MARGA – Monitor for AeRosols and Gases in ambient Air

Continuous Measurements of Aerosols and Gases

Metrohm Applikon

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Ambient air quality – critical for our health and the environment

For several decades, the emission of aerosols and their precursor gases has continuously increased due to growing populations, industrialisation and human activities. It has been known for some time that elevated concentrations of certain species in atmospheric aerosols have a negative effect on human mortality/morbidity rates. In addition to human health concerns, aerosols also affect atmospheric processes, having an impact on air quality, visibility, cloud formation and rainfall. Aerosols can influence the climate directly by absorbing and scattering light, thus changing the Earth's reflectivity or they can affect the climate indirectly via cloud formation and changing the property of clouds.

The chemical composition and size distributions of aerosols are highly variable and dependent on different factors such as the location, time, meteorological conditions, contribution of specific sources and altitude. Long term studies of the variation in concentration and composition of key components help in the understanding of the dynamics of air pollution and lead to ways of improving air quality to the benefit of our health and the environment.

Ambient air monitoring with MARGA quantifying aerosols and gases simultaneously

When considering the effects of aerosols on health and the environment, it is necessary to understand how they are formed and how their concentration and composition vary with diurnal and seasonal cycles. Continuous measurements of aerosols and their precursor gases are required with sufficient time resolution so that the various processes can be elucidated.

MARGA (**M**onitor for **A**e**R**osols and **G**ases in ambient **A**ir) has been developed by Metrohm Applikon in cooperation with the Energy Research Centre of the Netherlands. The instrument offers a new approach in which gases and aerosols sampled from the same air mass are separated from each other by selectively dissolving them in water. The resulting solutions are then analysed using ion chromatography with conductivity detection. Separating the two fractions from each other, allows the detection of important precursor gases and ionic species found in the aerosols.

Gases	HCl, HNO_3, HNO_2, SO_2, NH_3
Aerosols	Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}

Top shelf: Sample Box – separates and collects soluble gases and aerosols in solution. Eluents for chromatographs.

Middle shelf: Syringe pumps for collecting sample solutions, Metrohm ion chromatographs for anion and cation analysis and human interface.

Bottom shelf: UPS, additional liquid reservoirs and air flow control box (FCB).

MARGA – the concept

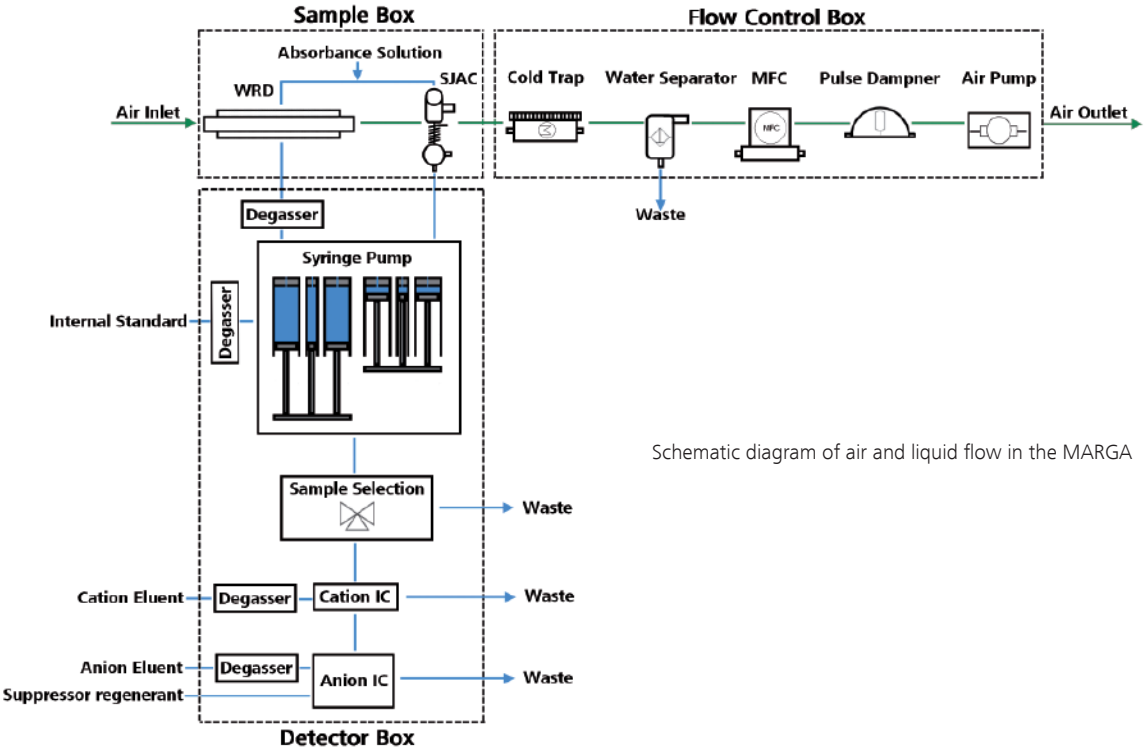
Air to be analysed enters into the Sample Box via an appropriate inlet, typically with a cut-off of PM_{10} or $PM_{2.5}$ (particle sizes less than 10 µm or 2.5 µm). The airflow is maintained at a constant 1 m^3/h by a mass flow controlled air pump. In the Sample Box water-soluble gases are quantitatively absorbed in a dilute (10 mg/L) solution of hydrogen peroxide by using a wet rotating denuder (WRD). Aerosols pass through the WRD and are subsequently collected in a steam-jet aerosol collector (SJAC).

