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Technical note

An autonomous aerosol sampler/elemental analyzer designed for ocean buoys and remote land sites

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Abstract

An autonomous aerosol sampler/elemental analyzer, that employs energy dispersive X-ray fluorescence spectrometry to determine the elemental (Fe, Si, S, Ca and K) concentrations of aerosols in near real time, has been designed, built and successfully tested on a roof. The ultimate technical goal is to deploy a buoy-mounted aerosol sampler/analyzer in order to make the long-term measurements necessary to quantify the deposition of mineral dust to the oceans. A major scientific goal is to address the question of enhanced biological production due to the release of dissolved iron from the deposition of mineral dust. Design and operating features are discussed and illustrated. This instrument has the sensitivity to measure the concentrations of mineral dust and Fe over the oceans with a time resolution of a few days during periods of moderate to high dust deposition. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

This note describes a new instrument that combines two capabilities: (1) the collection of a large set of time-series aerosol samples and (2) the in situ elemental analysis of the aerosol samples. The development of this instrument was a direct outgrowth of our buoy-mounted aerosol sampler (Sholkovitz et al., 1998a, b). This second-generation instrument is designed to operate in an unattended mode on ocean buoys and is capable of collecting up to 24 aerosol samples on filters over periods of days to weeks to months. Employing X-ray fluorescence spectrometry (XRF-S), the aerosol concentrations of Fe, Si, S, Ca and K are determined in near real time. Fe and Si are indicators of mineral dust, S has both biogenic, sea-salt and anthropogenic sources, and Ca and K have mineral and sea-salt sources.

While our instrument has not been tested at sea, it has successfully completed four months of testing on a local roof. This note is intended to inform the community of the design, the mode of operation and the capabilities of this new aerosol sampler/analyzer. Sea trials on a buoy are anticipated to start in 2001.

A major scientific goal is to address the *iron hypothesis* which argues that phytoplankton production in the high-nutrient and low-chlorophyll regions of the world's oceans is limited by iron, whose main source is atmospherically delivered mineral dust from the continents (Duce and Tindale, 1991; Martin et al., 1991). The IRONEX and SOIREE programs have demonstrated that enhanced productivity does occur when an iron sulfate solution is added to Fe-depleted surface waters (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000). In contrast, the enhancement of biological production due to the release of dissolved iron from dust events and/or rain events is poorly documented. Due to the episodic nature of the dry and the wet deposition to the oceans (Arimoto et al., 1992; Prospero et al., 1996), testing the iron hypothesis from ships is difficult. A buoy-mounted aerosol sampler/analyzer, along with simultaneous measurements of the physical, chemical and biological variability of the upper oceans, would provide the long-term measurements of mineral dust input

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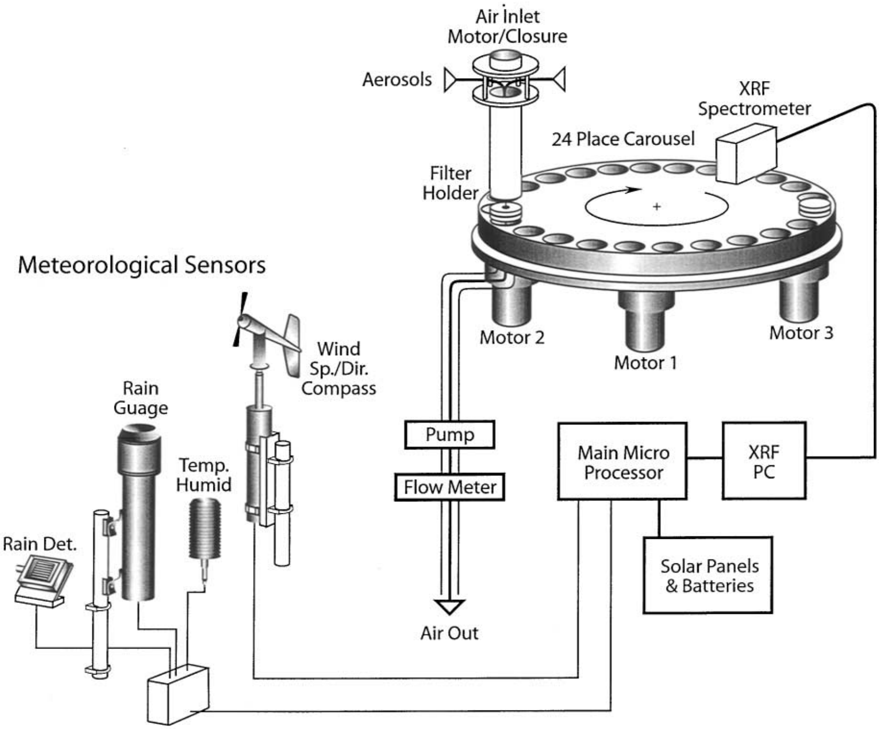

