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A Computer-Controlled Continuous Air Drying and Flask Sampling System

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ABSTRACT

A computer-controlled continuous air drying and flask sampling system has been developed and is discussed here. This system is set up for taking air samples automatically at remote places. Twenty glass flasks can be connected one by one or in pairs, and they can be filled at preset times, after preset intervals, or by online remote control. The system is capable of drying air continuously without operator intervention, with a flow rate of up to 4 L min^{-1}, to a dewpoint below $-50°C$. This enables continuous sampling, always retaining grab air samples of, for example, the last 24 h. This way, it is possible to decide afterward, according to online instrument records, if it is worthwhile to keep a single flask sample or even the whole diurnal cycle for later analysis at the laboratory. Dry sample air can be supplied to other analyzers. Four copies of the instrumentation are active at various places in Europe and have been shown to be able to run without servicing for periods of more than 1 month.

1. Introduction

Sampling of atmospheric whole air into glass flasks for later laboratory analysis of trace gas concentrations and isotopic ratios (commonly known as flask sampling) has proven to be a tool of major importance in global carbon cycle research (e.g., Conway et al. 1994; Keeling et al. 1995; Francey et al. 1995). In this way, air samples can be taken even at remote places with little infrastructure (and thus anthropogenic influences), providing better observation coverage of larger areas.

The simplest way to take a flask sample is to evacuate a flask in the laboratory, send it to the specific location, and have it filled by an operator by just opening the flask valve. Although this method is still successfully applied in one of the global networks (Keeling et al. 1995), it has some distinct disadvantages.

1) After an extended period of storage under vacuum, the inner surface of the glass flask is definitely not in equilibrium with the air that suddenly flows in, leading to several kinds of superficial de- and adsorption processes after evacuation and sampling, respectively, notably for CO_2 and its isotopomeres.
2) The air is not dried. This is unfavorable for the oxygen isotopic ratio $^{18}O/^{16}O$ in CO_2, being sensitive to oxygen atom exchange with traces of water (Gemery et al. 1996), and it impairs O_2/N_2 measurements on the air.
3) The sample quality depends critically on the vacuum integrity of the flask seal. Even without a leakage, there will be fractionating permeation going on through the applied elastomere O-rings.

All these effects tend to be more of a concern with lower flask volume. In the Keeling et al. (1995) network that uses 5-L flasks, the disadvantages are still manageable. However, for logistical reasons and the fact that less sample air is needed nowadays due to advancements in instrumentations, researchers strive for smaller sample flasks (down to 0.5 L). Unfortunately, the effects mentioned above then deteriorate the sample quality to an unacceptable point.

Thus, sampling strategies and techniques have changed. Most networks now use preconditioned flasks; that is, flasks filled with the appropriate pressure of dry air that resembles the expected sample air as well as possible in its analyzed constituents. These glass containers are filled in the field using a flushing device, which flushes the air at the sampling place through the flask for a certain period (15–30 min), after being dried by a chemical drying agent [usually magnesium perchlorate, $Mg(ClO_4)_2$] or by using a cryogenic cold trap if a power supply is available. The various networks have constructed very straightforward ''sampling suitcases,'' with which a minimally trained technician can easily and correctly perform this sampling procedure. All this has complicated the situation somewhat, since now some technical maintenance on the spot is necessary, such as leak tests, pump and battery maintenance, and above all frequent refreshment of the drying agent. Typical examples are the National Oceanic and Atmo-