The liquid samples from the WRD and SJAC are continuously collected during one hour by syringe pumps. After degassing and mixing with an internal standard (lithium bromide), the samples are analysed by two ion chromatographs for determination of anions and cations, respectively.

The bottom shelf accommodates various liquid containers, an uninterruptable power supply and flow control box. The entire instrument is controlled by a single software that runs on an integrated industrial PC.

Key Features

- Simultaneous measurements of gases and aerosols
- High temporal resolution – results every hour from same air mass
- High sensitivity for key parameters
- Unattended online operation
- Single software controls instrument and processes data
- Continuous calibration with internal standard
- All results validated by automated checks
- Results flagged with user-readable comments
- Detailed system diagnostics always available
- Results and all operation details recorded in easily accessible form
- Remote control and access of results possible
- Automated restart in case of temporary line power failure



Schematic diagram of air and liquid flow in the MARGA

MARGA is available with one or two Sample Boxes, the latter offering the possibility to distinguish between different size particulate matter in the same air mass (comparing $PM_{2.5}$ and PM_{10} for example) or to make gradient studies at the same location with inlets of variable heights.

Gas and aerosol sampling from the same air mass

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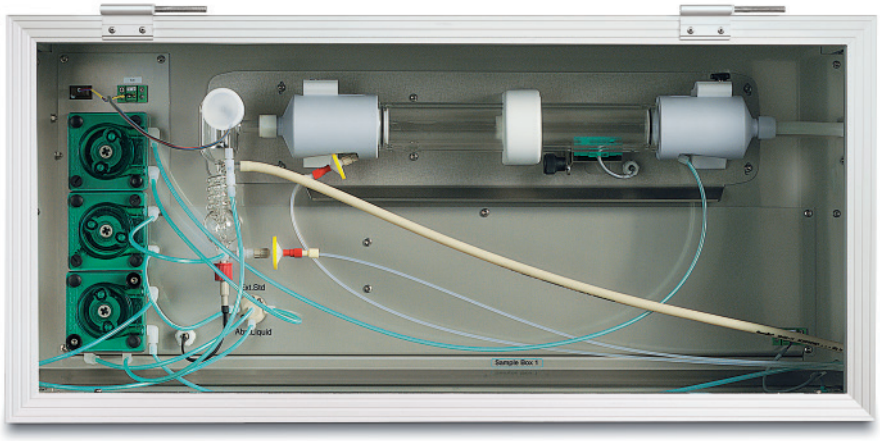


MARGA determines anions and cations in an aerosol and a gas sample taken from the same air mass every hour.