Fig. 1. Schematic diagram showing the main components of the aerosol sampler/X-ray fluorescence instrument and its linked meteorological sensors.

needed to test the iron hypothesis (Sholkovitz et al., 1998a).

The instrument described in this paper measures bulk aerosol concentrations; calculating dry deposition rates requires extra information on the size distributions of aerosols (Arimoto et al., 1997).

Wet deposition is also an important source of Fe to the oceans (Jickells and Spokes, in press). We are collaborating with Robert Byrne and colleagues at the University of South Florida to develop a buoy-mounted instrument that is capable of measuring the rainwater concentrations of Fe (II) and Fe (III) in an autonomous and real-time manner. This instrument uses a long pathlength spectrometer for measuring low concentrations of iron (Waterbury et al., 1997; Byrne et al., 1999).

2. Overview of the instrument and the basic operating procedures

Fig. 1 is a block diagram showing the major components of the instrument and the meteorological package. Fig. 2 provides a cross-sectional view of the sampler/sensor instrument only. Fig. 3 is a schematic drawing of the system mounted on a frame. A more complete description of the instrument, including photographs of the components and the whole system, can be found at www.whoi.edu/science/MCG/people/esholkovitz/index.html.

Main features include:

- Time-series sampling of up to 24 aerosol samples on 25 mm diameter filters.
- Near real-time elemental analysis of samples and filter blanks using XRF-S.
- On board standards for determining the stability and sensitivity of the XRF-S signals.
- Samples stored for additional analyses in the laboratory.
- Flexible software with direct internet connection to run the instrument, set the filtering parameters, and download the data.
- Autonomous and remote operations by batteries and/or solar panels.
- Rugged and watertight construction.
- Motorized valve on the inlet to protect the samples and instrument.
- Simultaneous measurement of key meteorological conditions.

The heart of the instrument is an X-ray fluorescence spectrometer that can measure the elemental