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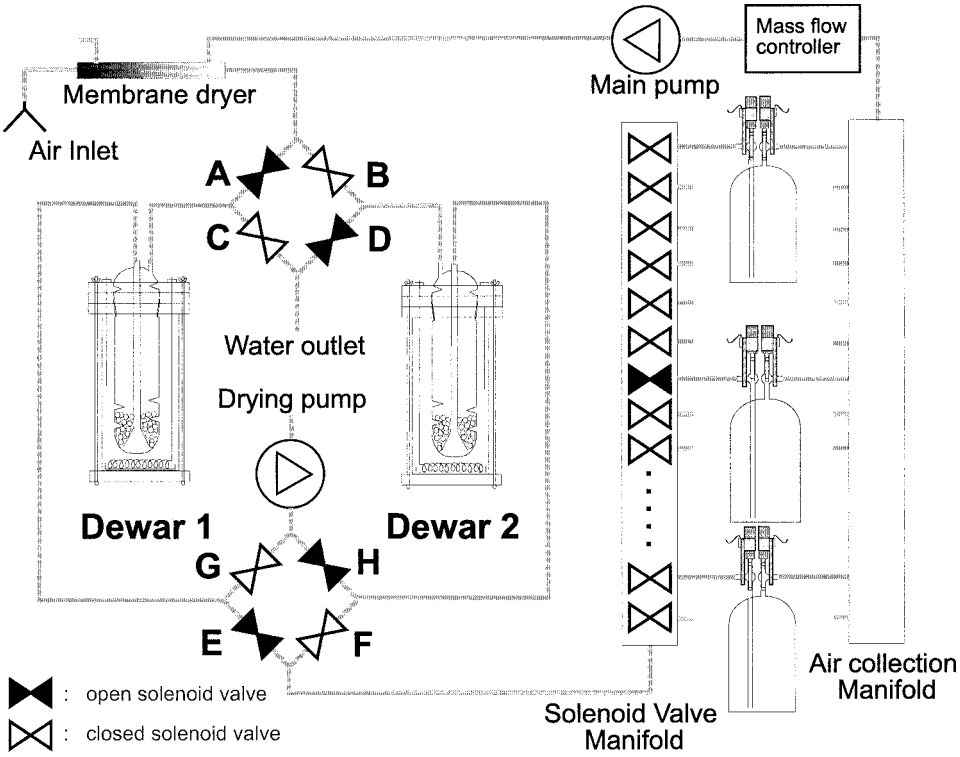

FIG. 1. Schematic drawing of the automatic flask sampling apparatus. After a predrying step (membrane dryer close to the air inlet) one of the two cold traps dries the sample air to a dewpoint below −40°C, while the other twin cold trap is regenerated at +40°C. The cryocoolers of the dewar vessels and the control electronics are not shown here. The detailed working scheme is explained in the text.

spheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) AIRKIT for weekly flask sampling at remote stations and their double-suitcase aircraft sampler, capable of automatically sampling flasks during one flight (Tans et al. 2001). The typical sampling frequency for a flask sampling site is preferably once a week, or at least once every fortnight. Depending on how remote the actual location is, this requires a significant amount of (traveling) time by the person responsible for the sampling. Further requirements on the moment of sampling, such as a minimum wind speed from a certain (clean air) wind sector or hour of day interval, can normally only partially be met by a person who can only devote part of his or her time to this work (again depending very much on the travel time that is required to the sampling place).

Another kind of study requires very frequent flask sampling, for example, studies using diurnal cycle characteristics (Zondervan and Meijer 1996; Meijer et al. 1996; Takahashi et al. 2002). Such sampling in diurnal cycles even can be ''continuous,'' as in the first two cited references above. That is, flask sampling goes on continuously, refilling the same flasks every 24 h, until an atmospheric condition, favorable for the specific experiment, has occurred. The confirmation that such an ''event'' has occurred can only be drawn in hindsight with the knowledge from online measurements. Thus, the storage of the last 24 h of air in flasks at all times is a necessity until confirmation is reached.

It is clear that an automated sampling apparatus supplying dry air samples would have considerable advantages, or would even be indispensable, for the purposes mentioned above. We have built such an instrument. Up to 20 flasks can be connected, a dry-air flow of up to 4 L min^{-1} can be supplied continuously, and the flasks can be filled with either ambient atmospheric pressure or with up to 150-kPa overpressure. Every flask is closed (electrically actuated) with its own two O-ring valves directly after flushing. The flask-filling schemes are totally flexible, and an online connection via the Internet or a modem and a mobile phone allows total control over the system, as well as the monitoring of all the critical parameters. This system is much more sophisticated, after further development of the equipment briefly described by Zondervan and Meijer (1996), which did not meet the above-mentioned requirements.