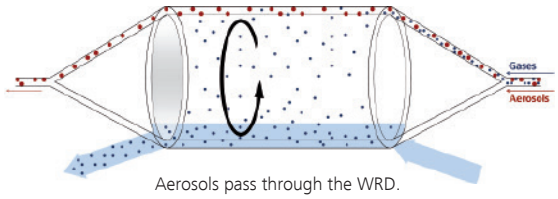
Wet Rotating Denuder (WRD)

The WRD consists of two concentric glass tubes, forming an annulus constantly fed with dilute H_2O_2 solution. These tubes rotate at 30 revolutions per min, forming a continuous liquid film on the inside of the outer cylinder and the outside of the inner cylinder. Ambient air is drawn in and, due to high diffusion coefficients, close to 100% of acid gases and ammonia are stripped from the air mass. The resulting solution of gases is continuously sampled by the Detector Box. Due to the design creating laminar flow and also the velocity of the air within the annulus, aerosols and particulates pass through to the SJAC.

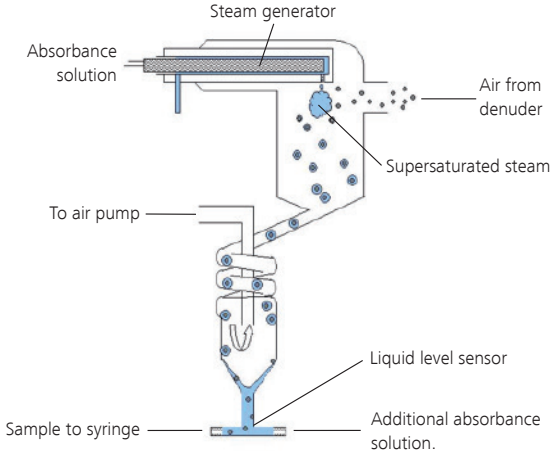
Steam-Jet Aerosol Collector (SJAC)

After the WRD, the ambient air, stripped of its gaseous water soluble components, enters the SJAC. Here super-saturated steam is introduced causing the aerosols to grow into larger, heavier droplets due to the process of deliquescence. Further on the air passes through a glass spiral tube, which acts as an impactor, breaking up the particles by inertial separation. The resulting solution of dissolved ionic aerosol species collects at the bottom of the SJAC which is then continuously sampled by the Detector Box.

Gases dissolve in liquid film because of high diffusion rates.



Aerosols pass through the WRD.



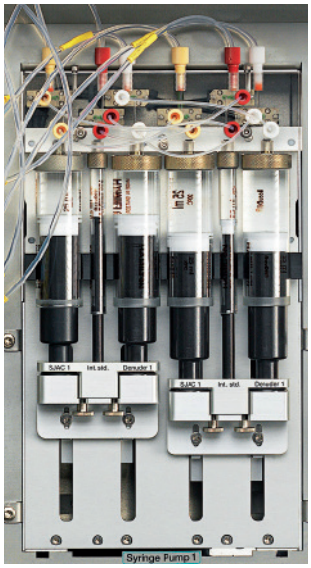
Working principle of WRD and SJAC

Automated analysis 24/7

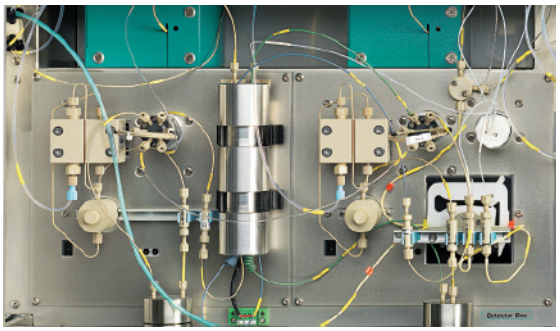
Detector Box

The Detector Box is fitted with two sets of alternating syringe pumps. Every hour, one pair of syringe pumps collect 25 mL of absorbance liquid each from the WRD (the gas sample) and the SJAC (the aerosol sample). Each syringe then contains a sample of gases and aerosols averaged over the one hour period. At the same time 2.5 mL of LiBr internal standard is drawn in, ready to be mixed with the samples before they are injected into the ion chromatographs. At the end of the hour the direction of the syringe pumps is reversed and the samples are passed to the sample loops of the ion chromatographs after first being degassed and mixed with the internal standard. Meanwhile the second set of syringe pumps are being filled with the next hour's sample.

