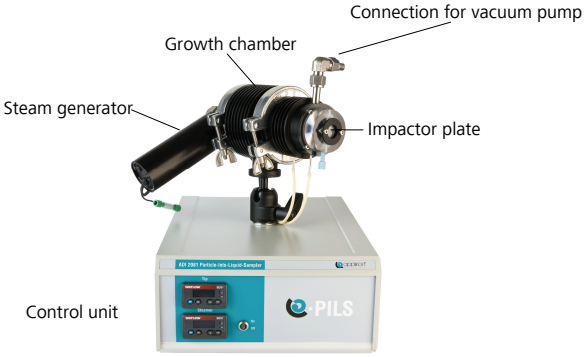
In contrast to the above, the particle samplers to be described allow semi-continuous sampling of aerosols downstream from two different denuder systems. Changes in the ionic composition of the aerosols can be sensitively monitored. The sampling systems can be coupled to an 850 Professional IC for anions and cations, which allows quasi-continuous measurements. The presented temporal resolution is 5 to 15 minutes. Rapid changes can thus be recorded immediately and correlated with meteorological and other data.

Particle-Into-Liquid-Sampler (PILS)

A vacuum air pump attached to the PILS draws the ambient air sample (16.7 L/min) through the whole system. While the size of the entering particulate matter (PM) is controlled by a cyclone (group of most concern is 2.5 µm and smaller; $PM_{2.5}$), interfering gas-phase nitrogen and sulfur species (NH_3, SO_2…) are removed by two consecutive static denuders. The remaining aerosols subsequently enter the growth chamber, where they are mixed with injected supersaturated steam. After the aerosol particles have grown to droplets, they can continuously be collected on the surface of the impactor plate. This impactor is surrounded by a stainless steel wicking mesh in which the collected droplets are mixed with carrier water that contains an internal standard (LiBr).

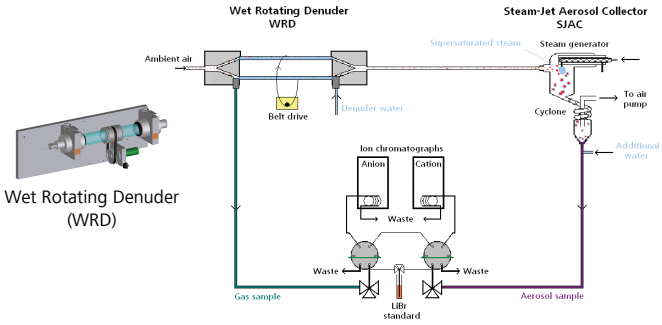


After air bubbles have been removed in the debubbler unit, the liquid sample containing the aerosols is transported to the loop or the preconcentration column of an IC. If both anions and cations need to be determined, the sample stream can be split into two.



Monitor for AeRosols and GAses (MARGA)

Whereas PILS exclusively aims at the determination of aerosols, MARGA measures components both in the gas phase and in aerosols. The main difference lies in the construction of the annular denuders. PILS uses two consecutive fixed denuders for the elimination of interfering gases. In contrast, MARGA uses a Wet Rotating Denuder (WRD) for the quantitative absorption of water-soluble gases in a thin water film on a rotating wall.

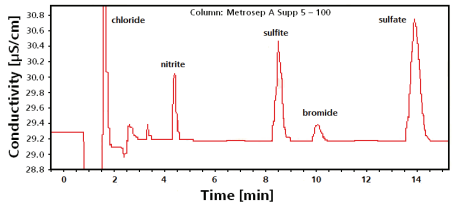


Wet Rotating Denuder (WRD)

Due to their low diffusion rate, aerosols do not dissolve in the WRD and arrive in the Steam-Jet Aerosol Collector (SJAC) where supersaturated steam condensation is used to grow the aerosol. Hence, MARGA provides two sample streams; one containing the dissolved gases and the other containing the dissolved particles.

Results

	Gas					Aerosol							
	HCl	HNO_3	HNO_2	SO_2	NH_3	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
Detection limit [µg/m³]	0.05	0.05	0.08	0.10	0.08	0.05	0.05	0.08	0.08	0.08	0.10	0.08	0.10



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(2) A. Khlystov, G.P. Wyers and J. Slanina, The Steam-Jet Aerosol Collector, Atmospheric Environment, **29** (17), 2229-2234 (1995).

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