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Review

Atmospheric Precipitation Sampling for Analysis

M. Grynkiewicz, Ż. Polkowska, B. Zygmunt , J. Namieśnik*

Department of Analytical Chemistry, Chemical Faculty,
Technical University of Gdańsk (TUG),
11/12, G. Narutowicz Str., 80-952 Gdańsk, Poland

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Abstract

This paper reviews collectors for atmospheric precipitation (rain, fog, and run-off water). Collection systems of a different degree of automation (from simple designs to highly automated costly collectors) are presented. In many papers on collecting atmospheric precipitation neither sampling procedures nor locations of sampling sites are given, although this information is necessary for producing correct and comparable results of physical and chemical analyses.

Keywords: atmospheric precipitation, run-off water, sampling, collectors, sample preparation

Introduction

Despite the general opinion that precipitation samples have a simple matrix, analysis of pollutants in precipitation water is a difficult task. The reasons can be:

- low and very low concentrations of analytes of interest;
- large time and spatial variability of analyte concentrations - the fluctuations are related to a season of the year and the phase of a given cycle of precipitation;
- different forms of precipitation (rain, snow, fog, hail);
- variability in ways precipitation reaches the ground (Fig. 1).

Atmospheric precipitation is a specific kind of environmental matrix and its collection must satisfy a number of conditions, especially with respect to a collection system. In compliance with recommendations of the European Monitoring Environmental Program (EMEP) the collectors for wet precipitation and total precipitation should be characterized by:

- large inlet area (1000-2000 cm^2) so that a sample of large volume could be collected even at a small precipitation rate;
- an appropriate container capacity to avoid any loss of a sample even when precipitation is very intensive;
- an appropriately selected construction material for particular parts of a collector – material should be resistant to chemicals and to low and high temperatures met under real conditions.

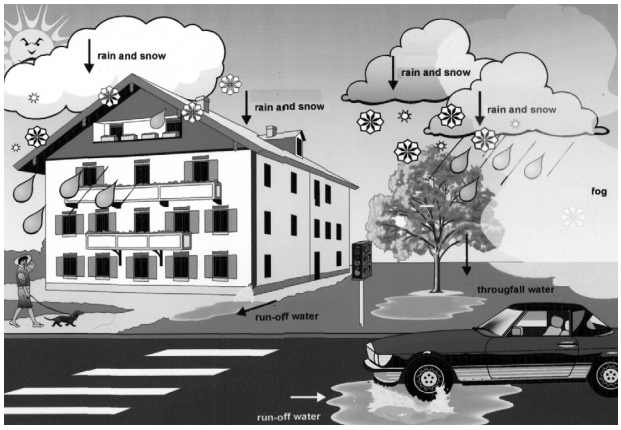

Fig. 1. Ways of reaching earth surface by atmospheric precipitation.

*Corresponding author; e-mail: chemanal@pg.gda.pl

Samplers should be placed ca. 1.5 m above the ground, in an open area, at best, overgrown with grass. This is aimed at avoiding contamination with leaves, twigs, and also with dust and sand from soil. The detailed conditions for collector location are given in the Polish standard [2] and discussed in many papers [1,3,4]. After a specified collecting period (week, month, etc.), samples should be transported to the laboratory and analysed as soon as possible, at best the same day (within a few hours after delivery). If immediate analysis is not possible samples should be stored under appropriate conditions (at a temperature of 4 ^{0}C in dark with addition of bactericides ($HgCl_2$, chloroform, isopropanol) or frozen at –20 ^{0}C) [5-9]. This is necessary to slow down or, at best, completely stop biodegradation of analytes of interest; many precipitation pollutants undergo biodegradation at room temperature [9].

An important operation is washing a collector before use. The rain droplets remaining on the collector wall can change new sample composition to a considerable degree, especially if a previous sample was strongly polluted and in this way affect analytical results. Collector washing procedures generally consist of a few steps including washing with hot water, detergents, deionised water, and organic solvents (CH_2Cl_2, isopropanol, etc.) [6].

Collecting a sample of run-off water is an important step of analysis. Errors committed at this step increase the total error of analysis and can not be eliminated in successive steps. The sample must be collected in such a way that it is representative of the population studied.