At the heart of the Detector Box are two Metrohm ion chromatographs, fitted with conductivity detectors. The samples in the filled sample loops are injected into cation and anion IC columns supported in a column oven. The addition of internal standard to the WRD and SJAC samples makes anion and cation IC data validation possible. It also allows for the retention times to be kept stable over long periods by comparing the relative retention times of Br^- and SO_4^{2-} and adjusting the column temperature appropriately. The timing of the analytical cycle is tightly controlled so that the anions and cations from both the aerosol and gas sample can be analysed within each hour or in the case of the two Sample Box version, two gas and aerosol samples within each hour. A preconcentration column can be added before the ion chromatographs in case lower detection limits are required.



Syringe block for collecting gas and aerosol samples.



Cation and anion chromatographs, with column oven and conductivity detectors.

Software for full control and visibility

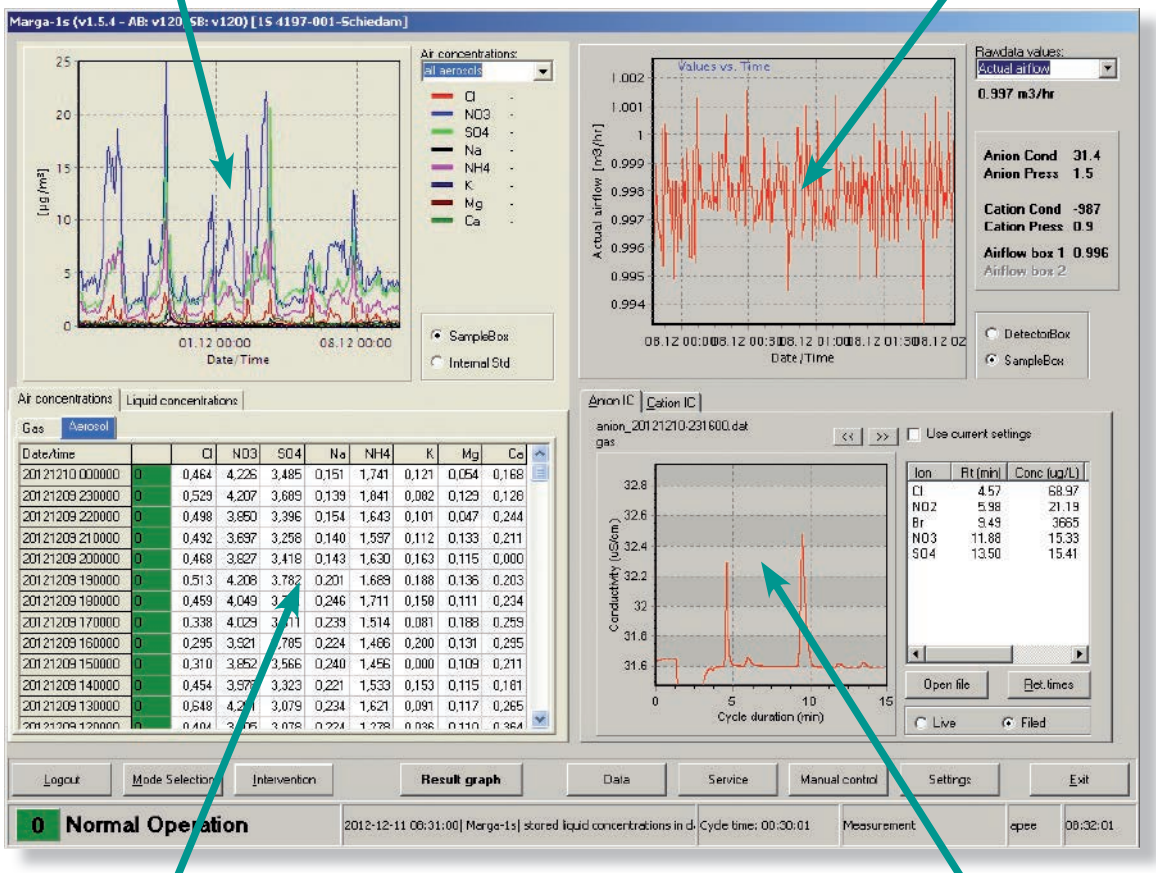
The MARGA software automatically opens when the instrument is switched on. The software allows for full control of the system from the industrial PC that acts as the human interface. The result graph screen shows up to one month's results for gases or aerosols and can be toggled with the operations details screen shown below. The operations details screen allows for a complete overview of the instrument operation at a single glance. The graphs can be zoomed for easy examination of details.

