

Sample Handling and Determination of Physico-Chemical Parameters in Rime, Hoarfrost, Dew, Fog and Cloud Water Samples - a Review

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Abstract

Our paper discusses many types of samplers used for collecting samples from precipitation and atmospheric deposits (fog and cloud water, dew, hoarfrost and rime). Equipment of various degrees of automation is presented. The paper also presents bibliographical information on the concentration range of inorganic and organic compounds in precipitation and atmospheric deposit samples, the storage and/or preparation of samples for analysis, and the techniques of final determination.

Keywords: fog and cloud water, dew, hoarfrost, rime, atmospheric precipitation, sample collection.

Introduction

The tremendous dynamics of the atmosphere make it the main propagation path for air pollution and its transport between the various elements of the environment in the form of dust, gases and aerosols. This pollution, depending on its properties and the meteorological conditions, is subject to scattering and transformation during transportation in the atmosphere. Moreover, most of the pollutants return to the earth's surface, often at great distances from the sources of their emission, together with precipitation or through absorption of gaseous pollutants and aerosols by surface waters, the vegetation cover or the soil. Wet deposition plays the most important role in feeding the pollutants from the atmosphere back to the earth's surface in regions distant from the sources of emissions. Atmospheric precipitation is the product of condensation of water vapour contained in the atmosphere. Rain, snow, drizzle, snow pellets and hail fall due to gravity. Clouds and fog are precipitation floating

in the air. Dew and hoarfrost are droplets that condense or freeze directly on the surface while rime is an impacted droplet. Characteristics of precipitation are presented in Fig. 1 [1].

Undoubtedly, the first stage of actions aimed at environmental protection is the identification and definition of the kind and degree of pollution. In the case of chemical contamination, this is certainly the field of analytics and monitoring. During the last 20 years the analytics of atmospheric deposition has been developing very intensively. An extensive review paper containing a description of the design and basic parameters of samplers for rain precipitation and runoff waters appeared in 2002 [2]. Since 1990 there has also been growing interest in the sampling of atmospheric deposits and fog. Because of the quantity and quality of transported substances, as well as the range of their interactions, they can be a good indicator of the degree of atmospheric pollution in a given geographical region.

The basic condition, which a sample has to meet to become a source of reliable analytical information, is its representative character for the object tested with regard

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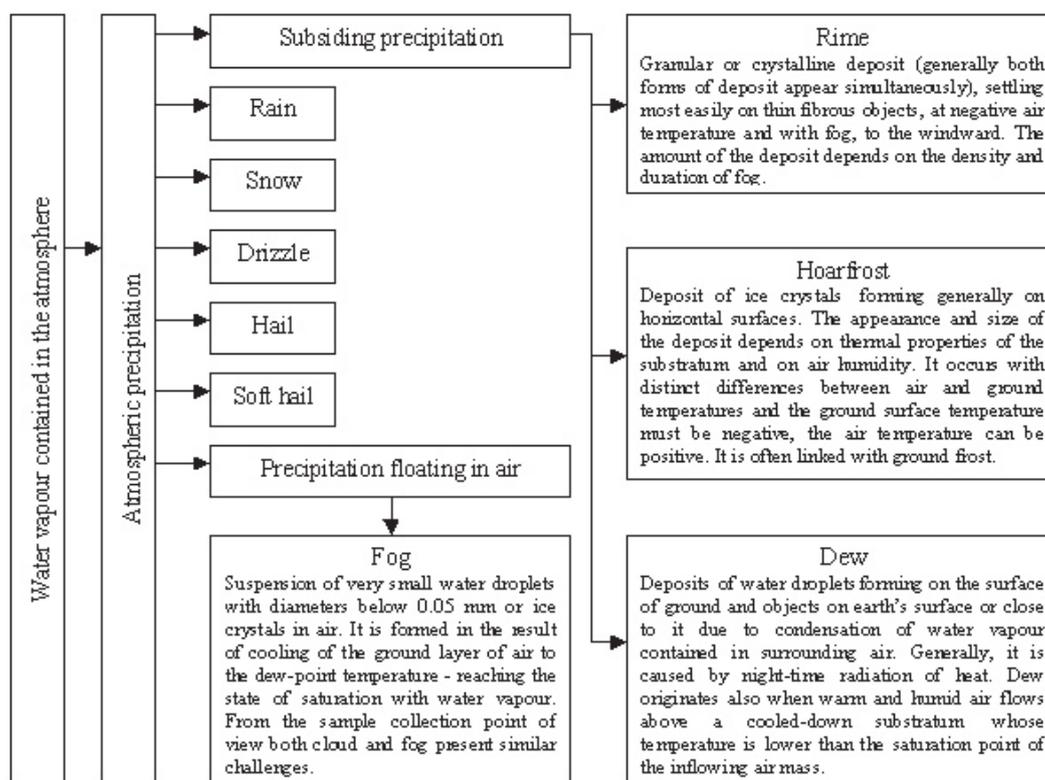


Fig. 1. Types of atmospheric precipitation and deposits.

to the problem under consideration. Information about the sample has to be an exact mathematical reflection of information about the tested object. This requirement is fulfilled completely only if all of the available material is analyzed. Since in practice usually only a sample which is a small fragment of the tested object is analyzed, this main requirement must be fulfilled as closely as possible [3]. Sampling has a special significance for the analytical process; in a sense, it is the critical point of analysis. Errors committed at this stage cannot be estimated, nor can their effect upon the result of the analysis be reduced. The proper preparation of the sampler is a very important factor in the sampling process. It consists mainly of the cleaning of the sampler before handling a sample. The cleaning procedure includes, among other things, washing in deionized water [4-6] and/or *e.g.* rinsing with acetone [7]. The collecting vessels are also washed in water with detergents [8], in aqueous solution of nitric acid [8], distilled water and eventually rinsed with deionized water [9, 10].

A necessary condition for carrying out analytical tests of atmospheric precipitation and deposits is the usage of appropriate equipment for handling and collecting samples in accordance with the principles of good laboratory practice. A study of available literature spurred the impulse to prepare a paper on the subject. This paper presents a review of the designs of samplers used for collecting liquid samples: fog cloud water, and dew, as well as hoarfrost and rime.

Fog and Cloud Water Collectors

The transport of anthropogenic pollutants through the atmosphere is an important means of their worldwide distribution. These airborne contaminants can be transferred to the aquatic and land environments via such mechanisms as wet and dry deposition and air/water partitioning. Fog has recently attracted the attention of the scientific community as a potentially important deposition mechanism. This liquid water in the atmosphere undergoes chemical exchange with the air. Organic and inorganic chemicals distribute themselves between the vapor and aqueous phases and between the particles present in both phases. There is also the possibility of chemical reactions occurring within a fog droplet. As the weather conditions change and the fog droplet evaporates, the chemicals contained in the droplet will remain on the surface with which the fog came into contact [11].

Over the last 20 years many investigators have examined the chemical compositions of cloud and fog and studied the processes occurring in atmospheric particles and the means of sample collection. Collecting samples of fog and cloud water is undoubtedly more complicated than collecting samples of precipitation or runoff water [2], while the designs of samplers are characterized by various degrees of automation. Usually, the instruments in question were originally meteorological instruments, serving for quantitative measurements of a given type of deposition. A fog and cloud water sampler to be used must meet a number of re-

quirements: efficiency in collecting fog and cloud droplets while avoiding the collection of submicron “nonactivated” aerosol, preservation of the size and chemical composition of droplets through all the stages of collection, and rapid collection of large amounts of liquid water for wet chemical analysis. The collector must be easy to use and automate, and should also require minimal maintenance. The cloud and fog water collectors operate primarily on the principle of inertial impaction on a plane surface, a standard technique for the collection of dry aerosol particles. It has been found that instruments based on this principle provided the most reliable results. This is indicated by the collection efficiency curves, which show the percentage of particles of any size which are collected as a function of particle size. For impactors, this efficiency curve shows a sharp division between the droplets collected and those which are not (cutoff). Marple and Willeke [12] formulated design criteria for the construction of inertial impactors. By applying these criteria to the construction of an impactor, the described cutoff characteristics can be achieved.

The technique had to be adapted, however, to the special needs of liquid water sampling. Single stage cloud water impactors, based on this principle, have been used for several years to perform studies of cloud and fog water chemical composition. They are used both as active, where flow of air containing the droplets is forced by means of a suitable mechanical device, and passive, where natural circulation of air (wind) is utilized. The latter are usually more simple in operation and may be used in windy environments, while the impaction characteristics (cutoff) is less controllable. Also, the collecting elements (impaction plane) may vary from flat surface to solid elements like rods, tubes as well as strings, ropes, filaments, screens and meshes.

Active collectors use either forced flow (fans, pumps) or motors moving the collecting elements in the air (usually rotating them) to achieve the same end. There is a wide variety of passive and active collectors available for varying ambient conditions. Typically, both passive and active samplers utilize flow past collecting strands or rods. Additionally, some active collectors use jet-driven impaction onto solid surfaces. Size-resolved cloud composition is usually obtained via active collectors with multiple jet/impaction surface combinations, or stages with varying cutoff diameters.

The simplest fog sampler is the deposition plate, typically a horizontal plate on which fog droplets are allowed to settle [13]. This sampler may suffer from contamination due to dry deposition and dew formation, which leads to significant biases toward errors with large particle measurements. The design is attractive for its simplicity and probably this was the reason it was tested relatively late in the history of passive sampler development but the aforementioned disadvantages restrict its applications.