2. The instrument

A schematic drawing of the system's main parts is shown in Fig. 1, and an overview photo of the instrumental arrangement is given in Fig. 2. Outside air is sucked through the drying system (including a membrane predrying step), through one or more of the 20

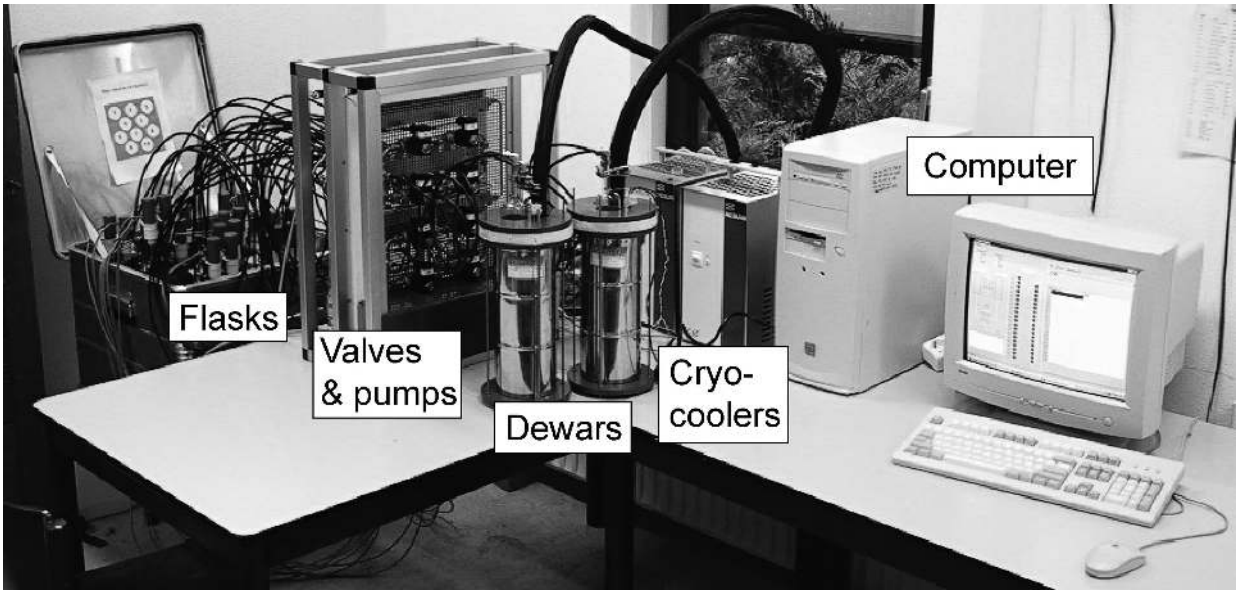

FIG. 2. Pictorial overview of the complete installation: the valve manifolds are hidden on the backside of the solenoid valve frame; only 10 of possible 20 flasks are connected.

sample flasks that is opened, to the pump. The dry air is then pumped out of the system again, and used as a ''drying agent'' in the predrying system. In the following, we will discuss the design of the different parts, namely, the drying concept, the airflow system including the flasks, and the electronics and software, including some remarks on installation tests. The valves in this drawing (shown as double triangles) are open when shaded black.

a. The drying concept

The system is designed to be able to dry, continuously and unattended, an airflow of up to 4 L min^{-1} under all meteorological conditions. This means that an automatic recovery of the drying mechanism must be included, and that during the recovery another means of drying must be provided. We chose a double cryogenic drying system as the most straightforward solution.

To freeze out the water vapor from the sample air, we use cold traps made of glass (drawn in the dewar vessels). They have an outer diameter of 5 cm and a total length of 28 cm. The airflow is forced through the entire cold trap from top to bottom, since the air exit is a small glass tube, with its entrance close to the bottom of the cold trap. The glass bodies have pencil-tip-like indentations at the top and three rows of indentations between 2 and 6 cm from the bottom to ensure turbulent flow and good contact of the air with the cold-trap walls. The lower 2.5 cm are filled with 3-mm-diameter glass spheres to prevent ice crystals falling to the bottom from being sucked through the center tube to the cold-trap air outlet. The lower 15 cm of the cold traps are immersed in a silicone-oil-based thermofluid (M60.115.05, Renggli, Rotkreuz, Switzerland); each in a separate 2-L stainless steel dewar vessel. A rubber-sealed plastic–foam–plastic sandwich lid insulates the top of the dewar from the outside air and facilitates all connections. The closure of the lid is very important, in order to prevent outside water vapor from entering the dewars, as it would gradually form a ''drop'' of water (or ice, respectively) at the bottom of the dewar and in between the heating wires. With time, even a volumetric problem would arise and make the thermofluid flow over. A Pt-100 sensor measures the thermofluid temperature. The fluid can either be cooled down to ≈ -55°C by an immersion cryocooler probe (CC-65 II-R, Neslab Instruments, Portsmouth, New Hampshire) or heated to $+40$°C by a resistance wire coil at the bottom of the dewar. The glass cold traps are designed such that they can take up to at least 75 g of water, which corresponds to an airflow of 4 L min^{-1} with a relative humidity of 90% at 25°C over a 15-h period.