Result panel

The results panel provides an overview of the measured gases, aerosols and internal standards.

Raw data panel

The raw data panel provides an overview of all the important raw data parameters.



Air and liquid concentrations panel

This panel displays up to the last 4 weeks of air and liquid concentrations. For each analysis a new line is created in the table. Coloured flags indicate the validity of each result.

Anion and cation chromatogram panel

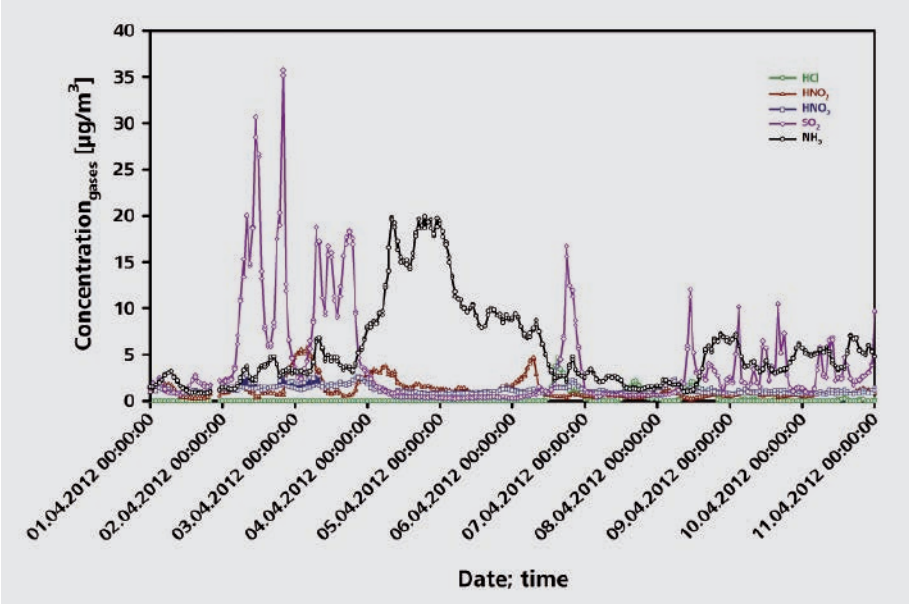
The anion and cation panel displays the anion and cation ion chromatograms. These can either be shown live or the user can page through previous results. Retention times of integrated peaks are also displayed.

The taskbar at the bottom of the screen allows the access to all the different functions, parameters and controls, while at the very bottom information is displayed on the current status of the instrument.