The next simplest samplers, where fog is collected through the impaction of droplets on a string screen, are string screen collectors. The fog droplets collide with and drop along the strings [14]. String screen samples can also

be in active and passive versions. The active fog sampler described by Jacob [15] consists of three parts: a series of three screens of Teflon wires where the fog condenses, a baffle which smoothes the air flow, and a fan which pulls the air past the Teflon wires. The fog water is collected on the wires until drops are formed, then they move down the wire, pool in a Teflon tray, and are collected in a clean glass jar or plastic sample bottle. The fog water comes into contact only with Teflon and glass during the sampling period. During sample collection the face velocity of the air through the sampler, the time of collection, and the air temperature were monitored. Typical sample collection volumes ranged from 50 to 200 ml, which took 50–180 min depending on the liquid water content of the fog event [11, 16]. Droplets in the range 3–100 μm diameter are efficiently collected.

Fig. 2 presents a schematic diagram of an active screen collector. The Teflon screen consists of four 4 mm thick copper rods, between which Teflon strings are strung [17]. Drops collected on the strings find their way to polyethylene collecting bottles. String screen collectors are also described in [18, 19].

The High-Volume Fog Sampler [20, 21] is a scaled-up version of the sampler described by Jacob [15], where a 50 cm diameter fan in the back draws air at the rate of 4400 m^3/h across a screen consisting of four layers of 0.28 mm Teflon filaments wound around threaded rods. Fog droplets impact on the Teflon filaments, coalesce, and flow down the filaments into a Teflon-coated funnel. The fogwater then drains by gravity through a Teflon tube to a Teflon bottle. The collection rate is approximately 1 l/h in fog with 400 m visibility.

Active string Cloud Water Collector CWP described by Daube [22], collects cloud droplets on a removable cartridge of 0.78 mm diameter Teflon strands. A fan inside the collector draws air and cloud droplets up through a ventral opening and then into the vertical collection strands. The collector excludes most rain droplets ≥ 200

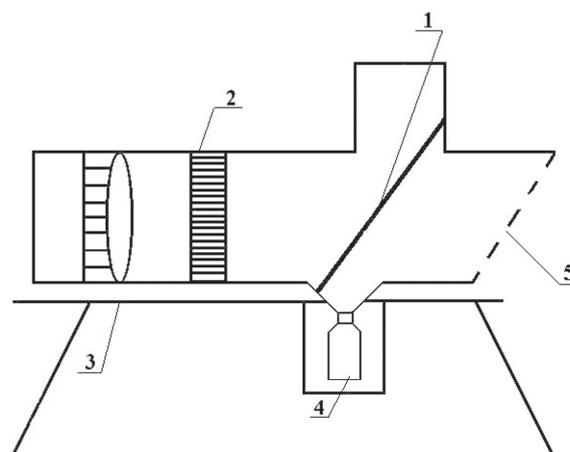


Fig. 2. Structure of an active fog water collector [17]: 1 – string screen, 2 – flow straightener, 3 – blower, 4 – polyethylene collection bottle, 5 – inlet.

μm at wind speeds ≤ 10 m/s. Cloud water collection was usually initiated within 15 to 30 min after the onset of cloud event, and the standard collection time was approximately 5 hours. The positioning of the air inlet on the bottom of the sampler makes it possible to avoid collecting rain [23-25].

The CalTech Active Strand Cloud Water Collector (CASCC) built at the California Institute of Technology (Fig. 3a), has been described in detail in publications [5, 26-30]. Cloud droplets are collected by inertial impaction on an angled bank of six rows of 508 μm diameter Teflon strands. A fan sucks in air through Teflon strings with the velocity of 8.5 m/s. The strands are inclined at an angle of 35 degrees from vertical. The collected droplets coalesce, and are drawn down the strands by gravity and aerodynamic drag into a Teflon trough. A Teflon tube delivers the sample from the trough to a collection bottle, which was emptied at 30-60 min intervals. The 50% collection efficiency size-cut, based on droplet diameter and predicted from impaction theory is 3.5 μm . A protective rain shield, which had its opening facing downward, was attached to the front of the collector to exclude large sedimenting droplets ($d > 300 \mu\text{m}$). The flow rate of air through the CASCC is 24.5 m^3/min , yielding a collection rate of approximately 2 ml/min when the liquid water content of the fog is 0.1 g/m^3 .

The CASCC is not functional when ambient temperatures fall below 0°C , since cloudwater droplets freeze on the collection surface. For this reason, a winter cloudwater sampler – the Caltech Heated Rod Cloudwater Col-

lector (CHRCC) was developed [31]. Stainless steel rods form the collection surface in this sampler and are internally heated on a periodic basis when temperatures fall below 4.5°C (Fig. 3b). When heated, accumulated frozen cloudwater on the rods melts and drains off the rods to the sample bottle. The fan draws air across an inclined bank of six rows of the 3175 μm diameter rods at a rate of 6.3 m^3/min . The corresponding cut-point of the rod bank is calculated to be 7.7 μm . The predicted collection rate in a cloud with a LWC of 0.1 g/m^3 is 0.44 g/min .

The active sampler described in [7] is a rotating screen device, 50 cm in diameter, in which four layers of stainless steel screen are rotated around a central axis at 720 rpm. Fogwater obtained from droplets impacting on the screen is centrifuged to the periphery, collected in a slotted aluminum tube, and drained into a collection vessel. A large fan pulls air through the device at a sampling rate of 160 m^3/min . This sampling rate typically allows 1 l of fogwater to be collected in 1-2 h, depending on the liquid water content of fog water. The CalTech, ASRC (Atmospheric Science Research Center) and AV (AeroVironment) instruments are rotating collectors, employing external surfaces for impaction of the droplets.

A device built at CalTech Rotating Arm Collector (RAC) is an external impactor that sweeps through the air at a high velocity (1700 rpm) in order to collect large particles [31, 32]. The arm (63 cm long) spins in a vertical plane, driven by a motor. Each end of the arm has a slot milled into its leading edge. Bottles (30 ml) are mounted at the ends of the arm to collect the water that impacts in the slots. Threaded Teflon tubes are screwed on the ends of the arm and extend inside the collection bottles, preventing the collected fogwater samples from running out after the instrument is stopped. Deflectors prevent water that impacts on the solid part of the arm from entering the slot. Small fins are welded to the back of the arm for extra strength. The entire arm is Teflon-coated to prevent chemical contamination and to facilitate cleaning. The rotating arm collector samples air at a rate of 5 m^3/min . Laboratory calibration has indicated a lower size cut of 20 μm diameter (50% collection efficiency). The sampler has been used, among others, in papers [30, 33-35].

The sampler built at Atmospheric Science Research Center (ASRC) consists of 150 0.41 mm diameter Nylon strings mounted between two plates. The sampler rotates about its vertical axis at 100 rpm [36]. Water impacting on the strings collects in traps on the bottom plate. Periodically, the sample rotation is stopped, and fogwater on the strings is coaxied into the traps by tapping the bottom plate with a mallet. At the end of the sampling period, water in the trap is manually transferred to polyethylene bottles. Two versions of the device exist, one of them passive, the other active.

The AeroVironment Rotating Rod Sampler (AV) collects droplets by impaction on a Teflon-coated rod rotated in a vertical plane at 3450 rpm. The outer part of the rod is 1.6 mm and the inner part is 19 mm in diameter to provide size cuts of 2.5 and 10 μm , respectively [36]. Water

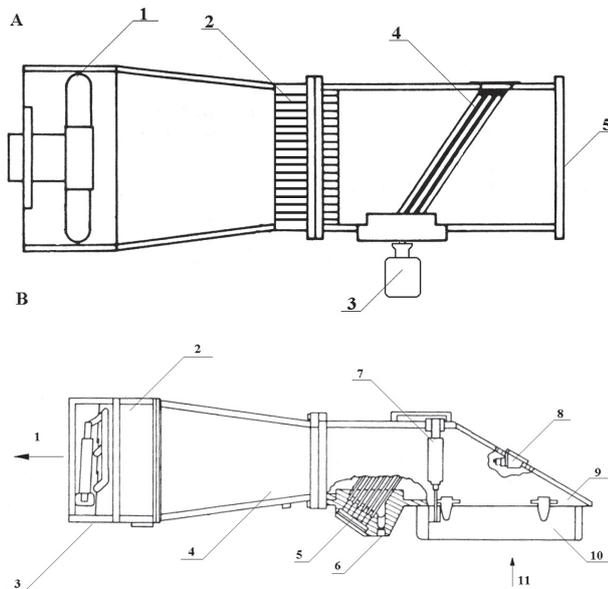


Fig. 3. Schematic diagram showing the construction of A: CASCC collector [30] (1 – fan, 2 – flow straightener, 3 – collection bottle, 4 – string screen, 5 – inlet); B: CHRCC collector [31] (1, 11 – air flow, 2 – fan, 3 – rear cover, 4 – diffuser, 5 – collection rods, 6 – drainage, 7 – pneumatic cylinder, 8 – rinse nozzle, 9 – inlet, 10 – inlet cover).