At the inlet of the autosampler valve frame, there is a cold-trap changeover valve setup, consisting of four single solenoid valves [Fluid Automation Systems (FAS), Versoix, Switzerland]. At a given time the sample air flows through valve A and cold trap 1 (with the dewar vessel at -55°C) to another similar four-valve installation and enters the solenoid valve manifold through valve E. At the same time, a small membrane drying pump (KNF Neuberger, Freiburg, Germany) pumps room air through valve H, backward through cold trap 2 (now heated to $+40$°C) and valve D to the water outlet. In this way, water that was trapped in cold trap 2 in an earlier stage is removed. Theoretically, the difference between the absolute humidities in saturated air at 40°C and the laboratory air can be removed per unit

flushed air. However, condensation will occur in the colder parts of the drying system and these water traces will only be removed again with the dry warm air as soon as the cold trap itself is dried. The energy consumption of the solenoid valves keeps their body temperatures during operation sufficiently high to prevent condensation in the valves. In the following, cold trap 2 has to be prepared for drying again. Valves H and D are closed, and dewar vessel 2 is cooled down to −55°C again. During this process, the remaining humid air in the tubing between valves H and F on the one side and D and B on the other side (twice ≈ 0.5 m of tubing in practice) is also effectively dried. The total regeneration of a cold trap takes less than 12 h: 1 h heating, 9 h flushing, and 1.5 h cooling down to −40°C (maximum flushing temperature) is sufficient. Depending on the environmental conditions, the cold-trap changeover time can be extended to 18 h (our normal setting) or even 24 h. This 18-h figure, combined with the moisture capacity of the cold traps, makes the system suitable for continuous dry air sampling in virtually every situation. Still, it is favorable to remove a part of the water vapor content already close to the air inlet of the system, especially if the inlet is far away from the autosampler, as is the case for air inlets mounted on masts and towers. The autosampler system is perfectly suited for the addition of a Nafion membrane predryer (MD 110-72-S, Perma Pure, Toms River, New Jersey) close to the intake. A Nafion dryer consists of a polymer membrane tube inside a stainless steel one. The membrane material is only permeable for water vapor, which is actively absorbed by sulfonic acid groups and moved along the water vapor gradient. The incoming air passes through the inner tube, while the volume between the inner and outer tubes is flushed with dry gas in the opposite direction to maintain the vapor gradient and remove the water vapor to the waste outlet. This dry air is, in our case, continuously supplied by the outlet of the autosampler. Since the composition of this dry air is almost identical to that of the inlet air (the dry air is actually the inlet air from a short time before), the risk of influencing the sample air composition due to eventual diffusion processes through the membrane is minimized. The dry air support to the Nafion dryer obviously requires double tubing between the autosampler and the inlet. In this arrangement, shown in Fig. 1 the air is used as a drying agent flowing from the upper-right to the upper-left connection, and the sample air from left to right. The Nafion predryer removes between a half and two-thirds of the water vapor content from the sample airstream, with the exact value depending on the respective temperature and humidity (den Besten and Neubert 1998). In setups with long inlet tubing, the major advantage of using a Nafion predryer is to prevent water vapor from condensing anywhere in the inlet line, for example, if it is installed underground between a tower and a laboratory building. We thereby exclude the possibility of oxygen atomic (and thus also isotopic) exchange between CO_2 and water close to or at the condensation conditions (Gemery et al. 1996), which might heavily alter the isotopic composition of atmospheric CO_2. The additional effect of lowering the water vapor load of the drying system is also welcome, although it is not strictly necessary, except under very hot and humid sampling conditions.