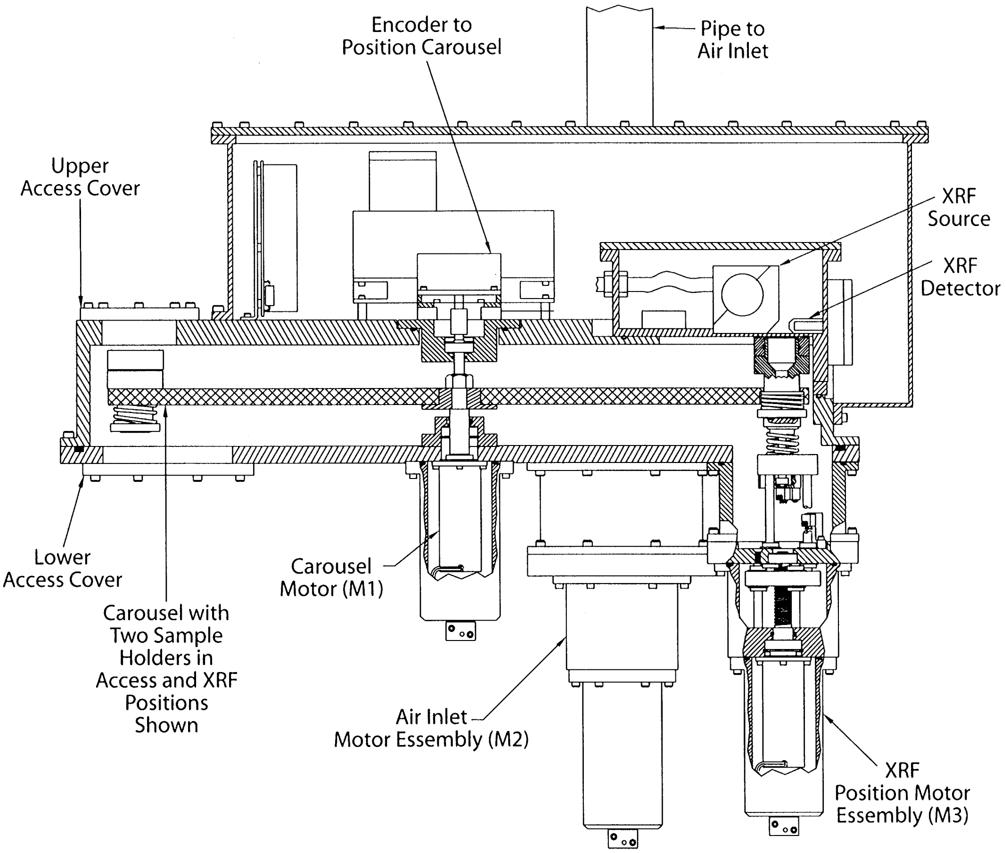

Fig. 2. Cross-sectional engineering drawing of the aerosol sampler/X-ray fluorescence analyzer instrument. The distance across the top most horizontal plate is 60 cm.

composition of filter-embedded aerosols. This analytical technique is well established (e.g., Camp et al., 1982; Haupt et al., 1996). Since XRF-S provides a non-destructive analysis (Jenkins, 1988), samples can be returned to the laboratory for the confirmation of the remotely derived XRF-S measurements and for additional measurements that cannot be made by XRF-S (e.g., Al, Na, trace metals).

To sample aerosols, the air inlet valve is opened and air is drawn into the 360° sandwich-shaped inlet. The air is then pulled vertically down a Ti pipe and through a filter holder, which is sealed against the bottom of the inlet pipe. When aerosols are not being sampled, the seal plate is moved down to seal the inlet pipe. The inlet closes when there is rain and/or when sea spray is produced by high winds. By linking the instrument to the meteorological sensors, the collection of aerosols can be programmed to occur only under pre-set conditions of wind direction, wind speed, humidity and temperature, and other environmental conditions.

Three motor assemblies drive the system. Motor M1 rotates a carousel carrying the sampler holders. Motor M2 moves a sample holder vertically to place the filter inline with the air inlet, pump and flow meters. Motor M3 moves a holder vertically to place the filter (or standard) against the window of the XRF-S. In practice, sample holders, containing 25 mm filters, are loaded into the carousel. One sample holder is then moved under and pushed tightly against the air inlet. Air is pulled through the filter for a set period of time, and the volume of air filtered is continually monitored by two mass flow meters. The aerosol-containing filter is then moved under and pushed up against the XRF-S for elemental analysis ($\approx$ 5–10 min). The elemental analysis results of filter blanks are obtained by performing an XRF-S measurement of each filter prior to collecting an aerosol sample.

The ability to make multiple measurements with the same filter extends the time-series capabilities in the following manner. Aerosols are collected for a set period of time, one day for example, and the filter is analyzed. If the Fe concentration is below a pre-determined level, then this filter is returned to the inlet position for another day of aerosol collection. This iterative process