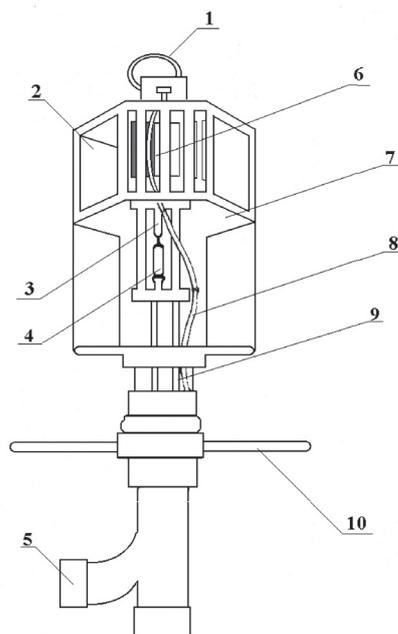


Fig. 4. A schematic diagram of DRI sampler [36]: 1 – deionized water system, 2 – inlet, 3 – central rod, 4 – to the collection bottle, 5 – PVC pipe for protection, 6 – impaction rod, 7 – outlet, 8 – deionized water tube, 9 – rotating rods, 10 – support rods.

impacting on the rods is transferred by centrifugal force to circular polyethylene troughs that drain to polyethylene collection bottles. Separate troughs and sample bottles are used for the two size fractions.

The Global Geochemistry Mesh Impaction Fog Sampler and DRI (Desert Research Institute) instruments are internal collectors, in which air is drawn into the instrument and extracted by surfaces internal to the device. The Global Geochemistry Mesh Impaction Fog Sampler is an internal impaction sampler that collects fogwater on a 10 cm diameter by 4 cm thick polypropylene mesh located at the entrance of a V-shaped Teflon-lined PVC pipe [35]. The mesh is made of interlaced filaments (410 μm diameter) and has a void volume of 96%. Air is drawn through the mesh at 1.7 m^3/min . Fog droplets impact on the mesh, coalesce, and then drain into a polyethylene bottle at the bottom of the V-tube. The sampler can effectively intercept droplets $>5.0 \mu\text{m}$, with a 50% collection efficiency at 2.4 μm . Liquid holdup on the mesh depends on the mass of liquid sampled. If $\leq 1 \text{ g}$ of water is sampled, all of it remains on the mesh. If 100 g is sampled, less than 5% remains [36].

The DRI (Fig. 4) is based on a jet impaction principle. Fog is drawn through three rectangular jets at a total flow rate of 20 l/s. The accelerated droplets impact on rotating Teflon rollers and are transferred to a central roller. Here, the fogwater is forced to accumulate in bulk form and is deposited into a polystyrene collection vessel. The impactor has a sharp cut-off at 5 μm diameter to allow efficient collection of droplets while rejecting small interstitial particles. The collector is housed in a shelter consisting of

an inverted, insulated 250 l drum to prevent collection of precipitation. Airflow up to the collector is provided by a fan [36-39].

Fig. 5 provides an example of a passive collector [38]. It consists of a Teflon support structure and 0.3 mm diameter Teflon strings, mounted 3.0 mm apart in a cylindrical configuration. Under appropriate airflow conditions, fog droplets are impacted on these strings, grow to larger drops, run down the strings and are collected into bottles. All droplets $>5.0 \mu\text{m}$ diameter are impacted, at normal wind speeds. In order to collect 15-25 ml it is necessary to collect samples for two hours. This collector is set out only in case of the occurrence of fog. In other situations it is enclosed inside a metal cylinder in order to prevent its contamination (rain and dry deposition). The sampler is activated and closed by a fog sensor based on the dew-point and a separate rain sensor. Modified dynamic versions of the passive sampler are the CalTech Active Strand Cloud Water Collector and a ground-based active collector [38].

A published paper [40] describes a passive collector (Fig. 6), consisting of a 2-m tall collection, of two horizontal disks 20 cm in diameter, installed vertically on frames at a distance of 40 cm from each other. Between the disks, Nylon strings of 0.2 mm dia. are stretched in two rows. The fog water collected on the strings is stored in a 500 ml polyethylene bottle. The collection area was 314 cm^2 . A hood above the collector prevents rain from diluting the fog sample. The sampler was set up in a 1m high PVC tube to protect it from direct radiation and light.

The principle of work of the collector described in [22] (Appalachian Mountain Club/Worcester Polytechnic Institute AMC/WPI) is based on the utilization of wind to transfer particles to Teflon collecting strands. The cloud water droplets are collected principally by the mechanism of inertial impaction on Teflon strings. Exclusion of the heavier rain droplets is accomplished by both the placement of the collection strands deep within the collection box and by a baffle system (Fig. 7). The air flowing through the baffles is restricted and forced to turn, causing it to accelerate. The rain droplets, with their greater inertia, overcome the viscous drag effects of the airstream and

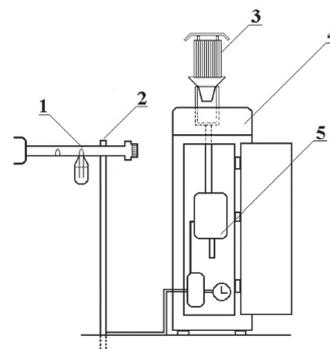


Fig. 5. Structure of a passive fog water system [38]: 1 – fog sensor, 2 – rain sensor, 3 – collector, 4 – shield, 5 – motor.

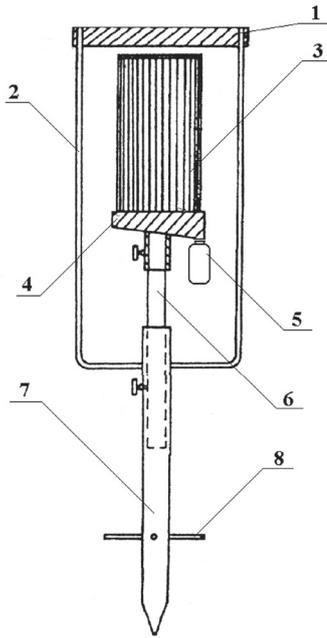


Fig. 6. Structure of a passive fog water collector [40]: 1 – hood, 2 – support, 3 – separator, 4 – funnel, 5 – collector bottle, 6 – support tube, 7 – stand, 8 – steel stabilizer.

pass out of it, impacting on the lower baffle. A drain below the baffle permits the separated rain water to leave the collector. The cartridge containing the collection strands is located behind the baffle to allow adequate expansion of the air flow and thus to maximize the utilization of the collection surface area. The distance back from the top of the entrance of the collection box to the upper lip of the lower baffle was selected for its theoretical ability to remove free-falling droplets >200 μm at winds of 0-10 m/s and droplets >500 μm at winds of 0-25 m/s. These values represent the minimum ability of the collector to exclude rain and drizzle. To prevent contamination of the cloud water sample by rain, baffles have lips to prevent the impacted rain water from running to the edge of the baffle and from becoming re-entrained in the accelerated air-

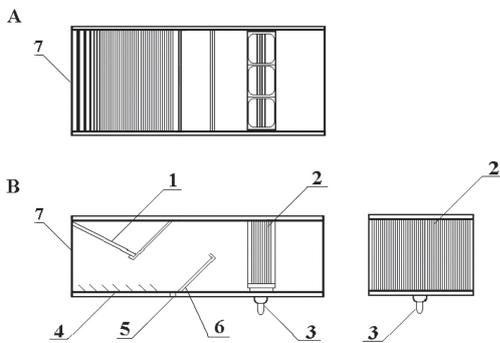


Fig. 7. Structure of a passive, cloud water collector AMC/WPI [22]: A – top view, B – side view, 1 – front baffle, 2 – collection cartridge, 3 – collection hose to bottle, 4 – splatter shield, 5 – drainage, 6 – rear baffle, 7 – inlet.

flow. The upper baffle has a small reservoir where water collects prior to draining out holes drilled on the side of the collector. To prevent rain splatter on the lower surface of the collector from re-entering the airstream, a series of vanes set at 40 degrees are positioned in front of the lower baffle. Rain water collected by these vanes leaves the collector at the base of the lower baffle.

In order to collect cloud water samples, another collector has also been used, consisting of 0.45 mm diameter Teflon coated wires, strung at 3 mm intervals around the perimeters of two 25 cm diameter plastic disks, held 1 m apart by plastic rods [41]. The surface area of the collector is sufficient to provide a sample of 50 ml in 3-30 min, depending on the wind speed and cloud liquid water content. The collection efficiency of this sampler indicates that cloud droplets of 10 μm diameter are collected with only 50% efficiency at wind speeds of 1 m/s, proving poor performance of the collector at low wind speeds. For 80% of the cloudwater samples, the wind speed was greater than 5 m/s, yielding 50% collection diameters below 5 μm.