The drying system has been extensively tested using flows of heated air (to over 30°C), and moisturized to virtually 100% relative humidity. The final design of the cold traps is able to effectively dry the air to a dewpoint of ≈−50°C under all normal circumstances. The moisture capacity of the cold traps is large enough to make continuous operation possible (especially with the assistance of the Nafion predryer). The drying system is very robust and normally works error free for several weeks without maintenance.

b. The airflow system and the flasks

The core of the airflow system is made of 6.35-mm o.d. stainless steel tubing. The two 10-port solenoid valve manifolds (distributing the air to the single flasks) and the air collection manifold (collecting the air after flushing through any one of the flasks) are custom made from aluminium. The solenoid valves are of the same type mentioned above. For connection purposes we use vacuum-tight tube fittings (Swagelok, Solon, Ohio). The tubing between the system and the flasks is 6.35-mm Dekabon 1300 (Saint Gobain Performance Plastics, Gembloux, Belgium), with 4.3-mm inner diameter and a length of ≈2 m per tubing. This is an aluminium tubing, coated with a thin polyethylene layer on the inside and a thick protective polyethylene tube on the outside. We selected this material because it is robust (very low risk of leak-causing damage) and yet flexible and lightweight. Furthermore, it is easy to connect, and thus a full set of 20 flasks can be exchanged in a short time. Any influence on the composition of the transported air is virtually absent, as aluminium strongly restricts diffusion into or out of the tubing. The relatively large inner diameter accommodates flows of several liters per minute over tens of meters with only a small pressure gradient. Such a high flow is desirable, since it minimizes the residence time of the air in the tubing (in particular if the inlet point is far from the autosampler). However, care must be taken to get the air into thermal equilibrium with the room air before entering the flasks (after all the air is cooled down to ≈−55°C), as otherwise mass-dependent isotope (or gas type) fractionation will occur.

The valve manifolds are made such that the dead volumes are minimal. Preventing considerable dead volumes (especially enclosing all tubing between manifold and flasks), as well as the risk of one leaking flask connection spoiling the whole series of samples, were the main reasons to have a solenoid valve (manifold) in addition to the flasks' own electrically actuated