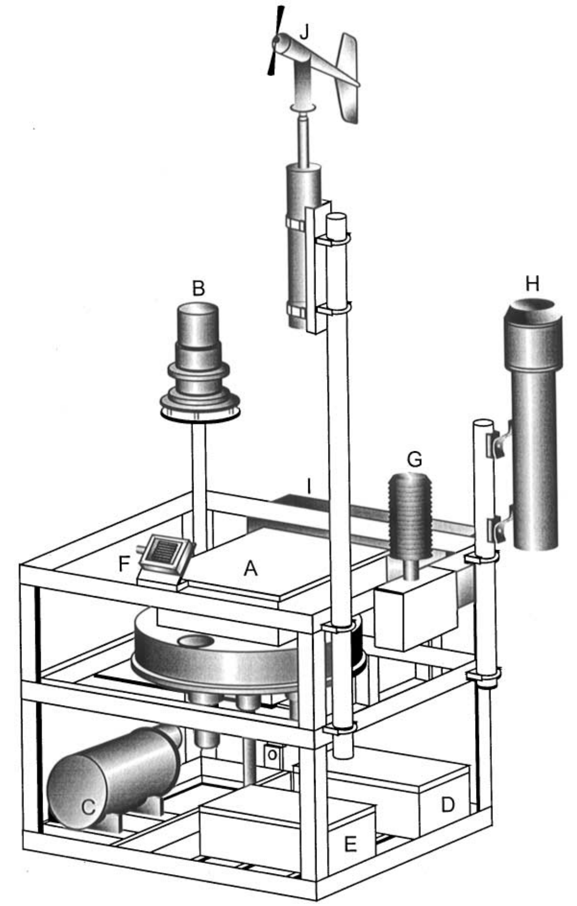

Fig. 3. Schematic drawing of the whole instrument mounted on an Al frame. The frame is 122 cm high and 84 cm × 92 cm on a side. The inlet is 50 cm above the top of the frame. (A) X-ray fluorescence analyzer sitting on top of the round sample-holder carousel, (B) air inlet with motorized valve, (C) pump, two flow meters and a local microprocessor, (D) voltage regulator, (E) main microprocessor, (F) rain detector, (G) relative humidity and temperature sensors, (H) rain gauge, (I) PC for X-ray fluorescence spectrometer and J. Anemometer. In an actual deployment, the meteorological sensors would be placed far from the aerosol instrument. The latter would also have a flat and heavy duty plastic sheet bolted to the top of the frame so that the inlet rises above a smooth surface.

of collection/analysis is repeated until the Fe (or any other elemental) concentration reaches a pre-determined level. A new filter then goes into use.

The development of intelligent software is a critical part of this project. We are currently able to use a direct internet connection to set the sampling parameters, collect samples, run standards and analyze samples. We can also follow the progress of the time-series collection and change sampling conditions. XRF-S spectra are stored on board the instrument for retrieval and analysis. Future plans call for developing two-way RF modem and satellite communication systems to remotely control the operating parameters of the instrument and to relay a subset of the XRF-S data back to the laboratory.

3. Major components

As shown in Figs. 1–3, the instrument consists of the following components: an air inlet, the sample handler and filter holders, the XRF spectrometer, the pump/flow meter unit, the meteorological sensor unit, a main microprocessor, the PC for operating the XRF-S, the power conversion/switching interface and a battery/regulator/relay system. Only the first three components will be discussed in detail here.

The air inlet has two components – an external unit and an internal unit. The external unit was modeled after the University of Minnesota's aerosol inlet (Liu and Pui, 1981). Their inlet has a dichotomous sampler and was designed for a flow rate of $1\,\mathrm{m^3\,h^{-1}}$ or $16.7\,\mathrm{l\,min^{-1}}$. Our external inlet does not have a dichotomous sampler, but it does retain the circular disk for 360° sampling. We added a mechanical valve that allows the inlet to be sealed from the atmosphere, thereby protecting the instrument and samples from rainwater, seawater and sea spray. This modification means that our inlet will not follow the performance of the original Liu and Pui inlet. The fact that our inlet will be on a 3D moving platform under variable wind speeds makes predicting its performance difficult. We have opted for a design that is simple, rugged and allows for a watertight seal. The pore size of filters determines the particle size cutoff of the aerosol collected. Our design allows for the possibility of adding different types of inlets (e.g., PM-10, PM-2.5 cutoffs) while keeping the sampling and sensing capabilities of the instrument intact. Plastics and Ti are used throughout in order to minimize contamination. The inlet pipe, the seal plate and circular inlet are made of Ti.

The main features of the sample handler are a carousel, three motor assemblies and a manifold that connects the filter holders to the aerosol inlet. The carousel is a circular 61 cm (24 in) diameter acetyl plate which contains 24 holes for the filter holders. Motor # M1 rotates the carousel and positions the filter holders at the air inlet, the XRF-S or the sample access port. An encoder provides feedback on the exact positions for each of the 24 holders.