The operation of the Two-Stage Fog Water Impactor (TFI) is also based on the principle of inertial impaction on a plane surface. This sampler (Fig. 8) consists of vertical slit impaction stages: one to collect the larger droplets, followed by two identical stages in parallel [42]. These collect those droplets which passed the first stage, but which are above a well-defined cutoff diameter. The cutoff diameters of the first stage are between 10 and 12 μm, and of the second stages are between 5 and 6 μm, calculated for flow rates from 150 to 200 m³/h. The air,

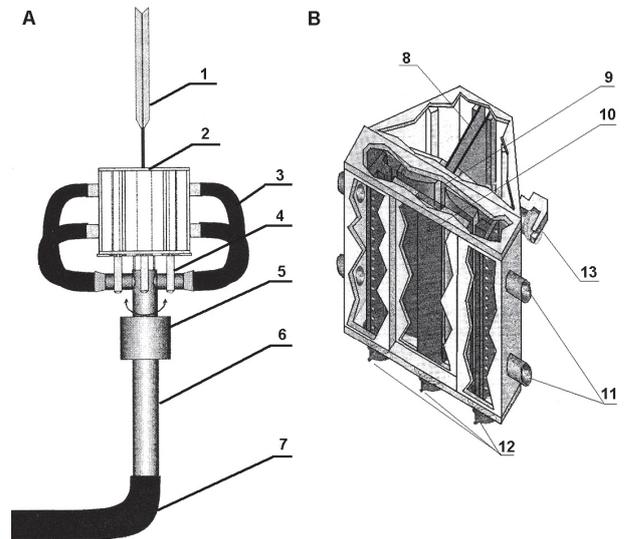


Fig. 8. Schematic diagram showing A: instrument set-up for size resolved cloud droplet measurements with TFI, B: the construction of a two-stage impactor [42]: 1 – wind vane, 2 – TFI, 3 – flexible tubing, 4 – sample vials, 5 – ball-bearing (gas proof), 6 – steel duct (fixed), 7 – tube to flow measuring unit and pump, B: 8 – inlet, 9 – nozzles, 10 – collection surface, 11 – connection to flexible pipes, 12 – connection to collection vials, 13 – inlet width regulator.

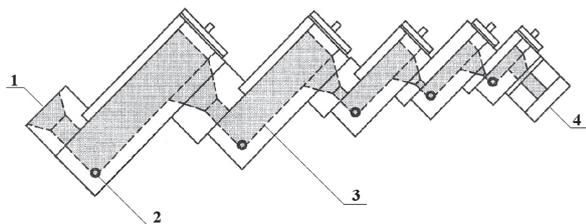


Fig. 9. Schematic diagram showing the construction of CSU 5 – Stage collector [43]: 1 – inlet, 2 – sample collection port, 3 – impaction surfaces, 4 – connection to pump.

together with smaller water droplets, leaves the impactor through holes in the plate and 4 suction pipes. The collecting of samples is forced by air flow to the external edges and to streams directed down the plates. Then the samples arrive into vials situated at the bottom of the device. The apparatus has the possibility of controlling the velocity of incoming air depending on the average wind speed.

Cloud chemistry can vary as a function of drop size. In order to investigate variations in chemical composition across the drop size spectrum, a new multi-stage cloud water collector was developed. The CSU 5-Stage collector (Fig. 9) is a cascade inertial impactor developed to obtain samples of cloud water in five independent size fractions for chemical analysis. Its design incorporates many features to facilitate its use in the field, and maintain both consistent performance between varying atmospheric conditions and the chemical and physical integrity of the collected sample. The sampler consists of five stages, each with a single, one-sided rectangular jet arranged in a cascade. The intensity of air flow rises as it passes through the sampler. Drops of progressively smaller diameters are collected in each stage as those with too much inertia cannot follow the fluid streamlines and impact. The collector is mounted at 45 degrees to the horizontal so sampled drops coalesce and run down to polypropylene vials threaded directly into each stage. The collector is oriented into the wind during operation, subject only to site restrictions and its own geometry. While the collector is designed for low wind environments, a baffle or windshield parallel to the inlet is added for higher winds. The experimentally determined 50% cut diameter for the first stage was 25.5 μm , while the second stage had a slightly higher 50% cut diameter of 29 μm [44]. Stages three, four, and five had 50% cut diameters of 17.5, 10.5, and 4.5 μm , respectively. Although some mixing between drop sizes occurs, the CSU 5-Stage effectively separates the largest drops (>30 μm in diameter) from the smallest ones (<10 μm in diameter).

An important drawback of most cloud and fog water samplers is their inability to separate completely the water particles from the surrounding air. The Counterflow Virtual Impactor (CVI) collector, which is shown in a schematic diagram in Fig. 10, offers a solution to this problem. Warm, dry, particle-free air flows through the annular region of two concentric tubes to the tip of the impactor [38]. The wall of the inner tube at the tip is made

of porous stainless steel, which allows the dry air to flow into the inner tube. A fraction of the air entering the inner tube is sucked back into the sampler, while the rest blows out the tip. A stagnation plane, where no net axial flow occurs, is formed inside the porous section of the inner tube. Tipward of this plane the air flows towards the tip, while inward of this plane the air flows back into the sampler. The distance from the stagnation plane to the tip can be varied by adjusting the air flow rates to the tip and back into the sampler. This plane is the virtual impaction surface. The device must be moving in the air tip onward (it is frequently airplane mounted). Cloud droplets approaching the CVI tip can either be deflected around the inlet (smaller ones, low inertia, also small solid particles) or swept into the inner tube (inertia sufficient to reach the stagnation plane). One can adjust the lower size limit of droplets being sampled (from 4 μm to 15 μm) by suitable positioning of the stagnation plane. The sampled cloud droplets evaporate quickly in the warm, dry air inside the CVI sampler. The maximum droplet radius that can be sampled is between 50 and 100 μm . Ambient gases and sub-micron aerosol particles are rejected in the CVI with almost 100% effectiveness. A measure of this effectiveness is the rejection ratio, defined as the ratio of the concentration of a species in ambient, cloud-free air to the concentration within the CVI sampler. The instrument requires a condenser for water collection and measurement. In this respect, a CVI collecting samples for chemical analyses must ensure total recovery from the gaseous phase of both water and other volatile substances (pollutants) contaminating original droplets caught by the device.

Specially designed equipment, consisting of a stainless steel cooling chamber (10 cm x 10 cm x 22 cm) and a collector for fog droplets utilizing the impaction technique, has also been used for collecting fog water [9]. Fog air is drawn at the rate of 0.2 m^3/min and the fog droplets impact on the collector, which is maintained at -15°C in the cooling chamber. The sampling period varies from 30 to 120 minutes, and in this time from 5 to 30 ml of fog water is collected. The volume of the sample collected depends on the duration of the fog event.

Another paper [8] shows a device consisting of two heads connected to a pump (Fig. 11). Air containing fog droplets is drawn in through the upper part of the collector. Droplets accumulating on the cones of the impactor

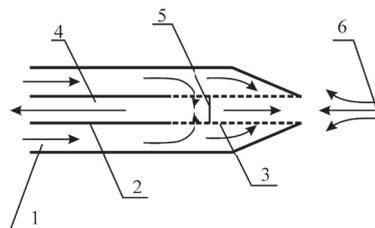


Fig. 10. A schematic diagram of CVI sampler [38]: 1 – warm, dry, clean air, 2 – inner tube, 3 – porous section, 4 – suction, 5 – stagnation plane, 6 – droplets of different size.

fall into polyethylene bottles. The sampling time is 5 to 16 hours.

In the available literature [38, 45] one can find information on an electrostatic precipitation method capable of sampling single cloud or fog drops. The precipitator is based on the corona discharge principle. A copper electrode is placed as a discharge electrode at a distance of 10 cm above an aluminium precipitation electrode. A 25-30 kV voltage is applied to the discharge electrode for 1 s to produce a spray of electrons or negative charge and the charge is transferred to the droplets by the action of the electric field. Charged droplets moving in the direction of the collecting electrode are captured on Petri dishes. The droplets are covered immediately with paraffin oil to prevent evaporation and contamination. Capillary electrophoresis is then used for the chemical analysis of the individual drops. This sampler can also be used for collecting bulk phase cloud or fog water, by increasing the time for the application of the voltage to the discharge electrode from 1 s to 5-15 min, depending on the density of the fog.

An automated system for the collection of cloud water samples directly from clouds has been described in various papers [4, 46, 47]. The system consists of a collector which uses wind speed to effect cloud impaction on 0.4 mm Teflon strings, a system for collecting, retaining and storing samples, and an electronic unit controlling the system. The equipment includes also a temperature sensor, a rain detector and a device for measuring wind speed. When there are no clouds, it is stored within a protective enclosure. During cloud events, a motor driven shaft elevates and exposes the collector. The sample storage unit consists of 24 l polyethylene sample bottles contained in a circular wire support and housed in a commercial refrigerator. When the liquid water content of a cloud exceeds 0.05 g/m^3 , the wind speed is higher than 2.5 m/s, ambient

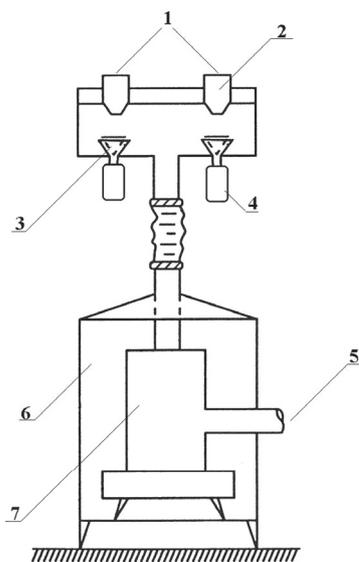


Fig. 11. Structure of a conical sampler to collect fog samples [8]: 1 – inlet, 2 – nozzle, 3 – impaction cone, 4 – collection bottle, 5 – outlet, 6 – shielding box, 7 – pump.

air temperature is above freezing and there is no rainfall, the cloud water collector is activated and projected out of its protective housing. The measurement of pH and conductance occurs automatically in real time during sampling. The indications of pH values are checked on a daily basis and the conductance value is indicated in relation to the external temperature.