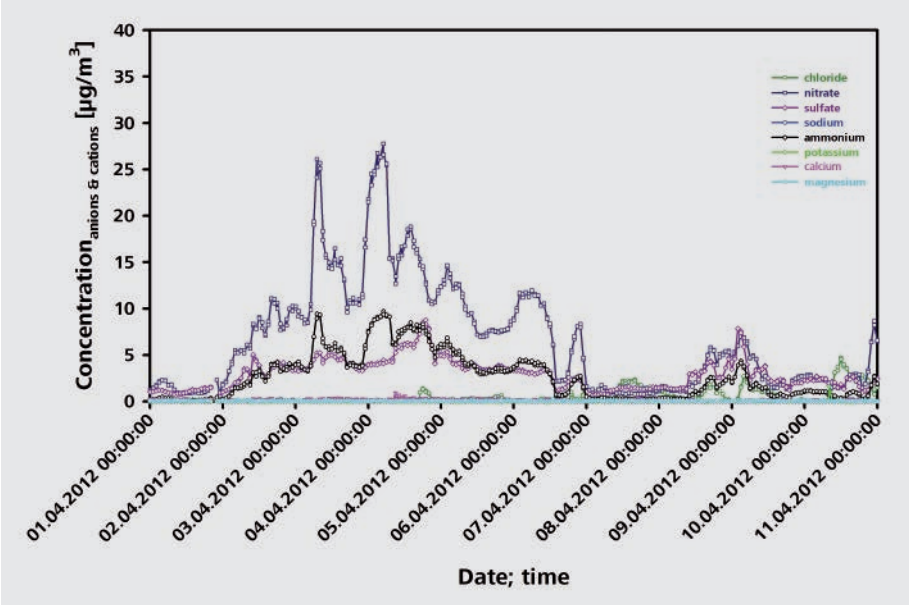
Data can be conveniently exported in .xml format, as well as status flags and log entries.

Monitoring trends in aerosols and gases over time

Once data on gas and aerosol concentrations are exported from MARGA then these data can be examined and graphed to determine trends, both seasonal and diurnal. Coupled with backward trajectories of wind direction valuable deductions can be made as to the possible sources of high pollution events.



Changes over time in the concentration of some gases in the ambient air in Schiedam (Netherlands), April 2012, determined by MARGA



Changes over time in the ionic aerosol constituents in the ambient air in Schiedam (Netherlands), April 2012, determined by MARGA

MARGA installation at Auchencorth Moss, Scotland, NERC Centre for Ecology and Hydrology. All rights reserved. Ian Leith. 2011.

Watch a video of a MARGA system operated by the Institute of Tropical and Marine Meteorology in Guangzhou, China: **http://metrohm.com/com/Company/testimonials/index.html?q=9**

MARGA of the German Federal Environment Agency (UBA) operating at research site Melpitz, of the Leibniz-Institute for Tropospheric Research (TROPOS)

MARGA installations run by USEPA at the USDA's Beltsville agricultural research site

MARGA installed in the laboratory of the National Institute of Environmental Research, Seoul

Typical detection limits with MARGA

Component	Detection Limit fixed loop (µg/m³)	Detection Limit Preconc. (µg/m³)
Gas		
HCl	**0.01**	**0.001**
HNO_3	**0.05**	**0.005**
HNO_2	**0.02**	**0.002**
SO_2	**0.03**	**0.003**
NH_3	**0.05**	**0.005**
Aerosol		
Cl^-	**0.01**	**0.001**
NO_3^-	**0.05**	**0.005**
SO_4^{2-}	**0.04**	**0.004**
NH_4^+	**0.05**	**0.005**
Na^+	**0.05**	**0.005**
K^+	**0.09**	**0.009**
Mg^{2+}	**0.06**	**0.006**
Ca^{2+}	**0.09**	**0.009**

Detection limits determined on an active MARGA system in Schiedam (Netherlands)

Specifications

Dimensions (rack included)	
Width	120 cm
Height	180 cm
Depth	60 cm
Weight	200 kg

Environmental conditions	
Shelter temperature range	25 ± 5 °C
Ambient temperature range	-30 to 45 °C
Shelter humidity	< 60%
Ambient humidity	0–100%
Altitude	Up to 2'000 m

Mains connection via UPS	
Required voltage	115–120 V/220–230 V
Required frequency	50/60 Hz
Power consumption	700 VA

Dimensions and power requirements given are for the MARGA 1S.

ETV Verification

The U.S. EPA Environmental Technology Verification Program (ETV) provides objective, third-party data to the environmental marketplace about the performance of new environmental technologies.

The MARGA instrument from Metrohm Applikon has been verified by this program. The full report can be found at **www.epa.gov/etv** or at **www.metrohm-applikon.com/marga.html**

ETV
www.epa.gov/etv

www.metrohm-applikon.com

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