The filter holder consists of a Ti cover, which slips over a PVC base. An internal o-ring creates an airtight seal between the cover and the base, and an external o-ring on the top of the Ti cover seals the filter holder against the inlet and the XRF-S window. The Ti cover has a 20 mm diameter opening and a filter area of $3.1\,\mathrm{cm}^2$. The 2.5 mm rim holds and seals a 25 mm filter between the cover and base. The area of the 20 mm collecting diameter exceeds the area (11×7 mm ellipse) of the filter that receives the primary X-ray beams. Each filter holder is held in place by a spring which also insures that the holders drop back onto the carousel after motors M2 and M3 are retracted.

Jordan Valley (JV) Applied Radiation, Inc. modified their model EX-310 XRF spectrometer by building a downward-looking X-ray tube and detector. Tight machining tolerances were necessary in order to push the filter holders up against the X-ray window. Model EX-310 can be run off batteries and contains a 12 kV rhodium X-ray tube and a Peltier-cooled energy dispersive detector. The remaining components of the EX-310 XRF-S were not modified but were reassembled to fit into a compartment that lies on top of the carousel (Fig. 2). The X-ray unit and carousel are covered with an o-ring sealed watertight cover. Electrical cables are fed through the side cover via watertight connectors. The X-ray tube is well shielded from radiation leaks.

4. Discussion

The instrument has undergone four months (May–August 2000) of testing on a roof in Woods Hole where it has been exposed to high winds and large rain storms. All aspects of the hardware and software worked as designed. That is, the instrument provided a time series of aerosol samples and XRF spectra. While this location receives little in the way of mineral dust, the spring bloom of local plants and trees in May provided a strong aerosol signal in the form of pollen. Summer haze, carrying grey aerosols from the combustion of hydrocarbons, elevates the sulfur content in July and August.

We opted to use Isopore membrane filters from Millipore Corp. Compared to most other types of filters these thin polycarbonate filters yield the lowest background scatter in their spectra (Fig. 4). The rate of filtration varied with the pore size of filters used and the loading on the filter. With no filter in place, the pump pulls about 16 l min^{-1} air through the instrument. A 3.0 μm pore-size Isopore filter (our choice for testing) yielded about 14–15 l min^{-1} at the start of sampling. In one case, large amounts of pollen in the air resulted in the flow rate dropping to 3 l min^{-1} after 3 days of pumping. In practice, the pump is hard pressed to handle the resistance to flow from filters with pore sizes below 0.4 μm. The resulting low flow rates yield small sample sizes per unit time and power.

The main consumer of energy is the air pump. Available power is the limiting factor with respect to the sampling endurance on a buoy that has battery and solar power. The volume of air filtered to power consumed is a fairly uniform ratio for diaphragm pumps with varying flow capacities.

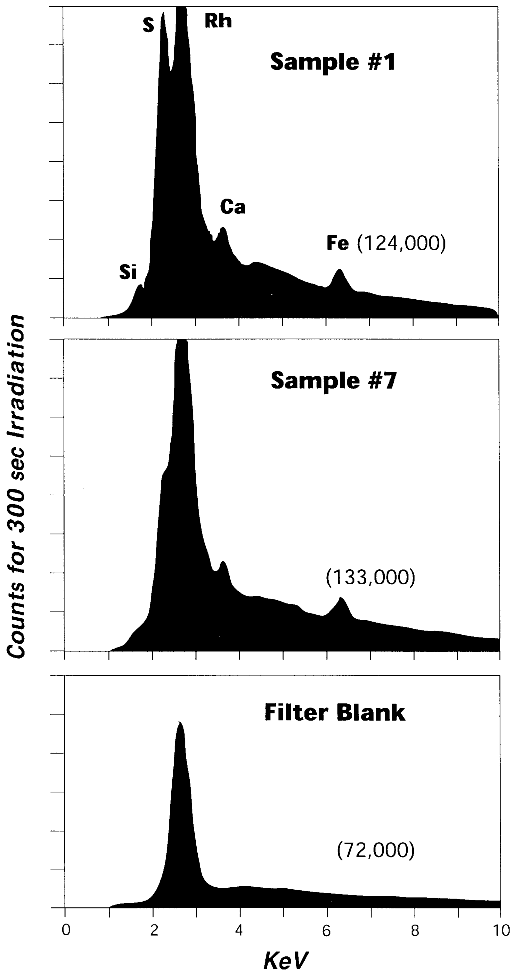

Fig. 4. 600 s X-ray fluorescence spectra of filter blanks and two aerosol samples (#1 and #7) collected at Woods Hole MA, USA at the beginning and end of May 2000. Each sample represents 3 days of air filtering at approximately 15 l m^{-1} for a total volume of approximately 66 m^3. Rh X-ray tube was run at 700 μA and 12 kV. Total counts integrated over the Fe peak are given. "Isopore" polycarbonate (Millipore Corp.) filters with a nominal 3.0 μm pore size were used.