An automated system for collecting and analyzing rain samples (Cloud and Rain Acidity/Conductivity Analyzer CRAC) has been adapted for the analysis of cloud water [6]. The system consists of a rain probe connected to an active CalTech collector. When cloud water samples are being collected, the rain detector is disconnected [15]. The instrumentation and the electronic section include a conductometer, a pH-meter and a microprocessor. Samples are collected sequentially in double accumulation vessels containing conductometric cells. After having collected 50 ml of samples, the system directs 12 ml to a chamber where pH is measured, while the remaining quantity goes to a vial which is kept in an automatic whirling arm. The whirling arm and the pH-meter are situated in the cooling section. This collector has a 50% cutoff size centered around $2 \mu\text{m}$ diameter.

Published papers [48, 49] describe an automatic device for collecting fog samples. Fig. 12 shows a block diagram of this instrument [49, 50]. The microprocessor, after receiving signals from three sensors: fog, temperature and rain, uses them to control the system of fog droplets collection. The fog detector, being an optical back-scattered sensor (Fig. 13), consists of two receivers, one of which measures the intensity of the light source and the other the intensity of light scattered by the fog droplets. Both signals reach the microprocessor and their ratio is compared with a threshold value. The system is activated when the detector signals the presence of fog. An active string collector was used to collect fog samples because of its simple structure and ease of automation. This collector consists of a polyethylene aerodynamic tunnel in which air is sucked in by a fan located in its rear part. Teflon strings (0.4 mm dia.) are strung 5 mm apart from each other in the form of a vertical shield, on three frames

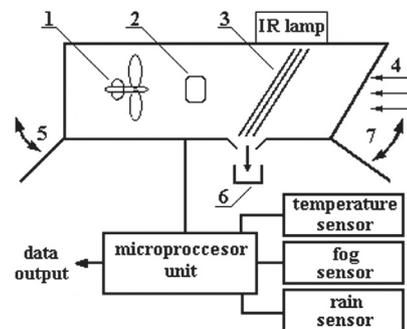


Fig. 12. Block diagram of the automatic system for fog water collecting [49]: 1 – fan, 2 – flow measurement, 3 – collection strings, 4 – air flow, 5 – rear cover, 6 – sample collection, 7 – front cover.

Table 1. Specifications for fog and cloud water collectors.

Type of sampler	Name of sampler	Collector surface	Collection rate [ml/min]	Cutoff [μm]	LWC [g/m^3]	Flow rate [m^3/min]	Reference
Active	String screen Sampler	Teflon wires	50-200/50-180	3-100	0.1-0.3		[15]
	High-Volume Fog Sampler	Teflon filaments	16.7			4400	[20-21]
	Rotating screen sampler	Stainless steel screen	8.3-16.7		0.024-0.08	160	[7]
	CWP	Teflon strands, 0.78 mm dia.					[22]
	CASCC	Teflon strands, 508 μm dia.	2	3.5	0.1	24.5	[5, 26-28]
	CHRCC	Stainless steel rods	0.44	7.7	0.1	6.3	[31, 42]
	TFI			5-12		150-200	[42]
	CSU 5-Stage Collector			4.5-29			[44]
Rotating	CalTech Rotating Arm Collector	Slotted, Teflon coated, stainless steel tube		20		5	[32-34]
	ASRC	Nylon strings, 0.41 mm dia.					[36]
	AV	Teflon-coated rod					[36]
Passive	Passive collector	Nylon strings, 0.2 mm dia.					[40]
	AMC/WPI	Teflon strands					[22]
	Passive sampling system	Teflon strings, 0.3 mm dia.	15-25/120				[38]
Mesh Impaction	Global Geochemistry Mesh Impactor	Polypropylene mesh		2.4		1.5-1.7	[36, 38]

placed at an angle of 30 degrees with respect to the direction of the stream. Fog droplets collide with them and once they reach an adequate size, they flow down into bottles. The velocity of air flowing through the tunnel is 6 m/s, which corresponds to an air stream intensity of 17 m^3/min . The collector is opened and closed automatically. At the end of fog occurrence the lid is closed in order to keep away impurities. In order to prevent the freezing of fog droplets on the strings, an infrared-emitting lamp is placed above the frames, which allows the hoarfrost on the strings to melt into the collecting bottles. A simplified version was used in [51].

In Table 1 parameters of samplers used for collecting fog and cloud were set together. The data presented makes it possible to select sampler depending on sample type as well as on cutoff, flow rate.

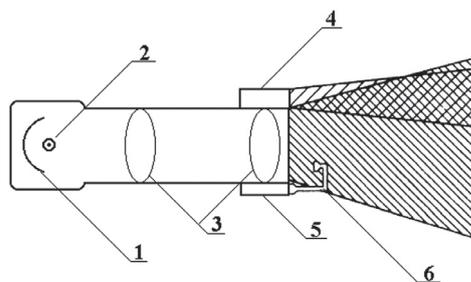


Fig. 13. Schematic diagram of the fog optical detector [48]: 1 – mirror, 2 – lamp, 3 – lenses, 4,5 – receiver, 6 – optical fibre.

Collectors for Dew Samples

Dew formation, cool nights and light breeze control the atmospheric chemistry at ground level where condensation occurs [52]. Therefore, the chemical process is highly influenced by the chemistry of the atmosphere in the related area, which can play an important role in the deposition of air pollution and role in arid ecosystems [13]. Dew may increase seedling survival, plant growth and crop yield, but it may also have a negative effect, promoting bacteria and fungal infections. As a source of information on the environment, dew samples have been a subject of interest for a long time [53]. During the night, the latent heat flux towards the soil surface is very small, and therefore the amounts of dew deposition are very small as well. This fact poses some very special technical measurement difficulties.

Various methods for measuring dew are described in the literature. The first publications presenting methods for determining the amount of dew appeared already at the end of the last century. Measurements were carried out using very simple methods, *i.e.* collecting dew from grass by means of a sponge or by placing absorbent paper on grass. The dew samples were collected early in the morning. Before the expected appearance of dew, the collecting surface was flushed with deionized water and subsequently dried. Dew collection took place only on rainless nights to eliminate any influence of rain droplets on collected dew samples.

Methods of dew sampling can be divided into three basic groups: optical, volumetric and gravimetric. Optical methods consist in visually estimating the amount of dew.

In this method the device Duvdevan is often used. Volumetric methods are connected with measuring the amount (volume) of the collected dew. Gravimetric methods rely on defining the increase of the weight of the collecting surface (without and with dew), which can be determined by means of analytical balance.

A typical example of a volumetric method is the use of a drosometer, where the collecting surface consists of a filter paper 9 cm in diameter, saturated with water [54]. This method can be used only at temperatures above 0°C and, in addition, the exact moment of dew formation has to be determined.

The gravimetric methods include the method using Leick's plates (made from a mixture of silicon dioxide dust, alabaster gypsum and water). The plates are weighed before being used and after they bedew. The increase in weight in mg is proportional to the amount of dew in mm. In research on dew samples a drosograph has also been used. The nascent dew settles upon a receiving plate and it can flow down to the collecting vessel located underneath. The plate and vessel are located at one end of a first-order lever, the opposite end of which ends in a small writing-pen. The movement of the pen, combined with the rotating movement of the drum, makes it possible to record changes in the quantity of dew. The drosograph described in [55] is built on the principle of an analytical balance; on its arm there is a metal box with turf which plays the role of dew collector and holder. In one of the papers [56], the direct weighing method was employed for collecting dew samples. The collectors were built in the form of containers made of polymethylmethacrylate (PMMA), with a diameter of 9.2 cm and a height of 10 cm, and with appropriate filling (a layer of thick gravel, sand, loess). The methods presented above permit continuous registration of the event in its nascent stage, measurement of the precipitation (dew) amount, its duration and evaporation time.

The dew sampling method most often described in the papers is the cloth plate method (CPM) [13, 57]. Velvet-like fabric (a square cloth, 6 cm x 6 cm), 0.15 cm thick, is placed in the centre of a 10 cm x 10 cm x 0.2 cm glass plate. The glass plate is placed on a 10 cm x 10 cm x 0.5 cm layer of plywood. The plate and the plywood form a homogenous base 0.7 cm thick. The material which ab-

sorbed the dew is changed every day, placed in flasks and weighed in order to measure dampness.

To collect the condensate of the water vapour rising from the ground, 50 µm thick plastic foil is used (2 m x 2 m, 2.5 m x 2.5 m) [58]. The plastic foil sheets are extended above a wooden frame and the edges are fastened to the ground. Dew drops form on surfaces slightly inclined down the foil, they are collected in the morning by means of a syringe and put into 100 and 250 ml bottles. Dew samples were collected using polyethylene trays. The tray was placed on a 1 m high iron stand on the roof of a single-storey faculty building [59]. After collection, the dew samples were transferred to polyethylene bottles.

In the collector described in paper [60] and shown in Fig. 14, the condensation surface is a rectangular foil sheet, 3 m x 10 m, made from TiO₂ and BaSO₄ microspheres embedded in polyethylene. The foil is fixed by lateral cables on a light grid attached by cables. The cables are fixed to beams anchored to the ground. This foil exhibits improved emitting properties in the near infrared (to provide radiative cooling of room temperature surfaces) and efficiently reflects the visible radiation (sun). A weak wind (<1 m/s) is necessary to provide sufficient humid air around the condenser, but strong wind increases heat losses. To minimize wind influence and recover water drops by gravity using a plane condensing area with an angle with respect to horizontal and thermally isolated from the ground with 2-cm-thick polystyrene foam. The placement of the collector at an angle of 30 degrees facilitates the flow of droplets (it seems the angle may be a critical value, too high leads to diminishing dew formation). Dew, accumulating in a groove along the lower edge of the collecting plane, flows off to a 25 l polyethylene bottle.