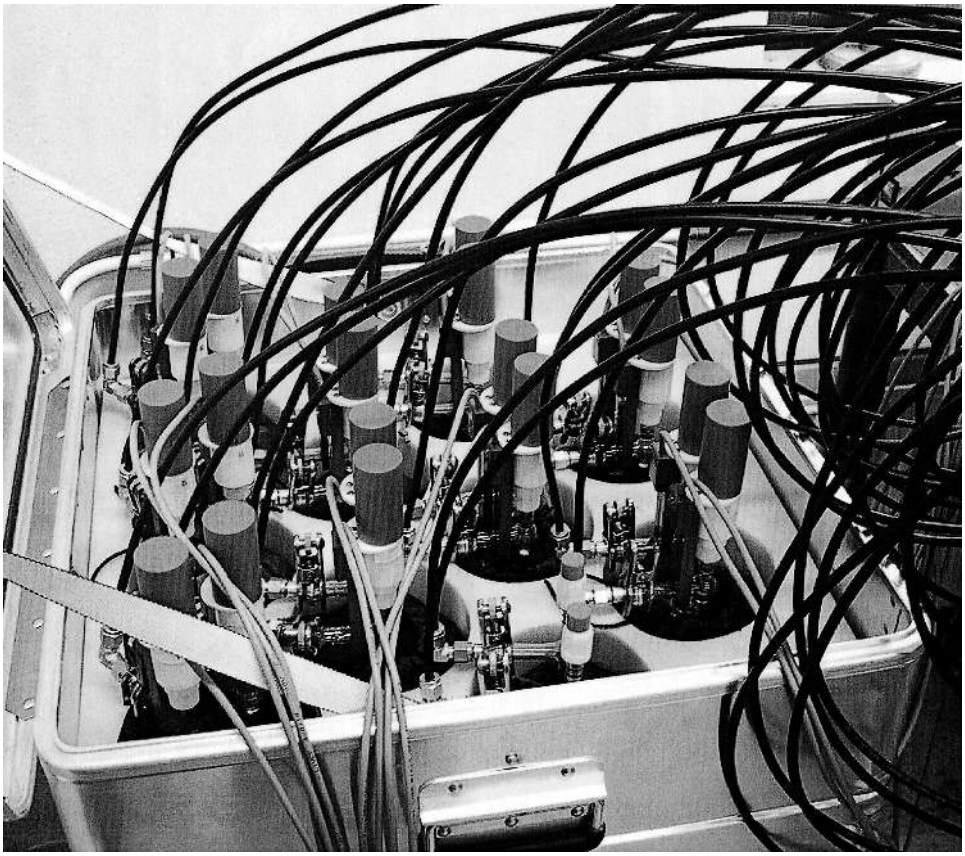

FIG. 3. Pictorial view of electric valve actuators in place on air sample flasks. One flask is shown without actuator; all of them are connected to the manifold by Dekabon tubing.

valves. Closing the flasks with their own valves after each flushing cycle is indispensable for reliable sample storage. Only then is the sample air closed off from any contact with metallic or plastic materials. Possible sample deterioration during months of storage in the flasks, and its dependence on O-ring material and filling pressure, have been carefully tested in another study (Sturm et al. 2004) and were found to be acceptable for all analyzed components under our regular sampling conditions. In this arrangement it is possible to flush just one flask, or two or more in series, if properly connected by glass tube shortcuts. We avoided splits from occurring anywhere in the airflow, since these can cause fractionation severe enough to be noticeable in the O_2/N_2 signal (Manning 2001).

The flasks we use are 2.5-L-volume glass flasks, with two O-ring high vacuum glass valves (Louwers, Hapert, Netherlands) and (one O-ring) Rotulex glass–metal connections. The commercially available manual valves were automated by home-built click-on electromotoractuators. Such actuators are put on each of the 20 O-ring valve sets. Their positions (open, closed, moving up, moving down) can be read back using microswitches or, in a newer version, a potentiometer. The actuators included in Fig. 1 and shown in Fig. 3, are installed on top of the flask valves. All O-ring material was Viton (quality K51414, Eriks, Alkmaar, Netherlands).

In the normal, ambient pressure filling situation, the main pump (KNF Neuberger) sucks the air through the system and is positioned behind the flasks. In this way, an eventual influence of the pump on the air's composition will not affect the sampled air. Pressure equilibration is reached by closing the flask inlet valve with a certain delay after the outlet valve is closed. In case the samples have to be filled with overpressure as compared to the actual ambient pressure (e.g., on board an aircraft) for a larger amount of sampled air, or according to the needs of applied analyzers, putting the pump before the flasks is unavoidable, and it is placed right before the solenoid valve manifold. In this arrangement special care must be taken to select a pump type with minimal influence on the air composition (most notably the O_2/N_2 ratio).

Finally, a mass flow controller (F-201C, range 0.1–5 L min^{-1}, Bronkhorst, Ruurlo, Netherlands) monitors and controls the airflow at a value preset by means of a potentiometer. For the overpressure arrangement the final filling pressure is regulated using a proportional relief valve (Swagelok RL3 series) or an absolute pressure relief valve (Tavco, Chatsworth, California). After

flushing the flasks and before being returned to the Nafion dryer, the dry sample air can be used to flush the online analyzers, for example, a gas chromatograph for CO_2, CH_4, and CO concentration measurements. A small flow might be branched off without negative consequences for the predrying step.

c. Electronics and software

Obviously, the system is fully automated. A microprocessor unit performs the low-level steering and controlling tasks for all valves, switches, temperatures, and flows. Several precautions have been built in to guarantee a safe and secure drying and sampling process. The electroactuators of the sample flask O-ring valves are provided with microswitches to report their position back to the microprocessor. The temperatures of the two cold-trap dewars are continuously measured; there is permanent double protection against overheating, both on a hardware basis close to the heater itself and on a software basis in the microprocessor, even if the connection to the computer should be broken (being the third safeguard in normal operation). The airflow in the system is continuously monitored and the operation will be stopped if the flow is lower than a preset minimum.