Commercially available thin-film standards (Micromatter Co.) were used to quantify the performance of the XRF-S. Fe, S and Si standards of 16, 6.8 and 15 μg cm^{-2}, respectively, yield approximately 290,000, 203,000 and 93,000 net counts for a 300 s irradiation time. Net counts for each element are determined by subtracting the integrated area under the peak of a filter blank from that of a sample. As illustrated in Fig. 4, spectra of Woods Hole aerosol samples, resulting from 72 h of filtering and 300 s irradiation, have peaks in Si, S, Ca and Fe. The K signal (Kα line at 3.31 keV) was too low to be detected. Note that the filter blank only contains the Rh tube line (Lα1 at 2.70 keV). Sample #1 has a well-developed peak in S (Kα line at 2.31 keV) which can be resolved from Rh. In contrast, S in sample #7 is lower in concentration and only forms a shoulder on the side of the Rh signal. The Fe Kα line at 6.40 keV lies in the low background/high-energy end of the spectra. For spectra with overlapping peaks in the low-energy range, the JV software allows one to mathematically separate the Si, S and Rh counts. The Woods Hole samples have a small but measurable Si signal (Kα line at 1.74 keV). We have measured strong and well-resolved peaks of Si and K with samples containing moderately more mineral dust (see web site in Section 2).

XRF spectra of the iron standard were taken eight times over the course of the four-month roof test. The precision on the Fe count rate was 3.3%.

The sampling resolution of our instrument will depend on the combination of the ambient concentration of aerosols and the detection limits of the XRF-S. Here, we compare the sensitivity of the XRF-S measurement with the aerosol concentrations at Barbados (Husar et al., 1997; Prospero, 1999). Sample #1, representing three days of filtering Woods Hole air, will be used as a gauge (Fig. 4). This sample contains an iron concentration of approximately 0.4 μg Fe m^{-3} or 8 μg mineral dust m^{-3}, assuming a 5% crustal content for iron; its sulfur concentration is approximately 1 μg S m^{-3}. The Barbados monthly means of dust concentration range from 2 to 22 μg m^{-3}. The majority of summer time and winter time values lie between 10–60 and 0.03–2 μg m^{-3}, respectively. African dust, transported across the Atlantic Ocean, lead to summer time pulses as high as 121 μg m^{-3}. Hence, the XRF-S in our instrument has sufficient sensitivity to measure the summer time Fe concentration of aerosols at Barbados with a resolution of a few days. During winter, 10–20 days of air filtering would be required to provide a quantifiable Fe XRF signal at the lower ambient concentrations. The same conclusions apply to the measurement of Si.

The non-sea-salt sulfur content of Barbados aerosols has a narrow range of monthly means (0.1–0.4 μg NSS-S m^{-3}). Summer time values can reach as high as 6 μg S m^{-3}. Again, the XRF-S in our instrument has the sensitivity to measure total S at Barbados throughout the year with a resolution of a few days.

Since our XRF-S operates in air, the X-ray energies of Na and Al are too low to be measured. Na concentrations must be measured in the laboratory before our data can be used to determine the concentration of non-sea-salt sulfur.

5. Summary

We have designed, built and tested an autonomous aerosol sampler/sensor that employs X-ray fluorescence spectrometry to determine the Fe, Si, S, Ca and K concentrations of aerosols. This instrument has the sensitivity to measure these concentrations over the ocean with a time resolution of a few days during periods of moderate to high dust deposition. A four-month roof test has successfully demonstrated that all aspects of the collection and analyses worked as designed. A sea test on a buoy is anticipated for 2001.

While this instrument was built for ocean buoys, its features – autonomous and remote operation, robust and weatherproof construction, time-series sampling, real-time elemental analysis, internet control – make it suitable for use on land, especially in remote or hostile environments. This instrument can also be used as an aerosol sampler only.

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