The glass collector described in [52], 100 cm by 100 cm and 1 mm thick, was placed on a frame at the height of 1 m. The accumulating dew finds its way to polyethylene bottles. In order to insure that dew will form, the back of the collector is made of aluminium.

Apart from glass collectors, also in use are collectors made with a polytetrafluoroethylene sheet (PTFE), a PMMA, a glass Pyrex plate, a sheet of stainless steel, an aluminium sheet, a PTFE sheet covered with stainless steel, or an aluminium-covered PTFE sheet. The collectors were placed on a 10 cm block of polystyrene foam [61].

Dew has been sampled by means of a collector, which consists of a pump, and a Teflon pipe terminated with a glass fibre filter [62]. The dew is sucked in by the pump together with air and flows through the pipe into a polyethylene bottle. Within 30 minutes, 1 ml of dew is collected.

Dew samples have also been collected using an instrument which consists of a 0.50 µm thick Teflon film attached to a 3 cm thick polystyrene block with double-stick tape. At sunset, the collector was placed on top of a 1 m high table and opened. Dew droplets <1 mm diameter were swept together with a chemically clean Teflon scraper, drawn up with a pipette and transferred to clean polyethylene bottles.

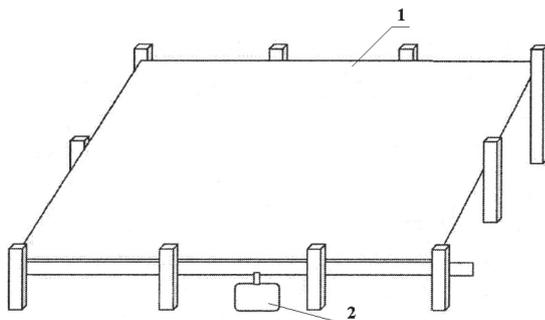


Fig. 14. Schematic diagram of a dew samples [60]: 1 – foil, 2 – collection bottle.

Table 2. Specifications for dew, rime and hoarfrost samples.

Type of collector surface	Comments	Dimension (mm x mm)	Reference
Dew			
PTFE sheet	The collectors were placed on a 10 cm block of polystyrene foam.	310 x 307	[61]
Pyrex glass plate		300 x 298	
Stainless steel sheet		303 x 228	
Aluminium sheet		303 x 226	
PTFE coated stainless steel sheet		303 x 228	
PTFE coated aluminium sheet		303 x 226	
Plastic foil	Dew drops form on surfaces slightly inclined down the foil, they are collected in the morning by means of a syringe and put into 100 and 250 ml bottles.	2000 x 2000 2500 x 2500	[58]
Glass	In order to insure that dew will form, the back of the collector is made of aluminium.	1000 x 1000	[52]
Rime/ Hoarfrost			
Polyethylene plates	It is also possible to measure the size of the collected deposit and to record its visual appearance by photographing it. Location at the height of 1 m	200 x 200	[67]
Polyethylene screen	Deposits are collected for the whole 24-hour period. Location at the height of 2-3 m	600 x 600	[68]
Polyvinyl chloride shield	at the height of 1 m		[69]
Teflon film	Teflon film attached to a 3 cm thick polystyrene block with double-stick tape		[70]

Dew samples have also been collected manually by means of a Teflon film (1 m², 0.4 mm wide) bent in the middle at an angle of 90 degrees [63]. The collected water flows off to a plastic 0.5 l bottle.

The parameters characterizing dew collectors are shown in Table 2.

Collectors for Hoarfrost/Rime Samples

In recent years has been an increase in the interest about chemical processes in cloud environments. Chemical deposition from cloud droplets appears to be an efficient process. Rime forms when supercooled cloud droplets in the basal cloud layer freeze on impact with vegetation or topographic surfaces. Rime is commonly observed on trees, towers, powerlines and other objects at high elevations exposed to high-velocity cloud airflow. The chemical characteristics of rime and glaze could mimic the chemistry of cloud droplets, and potentially affect vegetation adversely. If these deposits act as a biologically-inert, frozen protective shell, their role could be beneficial.

The simplest samplers used to collect samples of hoarfrost and rime consist of flat surfaces made from materials such as Teflon, galvanized steel or Nylon wires [64, 65]. Very often hoarfrost accumulates on some elements of cloud water collectors, e.g. the strings, and it is then collected manually into polyethylene bottles [24, 66].

In another published paper [67] an apparatus was described that consisted of four polyethylene plates (20 cm x 20 cm x 5 cm). The plates are fastened at the height of 1 m on an aluminium scaffold and positioned vertically facing the four cardinal points. The wind direction is estimated during sample collection by observing the wind vanes. It is also possible to measure the size of the collected deposit and to record its visual appearance by photographing it. Hoarfrost, which accumulates on the surface of the plates, is removed by means of a polyethylene scraper from the outer sides of the plates and collected into bottles.

For collecting samples of hoarfrost and rime, a passive collector is used with a string polyethylene screen. The collector mesh has 12 mm openings with 2 mm strands and overall dimensions of 60 cm by 60 cm (Table 2). Samples gathering on the screen are collected into 250 ml containers. The collectors are installed at a height of 2-3 m above the snow surface. The hoarfrost is collected for the whole 24-hour period [68].

In the passive shield hoarfrost/rime collector, made of polyvinyl chloride and placed on a square frame (929 cm²), the collecting area consists of 46 singular fibres 0.2 mm in diameter. This collector is placed at the height of 1 m above the snow surface. Rime is scraped off from its surface by means of a scraper. Subsequently, the samples are placed in polyethylene bottles and transported to the laboratory [69].

Table 3. Chemical composition of fog, cloud water, dew, hoarfrost and rime samples collect in various countries.

Name/type of sampler/ collection area	Site and period of sample collecting	Analytes	Concentration range	Storage and/or preparation of samples for analysis	Technique of final determination	References	
CASCC	New England 1990	SO ₄ ²⁻	0.00-1.3 ppb	Chemical conservation (chloroform), 4°C for 24h, then - 20°C	IC	[76]	
		Cl ⁻	0.00-2.7				
	pH	2.63-5.30	Chemical conservation (chloroform), below 10°C	pH-meter	[77]		
	NO ₃ ⁻	96-1167 µeq/l					
	SO ₄ ²⁻	54-678	No data	pH-meter	[78]		
	Cl ⁻	190-2437					
	NH ₄ ⁺	101-782					
	Ca ²⁺	5-53					
	Mg ²⁺	17-345					
	Na ⁺	142-1934					
K ⁺	6-49						
pH	2.74-4.37						
NO ₃ ⁻	128.6-1259.8 µN	Filtration of sample (0.45 µm), - 20°C				IC	[79]
SO ₄ ²⁻	18.3-4635.0						
Cl ⁻	1.5-117.2	Filtration with the use of quartz filters, extraction by means of solvent (dichloromethane)	GC-MS	[89]			
Ca ²⁺	2.2-68.2						
Mg ²⁺	1.8-34.4						
Na ⁺	NW-202.7						
K ⁺	NW-31.1						
NH ₄ ⁺	226.3-5897.2						
pH	4.97-7.43						
NO ₃ ⁻	75-2900 µM				pH-meter	[79]	
SO ₄ ²⁻	19-180						
Cl ⁻	10-82				n-Alkanes Naphthalene Phenanthrene Anthracene Fluoranthene Pyrene Benz(a)anthracene Benzo(e)pyrene Benzo(a)pyrene Benzo(ghi)perylene	pH-meter	[89]
pH	6.1-7.0						
NO ₃ ⁻	NW-5.1 ng/ml						
SO ₄ ²⁻	NW-0.1						
Cl ⁻	0.028-0.169						
pH	NW-0.040						
n-Alkanes	0.002-0.095						
Naphthalene	0.013-0.289						
Phenanthrene	NW -0.022						
Anthracene	NW -0.252						
Fluoranthene	NW -0.218						
Pyrene	NW -0.033						
Benz(a)anthracene							
Benzo(e)pyrene							
Benzo(a)pyrene							
Benzo(ghi)perylene							

Table 3 continues on next page...

	Germany 1997	NO_3^- SO_4^{2-} Cl^- NH_4^+ Ca^{2+} Na^+ K^+ Al Ni Pb Cd Cu Sb Se pH conductivity	20-1740 $\mu\text{eq/l}$ 55-1800 <13-389 <21-2580 <11-493 <9-664 <6.7-68.5 14-903 $\mu\text{g/l}$ 0.8-42.8 3.4-61.4 0.3-8.7 2.5-56.8 0.8-5.7 1.1-11.5 3.3-5.7 17-452 $\mu\text{S/cm}$	Filtration of sample (cellulose acetate, 0.45 μm), acidifica- tion, application of UV radiation, 48h extraction with hydrogen peroxide solution, - 18°C	IC - ICP-AES AAS pH-meter Conductometer	[85]
Cooling chamber	India 1989-1990	NO_3^- SO_4^{2-} Cl^- Ca^{2+} Mg^{2+} Na^+ K^+ NH_4^+ pH	233.9-514.5 $\mu\text{eq/l}$ 58.3-91.6 203.1-355.4 1412.2-2021.0 222.2-337.4 82.7-700.3 161.1-309.5 61.0-99.8 6.2-6.9	4°C (refrigerator)	No data	[81]
Passive	Canada 1991	NO_3^- SO_4^{2-} Cl^- NH_4^+ Ca^{2+} K^+ Mg^{2+} Na^+ pH conductivity	89.3-361.4 $\mu\text{eq/l}$ 230.2-336.6 5.8-45.0 183.6-345.6 17.7-82.8 2.6-5.6 4.3-21.9 4.7-52.8 3.71-3.97 81.1-155.3 $\mu\text{S/cm}$	Samples were not filtered, no reagents used to fix the sample, 4°C (refrigerator)	IC	[82]
	Chile 1989	NO_3^- SO_4^{2-} Cl^- NH_4^+ Na^+ Ca^{2+} Mg^{2+} pH	0.32-9.51 ppm 1.41-20.0 0.68-27.9 0.40-3.19 0.47-15.7 0.15-3.06 0.05-1.60 4.01-6.69	No data	pH-meter Conductometer HPLC	[84]

Table 3 continues on next page...