Collectors for Sampling Precipitation Water

Known atmospheric precipitation collectors are characterised by a different degree of automation; the most sophisticated can record meteorological data and also some characteristics of precipitation (rate, electrolytic conductivity, pH). Some permit simultaneously collecting precipitation and run-off water [10,11]. Below are described the samplers most widely applied.

The simplest collectors for precipitation water sampled for chemical analysis are glass, metal, and plastic containers. They are made of amber glass [6,10,12-17], stainless steel [7,18,19] or polyethylene [11,20-25]; the containers are equipped with glass, steel, or polyethylene funnels. Fig. 2 presents the scheme of a polyethylene collector [21]. Strachan [26] proposed a collector for total precipitation with a thermostated chamber to keep the sample temperature at 4^{0}C. The collector is also equipped with meters of wind velocity and direction [26].

An example of the simplest collector for total wet precipitation is an open container with a cover in a state of repose [27-31]. A collector of this type was used by Buijsman [32] to sample atmospheric precipitation in the northern Atlantic Ocean. The scheme of the sampler is given in Fig.3. The more complicated version has an automatic cover and a humidity sensor; in the system dry precipitation is excluded from a sample [10,33-41] (Fig. 4 [41]).

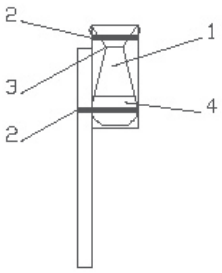

Fig. 2. Scheme of collector for sampling atmospheric precipitation [11]: 1 - polyethylene bottle, 2 - fastening band, 3 - band clip, 4 - rain water sample.

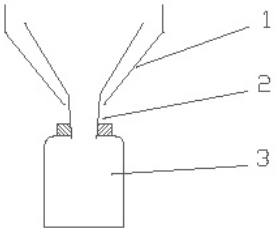

Fig. 3. Scheme of simplest collector for total precipitation samples: 1 - outer funnel casing, 2 - funnel (glass, steel or polyethylene), 3 - bottle (glass, steel or polyethylene).

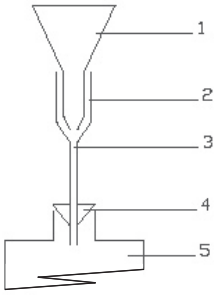

Fig. 4. Scheme of collector for sampling atmospheric precipitation: 1 - glass funnel, 2 - funnel fastening in glass sleeve, 3 - Teflon fastening of bottle capillary, 4 - glass bottle.

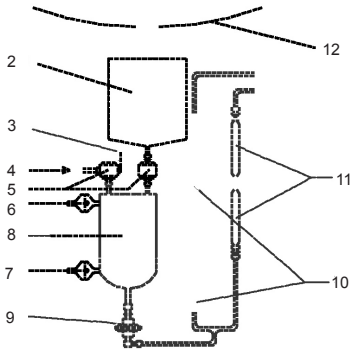

Fig. 5. Scheme of atmospheric precipitation collecting combined with pressure filtration [43]: 1 - Teflon collecting disk, 2 - collecting vessel, 3 - de-aerator, 4 - nitrogen inlet, 5 - electromagnetic valve, 6 - upper sensor, 7 - lower sensor, 8 - pressure container, 9 - membrane filter clamp, 10 - sorbent packed extraction columns (for further solvent elution treatment), 11 - sorbent packed extraction columns (for further thermal desorption treatment), 12 - tubes connecting collector with measuring devices.

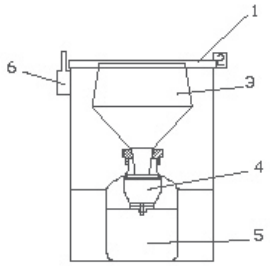

Fig. 6. Scheme of automatic collector for sampling atmospheric precipitation [31]: 1 - cover, 2 - electric motor, 3 - polyethylene funnel, 4 - filtration funnel, 5 - polyethylene bottle for collecting filtrate, 6 - humidity sensor.