The microprocessor unit communicates with a personal computer via an RS-232 serial connection, through a series of coded commands. The computer program (written in Delphi Pascal, Borland, Scotts Valley, California) performs all high-level automated tasks. This program gives continuous insight into the state of the system. It keeps track of all flask flushing and closing times, the status and history of the cold traps, the airflow, etc. It handles the sampling procedure according to the user-defined protocols. These protocols are very flexible, such that the autosampler system can be put to use for various purposes, such as continuous diurnal cycle sampling, (multiple) flask pair sampling once a week, sampling according to external criteria such as, for example, wind direction and wind speed, and constant or strongly varying CO_2 concentrations.

All of these settings can be changed in real time. Usage of a (cellular) phone and modem connection and a commercial software tool such as, for example, Virtual Network Computing (AT&T Laboratories, Cambridge, United Kingdom), by which the computer screen comes under direct remote control, leads to a fully remote-controlled autosampler system. One can then, from a distance, take one or more flask samples ''manually,'' decide whether to preserve samples that were taken before, change the automatic sampling sequence, etc. Finally, one can assure oneself of the error-free operation of the system or, if some error occurs, decide if one can solve or circumvent the problem by online manipulations, or if someone has to pay the system a service visit. The actual state of the system is saved in a file, which might be sent off by e-mail on a regular schedule. After a power failure at the remote station, the system can start up again automatically. According to the latest status information it can decide the appropriate action to be taken, like going on in the same configuration after a short break, or heating, drying, and cooling a cold trap first after a longer thawing period.

Figure 4 gives a snapshot of one of the screen setups of the computer program. The left-hand side of the screen always shows the schematic flow system, with indications of the present valve status and flow route [through which cooler, and which flask(s)], as well as the cold-trap temperatures and switching times, the sample airflow, and an activity log window. The right-hand side can either show (cf. the tabs on top) the actual state of flask filling and flushing or the filling history, the flask arrangement edit screen (single flasks, serial couplings, or flasks to be preserved or not in use), a valve test scheme, a graphical representation of the measured flow and temperatures of the last 7 days, the dryers' activity log, or the list of parameters (such as cold-trap switching times and temperature requirements) that can be altered. The software is currently in its second version. Further extensions are envisaged, especially concerning automatic, externally driven ''flask filling/saving'' decision algorithms.

d. Installation tests

Once the autosampler has been assembled, the full setup has to be leak tested. For the ambient pressure system, leak testing can be easily performed using the main pump and the flow controller of the system itself. Nearly all parts of the autosampler can be connected to the pump–flow controller combination, such that the flow through the system before the testing point is blocked, and any remaining flow in that case means a leak. Working one's way through the system from end to beginning, one can perform a reliable leak test without additional tools. Moreover, any leakage will be overestimated, as during normal operation (flushing sample air) there is only a small pressure gradient between the outside and inside of the tubing. The flow controller is sensitive down to about 20 mL min^{-1}, which is sufficiently low for leak-testing purposes, though the use of a bubble flow meter is recommended. Usually, there are a few leaks to be discovered the first time a complicated system like this is assembled, with many valves and connections. These sorts of leaks, however, can be easily identified and eliminated. Once leak free, the system will reliably remain so as long as the tubing of the system is left in place. The flask connections, for which we use O-ring Rotulex connections, are not problematic. Moreover, since they are near the end of the system, it is easy to test their vacuum integrity every time new flasks are connected. For overpressure systems, the same procedure applies for the air-drying part, still working at lower than atmospheric pressure. The overpressure part downstream of the pump, including the solenoid valve manifold, all flask connections, and the air collection manifold, can be checked by applying leak detection fluids.