Passive	Chile 1987-1989	Fe As Cd Pb Al Ti V Mn Ni Cu Zn Sr Sb Ba	<50-70 ppb 1.8-20.3 <0.5-1.2 <0.5-36.1 4.3-65.1 <2.0-3.8 0.5-7.9 3.0-35.4 <2.0-6.0 <1.0-44.4 4.1-78.2 0.7-18.3 <0.5-0.8 0.6-8.1	No data	FAAS pH-meter ICP-MS	[84]
	Namibia 1994-1995	NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ pH	0.22-0.72 ppm 0.58-6.71 0.38-10.0 0.81-1.05 0.3-2.48 0-0.5 0.03-0.98 0.36-6.11 5.6-6.6	Refrigerator	IC pH-meter	[88]
Screen	Japan 1991	NO ₃ ⁻ NO ₂ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ Na ⁺ K ⁺ pH	0.0-3211.3 µeq/l 0.0-1.1 42.9-3625.4 7.2-1414.1 0.2-2300.0 0.3-67.2 1.8-991.3 0.0-36.5 3.30-4.25	Refrigerator	IC pH-meter	[86]
	Automatic	Italy 1994	NO ₃ ⁻ NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ Ca ²⁺ Mg ²⁺ Na ⁺ K ⁺ NH ₄ ⁺ pH conductivity	0.37-6.33 meq/l 0.01-0.12 0.26-3.40 0.06-0.40 0.04-0.17 0.01-0.09 0.02-0.15 0.01-0.18 0.81-7.16 2.60-7.03 106-1760 µS/cm	No data IC/AAS IC/Colorimetry pH-meter Conductometer	[87]

Table 3 continues on next page...

Automatic	Italy 1999-2001	TOC	30-215 ppm	Filtration with the use of quartz filters (47 mm), refrigerator	Analyzer Shimadzu TOC 5000A	[91]
RAC	California	Formaldehyde Acetaldehyde n-pentanal n-butanal	0-2.30 µg/ml 0.06-0.17 0-0.15 0-0.052	Derivatization (2,4-dinitrophenylhydrazine), acidification (HCl), extraction by means of solvent (hydrazine), dark place, refrigerator	HPLC-UV	[90]
	Congo 1986-1987	NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ Na ⁺ K ⁺ pH	61.4 µeq/l 114.5 42.3 75.3 82.6 69.9 19.0 4.92	Refrigerator	IC AAS pH-meter	[83]
CLOUD WATER						
RAC	California 1982	NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ Fe Pb pH	191-9500 µeq/l 128-7310 21-1965 128-3130 5-975 1-161 2-762 5-2465 200-6880 µg/l 80-2780 2.06-3.65	Filtration with the use of Teflon filters	IC Colorimetry AAS - - pH-meter	[92]
	RAC/ CASCC	California 1985-1986	NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ Ca ²⁺ Mg ²⁺ Na ⁺ pH	<1-1140 µN <1-665 <1-491 2-308 1-266 1-680 4.4-5.7	No data	IC AAS pH-meter
CASCC	California 1988	NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ Mg ²⁺ Na ⁺ pH	164-336 µN 142-236 NW-30 303-584 8-18 5-12 14-35 4.34-4.75	Filtration with the use of Teflon and Nylon filters, 4°C (refrigerator)	IC Colorimetry AAS pH-meter	[97]

Table 3 continues on next page...

CRAC	North Carolina 1987-1989	NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ pH	14-556 µeq/l 52-1814 2.0-121 2-716 6.0-108 1.0-8.0 0.5-30 0.2-82.0 2.87-4.21	4°C (refrigerator)	IC Colorimetry AAS pH-meter	[96]
	North Carolina 1986-1987	NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ pH conductance	11.90-854.4 µeq/l 21.00-1200.00 0.5-151.75 5.8-567.10 1.80-296.00 1.40-17.00 0.60-66.40 1.40-162.68 2.83-4.55 12-583 µ Ω ⁻¹ cm ⁻¹	No data	No data	[94]
ASRC	1986-1988	NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺	91-205 µeq/l 245-576 6.49-32.9 119-218 13.9-55.1 2.59-7.78 4.1-13.9 3.65-19.4	4°C (refrigerator)	IC	[95]
	Indiana, Ohio, West Virginia, Kentucky 1990	NH ₄ ⁺ pH	0.49 -3.8 mg/l 3.53-4.05	Refrigerator, analysis carried out within 24-48 h from drawing sample	IC pH-meter	[98]
	North Carolina 1993-1994	NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ pH	8.00-113.10 µeq/l 105.00-1110.21 8.00-420.82 25.50-291.61 7.10-82.80 2.05-15.32 1.20-105.30 3.91-154.85 2.84-3.77	4°C (refrigerator)	IC	[99]
	Costa Rica 1988-1992	NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺	47.2-739.4 µmol/l 8.7-70.1 7.7-76.5 18.1-121.8 144.4-713.4	4°C (refrigerator)	pH-meter Colorimetry AAS	[101]

Table 3 continues on next page...

	Japan 1994-1997	<p>12-383 meq/l 85-3640 180-26500 56-330 26-933 13-425 45-5370 160-23000 3.8-5.2</p>	<p>NO₃⁻ SO₄²⁻ Cl⁻ NH₄⁺ Ca²⁺ K⁺ Mg²⁺ Na⁺ pH</p>	<p>IC</p>	[103]
ASRC	Germany 1997	<p>1730-99100 µg/l 1230-28110 40-10450 380-29500 10-7310 <5-800 <5-740 70-6220 9-15500 316-35220 <5-580 1.0-158 29-10430 <0.05-3.6 <0.05-0.18 <0.3-9.0 <0.02-2.1 0.2-11.4 0.5-173 3.1-910 0.1-6.6 0.1-68.7 <0.05-3.4 0.05-2.0 0.02-5.5 <0.05-1.0 1.97-84.0 3.4-6.8 19.3-316 µS/cm</p>	<p>NO₃⁻ SO₄²⁻ Cl⁻ NH₄⁺ Ca²⁺ K⁺ Mg²⁺ Na⁺ pH conductivity</p>	<p>IC ICP-OES ICP-MS ICP-OES ICP-MS pH-meter Conductometer Spectrophotometry UV-VIS AAS pH-meter</p>	[104]
String	India 1983-85	<p>29 µeq/l 31 251 55 274 37 96 196 6.9</p>	<p>Filtration of sample (Whatman 41), 4°C</p>	<p>AAS</p>	[100]

Table 3 continues on next page...

Passive	Oman 1990	NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ Fe As Cd Pb Be Al Cr Mn Ni Cu Zn Ag Ba pH	0.70-12.3 ppm 0.45-6.70 5.85-84.3 0.00-0.65 2.08-42.7 0.14-2.12 0.46-5.73 3.36-46.0 <60 ppb <1 <0.5 <0.5 <0.5 2.2-19.5 <5 5.4-34.5 <2-7.36 <5 <2-25.6 <0.5 1.5-22.5 6.96-7.94	Samples were not fixed, 4°C	HPLC FAAS HPLC FAAS HPLC ICP-MS	[102]	
		DEW			pH-meter		
Teflon layer	Indiana 1987-1988	NO ₃ ⁻ NO ₂ ⁻ SO ₄ ²⁻ SO ₃ ²⁻ Cl ⁻ F ⁻ PO ₄ ³⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ pH	2.2-78 µmol/l 0.9-9.6 1.9-53 0-1.7 3.3-16 0-10.3 0-6.1 3.7-105 25-133 2.8-26 6.1-35 1.4-8.9 6.2-6.8	Dissolution filtration of sample, chemical conser- vation (chloroform), 4°C, dark place	IC AAS	[70]	
		Chile 1995-1999	NO ₃ ⁻ NO ₂ ⁻ SO ₄ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ pH	47-177 µeq/l 93-238 177-901 28-86 419-748 284-703 7-80 25-103 15-128 5.4-6.6	5°C	Capillary electrophoresis Spectrophotometry FAES	[63]

Table 3 continues on next page...

