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**SEQUENTIAL, TIME-INTEGRATED  
COLLECTOR OF PRECIPITATION, GROUND  
WATER, AND SURFACE WATER FOR  
ANALYSIS OF ISOTOPES**

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for government purposes without the payment of any royalties therefore.

BACKGROUND

The present invention is directed, in general, to water sample collectors and, more particularly, to the sequential, time-integrated collection of precipitation, surface water, and ground water samples for analysis.

Large land-falling cyclones produce more than 8 inches of rain in 24 hours and impact the West Coast of the United States, particularly Northern California. In such hydrologic events, the amounts of chemicals and the amounts of isotopes vary in precipitation. The concentrations or relative changes in amounts of chemical constituents or isotopes may provide information to understand physical processes in these complex systems. To determine the relative amounts of oxygen and hydrogen isotopes, precipitation samples need to be collected from these storms at 15- or 30-minute intervals over a period of 24 to 48 hours. Increased understanding of these storms should improve forecasting and allow the National Weather Service of the National Oceanic and Atmospheric Administration (NOAA) to alert earlier the public, the military, and emergency services of these storms.

Various types of liquid sample collectors have been designed. Some collectors contain only one collection vessel, such as a bottle, and are used in bulk precipitation collection for acid-rain studies, for example. While other collectors contain 8 or 24 bottles, these collectors only allow 4 or 12 hours worth of collections, respectively, assuming 30-minute collection intervals. These collectors are inadequate for applications in which 48 hours worth of collections at 30-minute collection intervals are needed. For these types of applications, at least 96 collection vessels are needed to collect at least 96 separate water samples.

Collectors with sample vessels having volumes of 0.5 liter or greater have been used. These sample vessels are unsatisfactory due to the amount of headspace and consequent evaporation that results when low volume (e.g., 0.5 mL to 1 mL) precipitation samples are collected. Evaporation of water from a sample vessel after collection leads to isotopic fractionation, which changes the relative amounts of the hydrogen and oxygen isotopes of the water. To minimize evaporation of low volume samples, collectors are needed that use small bottles (e.g., about 20 mL in volume) to reduce headspace, and also that seal the bottles after collecting each sample.

There are also collectors that collect samples instantaneously or intermittently. These types of collectors typically load a fixed quantity of water at a specific time or at specific times, without collecting and homogenizing the fluid over a time interval before drawing a sample. These types of collectors are inadequate to accurately determine the relative amounts of isotopes in precipitation. To accurately determine the amounts of isotopes, time-integrated samples are needed. In other words, each sample collected needs to be representative of the entire collection interval for that sample. Otherwise, important information can be missed if the fluid is

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changing, such as the precipitation during a storm. For example, a narrow peak can be missed in a ground water or surface water tracer test when an instantaneous sample is collected at a predetermined interval.

Thus, a precipitation collector is needed that can collect multiple sequential, time-integrated samples as small as 0.5 mL at, for example, 30-minute intervals over an extended period of time, such as 48 hours or longer, and that can also minimize sample evaporation or hold it as close to zero as possible.

SUMMARY

It is an aspect of the present invention to provide a method and apparatus for the unattended collection of sequential, time-integrated water samples at preset time intervals over the course of a hydrologic event or test to determine amounts of isotopes or water quality.

Another aspect of the present invention is to provide a method and apparatus for the unattended collection of sequential, time-integrated water samples for ground water and surface water tracer tests.

Another aspect of the present invention is to provide a method and apparatus for the unattended collection of sequential, time-integrated water samples as small as about 0.5 mL at 15- to 30-minute time intervals over 24- to 48-hour periods or longer.

Another aspect of the present invention is to provide a method and apparatus for the unattended collection of sequential, time-integrated water samples in which multiple sample vials are sealed after each vial receives a sample to prevent evaporation.

These and other aspects are achieved according to the present invention by providing a sequential, time-integrated collector that collects multiple water samples as small as about 0.5 mL in multiple sample vials at preset intervals over an extended period of time. The collector includes an electronic controller that receives a start signal from various inputs, such as a manual push button, a timer, a cell phone, or a rain sensor. Once started, the controller actuates either of two electrically-actuated valves, each connected to a water reservoir. At preset intervals, water samples are transferred into plastic or glass sample vials in a multi-sample carousel. Evaporation that could change the isotopic composition of a precipitation sample is minimized by sealing the opening of each sample vial after it is filled by pressing the mouth of each vial against a flat, low-friction surface, such as a Teflon® sheet. Thus, after loading with a water sample, each vial is exposed to the air for less than 5 minutes, eliminating evaporation. With this approach, 96 or more vials can be used, and samples as small as 0.5 mL can be collected with no change in the relative amounts of hydrogen and oxygen isotopes of the water samples.

According to an embodiment of the present invention, there is provided a water collector for collecting multiple water samples over multiple preset time intervals. The water collector includes a first reservoir that captures water over a preset time interval and homogenizes the water during the preset time interval. A second reservoir receives a predetermined amount of a water sample from the water in the first reservoir at the end of the preset time interval, and any excess water is discharged from the first reservoir. A carousel contains multiple vials, including a first vial and multiple second vials. A sealing plate rests on top of the carousel and has a first opening under which the first vial is positioned. The carousel rotates after the first vial receives the water sample from the second reservoir to move the first vial underneath the sealing