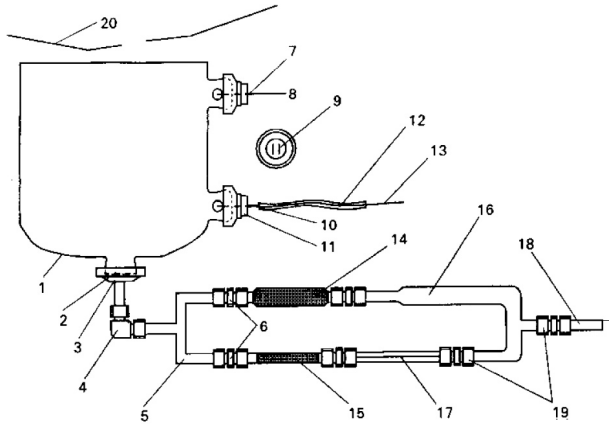

Fig. 7. Scheme of collector for sampling rain water for determination of dissolved organic compounds [43]: 1 - glass bottle, 2 - glass fibre, 3 - filter clamp, 4 - connector, 5 - T-tubes (of glass), 6 - Teflon connectors, 7 - spherical ground joint, 8 - upper electrode, 9 - set of electrodes (front view), 10 - stainless steel tube, 11 - lower electrode unit, 12 - Teflon coating, 13 - electric cable, 14 - tube with sorbent (Tenax-GC) for further solvent elution treatment, 15 - tube with sorbent (Tenax-GC) for further thermal desorption treatment, 16 - connecting glass tube, 17 - stream splitter, 18 - Teflon tube (to pump), 19 - Teflon connector, 20 - collecting plate.

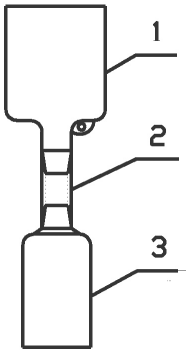

Fig. 8. Scheme of collector for sampling wet atmospheric precipitation for mercury compounds determination [51]: 1 - polypropylene funnel, 2 - connector with vent opening, 3 - polypropylene bottle.

Rain water is collected on a specially shaped Teflon disk [42-44] or a glass funnel [8,10,45-47]. Pumps are used to force sample flow to a bottle made of glass, stainless steel or aluminium. The sample is passed through filters to separate solid particles. The filters are made of glass fibre [46], Teflon [42,44], or silver membrane [42-44]. The collectors are often equipped with sorbent (Tenax-GC, Amberlite XAD) packed tubes (cartridges), which permits to simultaneously extract analytes [8,42,44,48]. Examples of collectors for atmospheric precipitation are presented in Figs. 5 [31] and 6 [43].

In the Brookheaven National Laboratory a sequential automatic collector was designed. It can be applied to collect samples of precipitation water as well as snow. Samples are protected from contamination in the periods between precipitation. The collector consists of a large case with a rotating support inside on which 30 Teflon bottles are situated. Precipitation enters the bottle through a Teflon funnel. When precipitation stops the funnel is closed by a cover equipped with a sensor which triggers moving the cover over the funnel when it becomes dry. The bottles are automatically exchanged after each precipitation event. Closing and opening the collector as well as bottles exchange are automatically recorded [49].

Some precipitation water collectors are even more complicated. Fig. 7 presents the scheme of a collector for sampling rain water to determine dissolved organic compounds [50]. It consists of the following parts:

- appropriately shaped Teflon disks with an opening in the centre which collects precipitation;
- a glass bottle with two stainless steel electrodes at different heights which detect the water levels in the bottle;
- a system for isolation and enrichment of organic compounds from samples of precipitation water (sorption tubes).

Passage of water through the sorption system is forced by a peristaltic pump switched on and off in response to a signal from the lower electrode. When the water level reaches the upper electrode, pumping rate increases twice [50].