Glass	Jordan 1999-2000	NO_3^- SO_4^{2-} Cl^- F^- NH_4^+ Ca^{2+} K^+ Mg^{2+} Na^+ Pb Co Cd pH	0.5-15.7 ppm 2.9-49.0 0.3-59.9 1.1-5.6 NW-3,48 0.7-37.8 0.2-4.8 0.1-9.8 0.3-36.7 0.30-32.3 ppb 0.24-3.1 0.01-3.8 6.1-7.4	Refrigerator, analysis carried out within 48h from the moment of drawing the sample	IC Spectrophotometry IC AAS pH-meter IC	[52]
PTFE sheet	Japan 2000	NO_3^- NO_2^- SO_4^{2-} SO_3^{2-} Cl^- NH_4^+ Ca^{2+} K^+ Mg^{2+} Na^+ pH	0.024 $\mu\text{mol}/\text{cm}^3$ 0.067 0.032 0.033 0.099 0.265 0.054 0.006 0.011 0.078 6.80	Filtration of sample (0.22 μm , membrane from PTFE)	pH-meter IC	[61]
Pyrex glass plate		NO_3^- NO_2^- SO_4^{2-} SO_3^{2-} Cl^- NH_4^+ Ca^{2+} K^+ Mg^{2+} Na^+ pH	0.029 0.061 0.037 0.034 0.122 0.240 0.064 0.011 0.017 0.128 6.61		pH-meter IC	
Stainless steel sheet		NO_3^- NO_2^- SO_4^{2-} SO_3^{2-} Cl^- NH_4^+ Ca^{2+} K^+ Mg^{2+} Na^+ pH	0.064 0.010 0.069 0.011 0.326 0.119 0.206 0.022 0.034 0.244 7.04		pH-meter IC	

Table 3 continues on next page...

PTFE coated stainless steel sheet		NO ₃ ⁻ NO ₂ ⁻ SO ₄ ²⁻ SO ₃ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ pH	0.025 0.097 0.025 0.037 0.053 0.368 0.075 0.003 0.008 0.048 7.08	IC	IC	
PTFE coated aluminium sheet		NO ₃ ⁻ NO ₂ ⁻ SO ₄ ²⁻ SO ₃ ²⁻ Cl ⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ pH	0.022 0.056 0.023 0.034 0.056 0.244 0.067 0.005 0.006 0.055 7.06	IC	IC	
RIME/HOARFROST						
Teflon layer	Indiana 1987-1988	NO ₃ ⁻ NO ₂ ⁻ SO ₄ ²⁻ SO ₃ ²⁻ Cl ⁻ F ⁻ PO ₄ ³⁻ NH ₄ ⁺ Ca ²⁺ K ⁺ Mg ²⁺ Na ⁺ pH	6.7-41 µmol/l 0-7.6 4.4-46 0-3.4 0-223 0.6-12 0-5.1 0-169 17-234 0.8-31 4.6-25 2.0-203 6.2-7.5	Disso- lution, filtration of sample, chemical conser- vation (chloroform), 4°, dark place	AAS	[70]
Polyvinyl chloride	Washington 1989	SO ₄ ²⁺ H ⁺ Cl ⁻ Na ⁺ K ⁺ Mg ²⁺ Ca ²⁺ NH ₄ ⁺ NO ₃ ⁻ pH	18.3 µeq/l 2.0 18.4 12.5 3.6 2.2 10.5 17.2 12.4 5.69	Low temperature	No data	[69]

Table 3 continues on next page...

CWP	Czech Rep. 1988-1991	NO ₃ ⁻ SO ₄ ²⁻ F ⁻ Cl ⁻ Zn ²⁺ Mn ²⁺ Mg ²⁺ Na ⁺ K ⁺ Ca ²⁺ NH ₄ ⁺ Fe ²⁺ Al ³⁺ Si ²⁺ pH conductivity	0.30-17.9 mg/l 0.70-48.8 0.02-0.98 1.47-28.6 10.0-1490 µg/l 5.00-184 0.02-1.56 mg/l 0.07-17.6 0.10-9.14 0.06-7.38 0.02-12.5 0.02-0.57 0.02-1.29 0.03-0.05 3.47-6.87 6.65-252 µS/cm	No data	No data	[24]
Grunow's thimble	Poland 1990/1994	pH SO ₄ ²⁻ H ⁺ Cl ⁻ Na ⁺ K ⁺ Mg ²⁺ Ca ²⁺ NH ₄ ⁺	2.23-7.04 480 µM 220 160 20 20 20 40 140	No data	No data	[71]
Nylon wires	Poland 1994	H ⁺ Cl ⁻ SO ₄ ²⁻ Na ⁺ K ⁺ Mg ²⁺ Ca ²⁺ NH ₄ ⁺ Zn ²⁺ Fe ²⁺	208.3-211 µM 0-158.3 466.7 166.7-225 0-20.8 12.5-19 5-33.3 100-125 0.5-0.9 1.5-2.5	Filtration of sample, acidification of samples designed for analysis of metals (HNO ₃)	Spectrophotometry	[65]
Galvanized steel layer	Austria 1992-1996	H ⁺ NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ Na ⁺ K ⁺ Mg ²⁺ Ca ²⁺ NH ₄ ⁺	45.5-45.90 µmol/l 29.1-29.36 29.3-31.14 5.03-6.1 4.73-5.6 0.92-1.0 1.44-1.5 7.39-8.8 44.4-51.38	Low temperature, analysis carried out within 72h from the moment of drawing the sample	IC	[64]

NW – below the threshold of determination ability of the applied analytical procedure, TOC – Total Organic Carbon, IC – Ion Chromatography, AAS – Atomic Absorption Spectrometry, ICP-MS – Induced Coupled Plasma Mass Spectrometry, ICP-AES – Induced Coupled Plasma Atomic Emission Spectrometry, GC-MS – Gas Chromatography with Mass Spectrometry, HPLC-UV – High Performance Liquid Chromatography with UV detector, HPLC – High Performance Liquid Chromatography, FAAS – Flame Atomic Absorption Spectrometry, ICP-OES – Induced Coupled Plasma Optical Emission Spectrometry, PTFE – Poly(tetrafluoroethylene)

In literature [70] another collector has been described, consisting of a 0.50 μm thick Teflon film attached to a 3 cm thick polystyrene block with double-stick tape. Before an expected light freeze, the collector is cleaned by means of distilled deionized water and dried off. Hoarfrost is removed by means of a Teflon scraper into plastic containers, melted at room temperature and transferred into bottles.

To measure liquid and solid atmospheric deposits, also the instrument known as the Grunow thimble is used. It consists of a wire mesh in the form of a cylinder with a diameter of 10 cm and a height of 20 cm [71, 72]. This thimble is laid over a rain-gauge, *e.g.* of the Hellman type (the instrument consists of a metal cylinder ending in a funnel and the precipitation – depending on its kind – flows down into the container or accumulates above the funnel).

Measurements of solidified atmospheric deposits (hoarfrost, rime, freezing rain, glazed frost) can be of substantial significance for certain branches of the economy, such as the power industry, or air and road transport. A sufficiently thick layer of the deposit can overload and possibly break electric power lines. In a published paper [73] a method is presented for measuring the process of accretion of solid deposits on specific surfaces. The method relies on the measurement of the weight of ice deposits, the visual description of their appearance and the time and duration of their occurrence. For this purpose, several pairs of electric power line sections of different diameters are used. A single measurement set consists of four conductor sections of a specific diameter and length, suspended in pairs at some set height above the ground. During the observation, the thickness of the deposit on the conductors is measured with a pair of calipers. When the thickness exceeds 10-20 mm both conductors are taken down and transferred indoors for the purpose of melting and weighing, or measuring the volume of water by means of a laboratory graduated cylinder. A published paper [74] presents an installation for the measurement of frosting on power lines. It must be said that some problems may arise to differentiate between solid deposited precipitation and freezing fallen precipitation (freezing rain), both contributing to the icing events.

Hoarfrost and rime constitute an important element in water circulation, particularly in mountainous regions where they occur quite frequently. They contribute to the process of cleaning the atmosphere and of transferring impurities from air to the soil.

Measurement methods are usually based on the determination of the weight of hoarfrost (icing) per unit of area or length (the latter value is important for the power industry). This weight may be determined by means of a device [75] which consists of two wooden rods, where frost/ice formation occurs, laid perpendicular to each other, the first pointing north-south, the other east-west. The modified version of the device utilizes a strain-gage beam force sensor connected to the cylinder collecting the ice. The necessary electronics are located in another part of the apparatus to minimize heat flow to the ice collecting element (the principle of operation is somewhat obscure).

In paper [73] a system is presented which is used to measure frosting. It consists of continuously operating vibrational sensors of freezing rain and frosting. The sensor is a small cylindrical metal core, electromagnetically excited to vibrate at a nominal resonance frequency of 40 kHz. Two feedback coils co-vibrating with the core, placed in it, permit the measurement of the actual frequency of core vibrations through a microprocessor-based measuring and control circuit. When frosting (freezing rain, rime, hoarfrost) starts to form on the core – the mass of the vibrating object increases, which leads to a proportional reduction of the frequency of core vibration. When the frosting reaches a thickness of 3.8 mm, heating of the sensor is switched on automatically in order to melt the deposit and to restore the resonant frequency. Periods of de-frosting and renewed frosting build-up last for 5-10 minutes, depending upon the wind speed and temperature of the environment. Once every a minute a signal appears at the output of the sensor indicating the frequency of vibrations of the sensor.

In the recent years an increased interest is observed in the chemistry of atmospheric precipitation and deposits, as the impurities and pollutants undergo complicated chemical and biochemical reactions in the aquatic and soil ecosystem due to which they enter into biogeochemical circulation, disturbing the environmental balance. For this reason, the pollution of atmospheric air, as well as the pollution of atmospheric precipitation and deposits which follows, constitute a problem on an international scale, requiring constant monitoring, as confirmed by national and foreign studies collected through literature research. In Table 3 results of measurements of inorganic and organic compound concentrations determined in non-typical samples are presented together with the methods used for their final determination.

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