In the University of Michigan Air Quality Laboratory a new model of an automatic collector was designed for sampling wet precipitation to determine mercuric compounds. In this model mercury is prevented from adsorption on collector parts. Construction materials of the sampler presented in Fig. 8 are carefully selected and collector parts contacting with a sample are rinsed with nitric acid (pH<5) [51]. Baumgardner and co-workers proposed an automatic system for sampling rain water directly from clouds. They used the information collected by Mohnen [52] and Vong [53] within the Mountain Cloud Chemistry Project (MCCP). Electrolytic conductivity and pH are automatically measured in real time during sampling. Indications of pH are automatically controlled every day. In conductivity measurements outer temperature is taken into consideration. Samples are stored in 4 one-litre polyethylene bottles in a refrigerator. Electronic system con-

trol is based on the authors experience within the MCCP project and on literature studies. The sampler is equipped with temperature sensor and a system to measure wind speed. Fig. 9. presents the scheme of the collector for sampling precipitation water directly from clouds [54].

Fog Water Collectors

Fog sampling is more complicated than sampling atmospheric precipitation. A fully automated fog collector is described below. A component part of the collector is an aerodynamic tunnel through which atmospheric air containing fog droplets is sucked by a pump. Water droplets impinge Teflon strings which form a vertical screen. Larger droplets formed on impinging drain off to a sampling bottle. An average speed of air stream through the tunnel is 6 m/s. All collector parts which are in contact with fog droplets are made of either Teflon or polyethylene. At sub-freezing air temperature fog droplets are frozen and formation of larger droplets on the screen is not possible. Therefore, the system is equipped with a temperature sensor. When temperature drops below 0ºC, then a different sampling program is operated (atmospheric air flows through the tunnel for 30 min, and the screen is heated for 2.5 h; as a result, fog droplets flow down to the bottle). A precipitation detector is also installed which prevents samples from being collected during rain or snow [55]. A similar collector was applied by Collet [56]. Similar designs were also proposed by other authors [57-60].

Another type of collector is the Aerovirnoment Collector (AV). Fog collection is based on droplet impact upon a Teflon-coated rod moving at a rate of 3450 rotations per min. Centrifugal force moves the impinging droplets to polyethylene circle channels and then to polyethylene collection bottles. The scheme of the collector is given in Fig. 10 [61].

A string collector designed at the Atmospheric Science Research Center (ASRC) is composed of 150 strings (0.41 mm in diameter) spread out between two plates (Fig. 11). The collector rotates around vertical axis at a rate of 100 rotations/h. Due to impact upon rotating strings fog droplets are collected in the lower part of the collector (on the plate). Collector rotation is stopped periodically and water removed from the strings by means of a wooden hammer. After sampling, water from traps is transported into polyethylene bottles [61].

Fig. 12 presents the construction of a collector with a rotating outer arm designed in the California Institute of Technology. The rate of arm rotation is adjusted to sampling fog droplets which, via an inlet port, are collected in the bottles of a volume of 30 cm^3 fastened at the arm ends [62].

The detailed description of a collector of the same type was given by Keamer in 1993 [63]. The collector design is based on the former designs described by McFarland in 1984 [64] and by Jacob in 1984 [65].

Operation of the collector designed in the Desert Research Institute (DRI) is based on impact of fog droplets

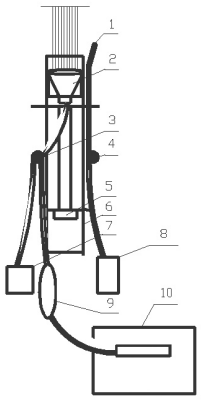

Fig. 9. Scheme of collector for sampling precipitation water directly from clouds [54]: 1 - deionised water spray nozzle, 2 - collector funnel, 3 - three-way solenoid, 4 - rinse pump, 5 - motor, 6 – collector tower, 7 - waste water container, 8 - de-ionised rinse water container, 9 - accumulator, 10 - refrigerator.

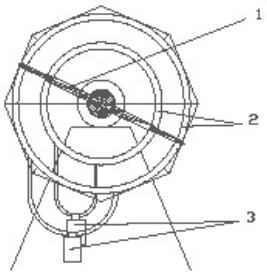

Fig. 10. Rotation collector for sampling fog [61]: 1 - rotating rod collecting fog droplets, 2 - channel collectors, 3 - bottles for collected samples.

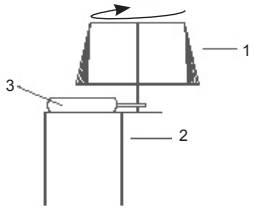

Fig. 11. Scheme of string collecting for sampling fog water [61]: 1 - nylon strings, 2 - motor.

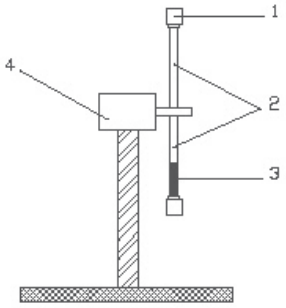

Fig. 12. Scheme of collector with rotating arm for sampling fog [62]: 1 - bottle for collecting fog sample, 2 - arm, 3 - inlet port, 4 - motor.

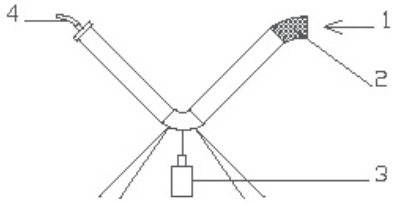

Fig. 13. Scheme of collector for sampling fog [62]: 1 - fog droplets inlet, 2 - polypropylene gauze, 3 - collecting bottle, 4 - vacuum channel.

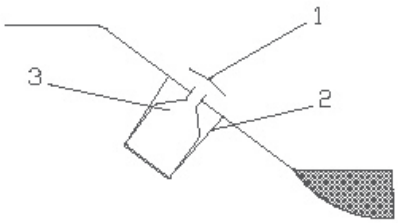

Fig. 14. Scheme of collector for sampling run-off water [78]: 1 - screen, 2 - plastics container, 3 - glass bottle.

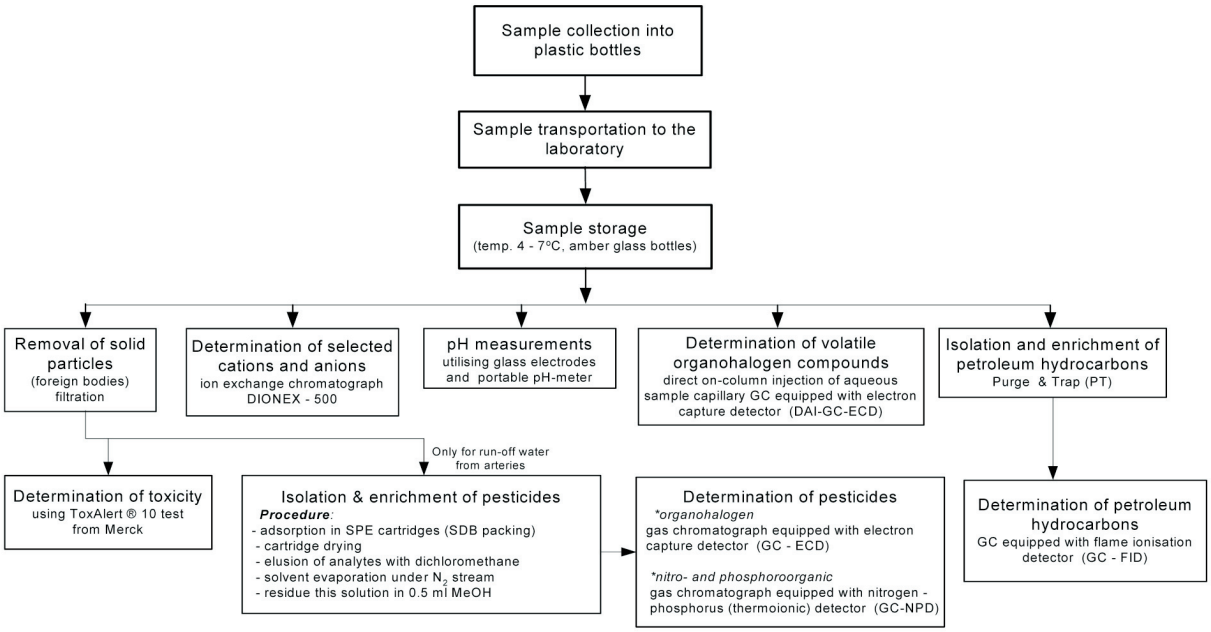

Fig. 15. Scheme of analytical procedure for atmospheric precipitation developed at Department of Analytical Chemistry, Chemical Faculty, Technical University of Gdansk [98].

on rotating rollers. The sample moves to a central roller and then directly to a polystyrene bottle [64].

In a collector presented in Fig. 13, fog droplets are collected on a polypropylene gauze (diameter 10 cm, thickness 4 cm) situated at the end of a V-shaped tube in V form made of PCV coated with Teflon. Flow rate of air stream in the tube is 1.7 m^3/min. Fog impinges the gauze; droplets which are formed in the process flow down to a bottle placed at the bottom of the tube [65].

Fog collectors of more complicated designs were proposed by Schell [67], Hoffmann [68] and Fuzzi [69]. Very often simple collectors are used in which fog droplets are collected on gauze screens made of either plastic materials (Teflon, polyethylene) [70-75] or steel [76,77].

Collectors for Run-off Water

Samples of run-off water are usually collected by the formation of an appropriate drainage system. Such an approach is most often applied for run-off water from arteries of traffic and arable land [78-81]. A sample of run-off water is collected from a specially prepared erosion ditch (a site selected after observation of groove erosion) manually by means of a scoop and delivered to the laboratory for analysis. Another approach is to place a glass bottle – a collector in an embankment [78,79]. The bottle is placed in a plastics container with a metal cover to protect the bottle from destruction. Due to application of the cover precipitation water cannot enter the bottle. The bottle neck is ca 2 cm above soil surface to prevent insects from entering the bottle [78]. The scheme of placing the collector is given in Fig. 14.

Fully automated collection systems are also available, which also enable measurement of some sample parameters [81-84]. The system designed by Striebel et al. [85] makes it possible to measure run-off rate, temperature, and pH of run-off water. The samples collected were transported to the mobile laboratory and subjected to analysis for the content of organic pollutants (PAHs,

nitrophenols, TOC, AOX) and inorganic ions (Cu, Cd, Zn, Fe, Pb). The main component of the system is a 10 l vessel connected by means of polyethylene tubes with devices used to measure physical and chemical sample parameters on-line. The whole system is mounted in an erosion tube placed in the ground at a depth of 0.5 m. Run-off water samples are transported via rubber tubes from the glass vessel to appropriate bottles (glass for organic analytes and polyethylene for inorganic analytes). To protect the tubes from clogging and damage, particles of a diameter larger than 5 mm are trapped on gauze filters. The analytical data are recorded and stored on computer disks. The collection system described above is quite complex and costly and therefore rarely used in practice [84]. A simple design collector for run-off water and its situating for sampling was presented by Perry [85].

Other designs of automatic collectors for sampling run-off waters were proposed by Kohonen [87] and Newburn [88]. Simpler and cheaper designs were proposed by Nieminen [89].

The collector described above is mainly used to collect run-off water from river surface during precipitation. The device can be installed where depth is not less than 50 cm. Precipitation water is collected via the upper funnel (area of 0.50 m^2) into the lower funnel (area of 0.09 m^2), which starts sinking. When the lower funnel goes down to the level that run-off water reaches an opening in a collecting tube of the first bottle, automatic sampling starts. When completely filled, the bottles are closed with the use of a stop valve. The successive flasks are filled as water collects in the lower funnel. The successive samples correspond to precipitation water columns of 1-2 , 4-5, 7-8, and 10-11 mm in the lower funnel.

Sampling of run-off water from building roofs is less complicated than from the arteries of traffic. A system for collecting water can easily be set up. A glass bottle is placed at gutter outlet; it collects water rinsing the roof surface. To protect the bottle from destruction it is appropriately situated in the ground or placed in a plastic container fixed to ground. If concentrations of a given analyte in rain water and roof run-off water are to be compared an additional collector is placed on the roof [90-98].

Summary

This work is a review of commonly used collectors for sampling atmospheric precipitation. Literature studies help select the most suitable collecting system as a procedure of sampling depending on research project, kind of sample and analytes.

Development of the analytical procedure for collected samples is also very important. The scheme of analytical procedure was developed at the Analytical Chemistry, Chemical Faculty, Technical University of Gdansk in Fig. 15 [98].

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