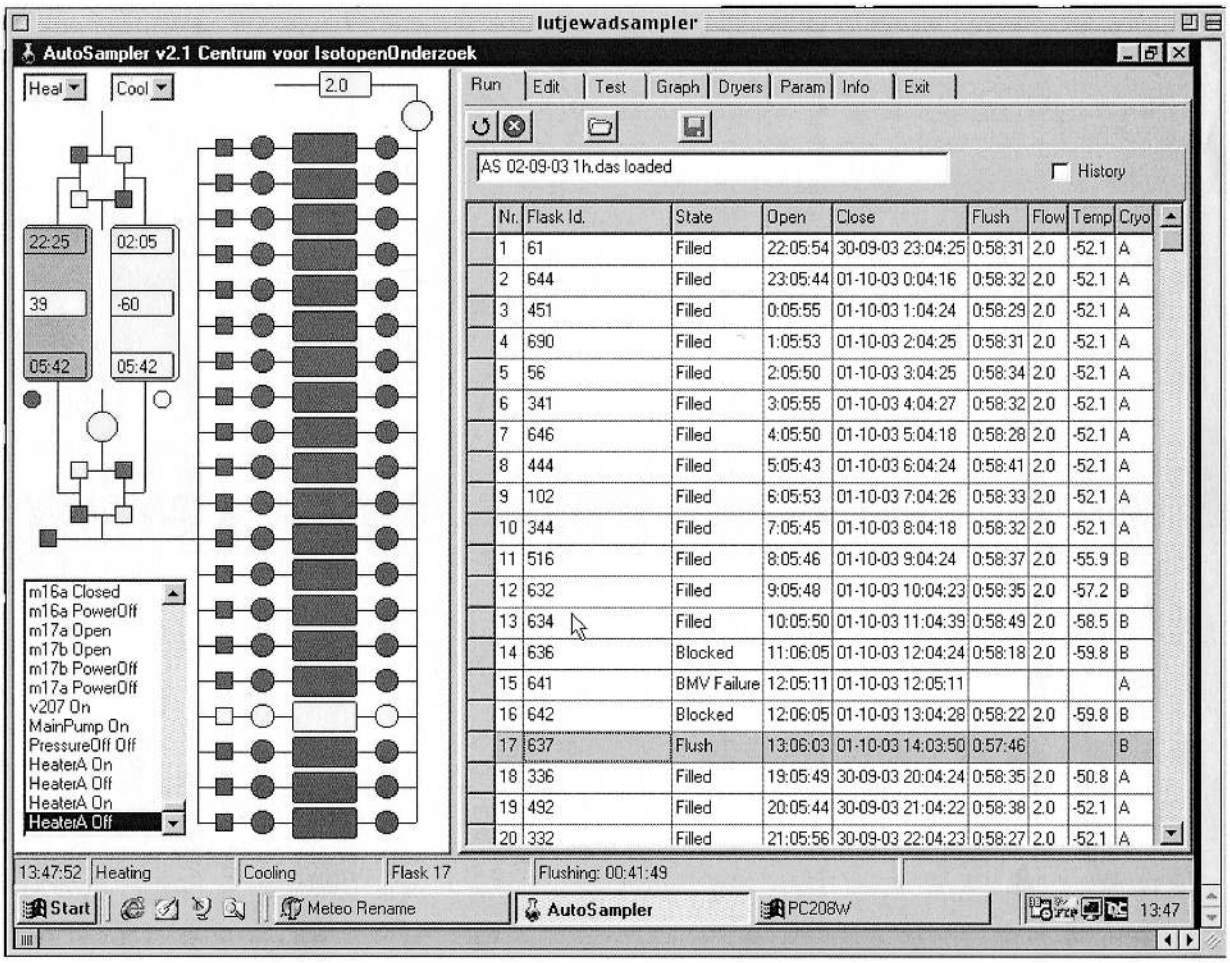

FIG. 4. The main screen of the computer program; on the left side showing the state of the dryers and the gas flow through the system (open valves are shown in light gray), including flask number 17. An activity log is kept in the lower-left corner. The right side shows either the actual flask filling details (given here) or auxiliary information as described in the text.

3. Example of results

Since the second half of 2001, four copies of the autosampler system have been deployed and are functioning within the European Union (EU) Environment and Climate project Aerocarb, which is part of the Carbo-Europe cluster of projects. The systems were installed in Hegyhatsal, Hungary; Saclay, France; Heidelberg, Germany, and at our atmospheric monitoring station in Lutjewad, at the North Sea coast close to Groningen in the Netherlands. They are used for continuous diurnal sampling, with the main goal of trapping ''pollution events,'' in which a diurnal cycle shows a relatively large excursion in CO_2 mixing ratio, that is, from near-background conditions to much higher values and back again, and a concurrent excursion in CO, while at the same time the wind direction and velocity remain relatively constant. Such conditions are a firm indication that a considerable amount of fossil-fuel-derived CO_2 is present in the specific air mass. The analysis of these events is used to determine the relation between the CO mixing ratio and the amount of fossil-fuel-derived CO_2 that is present. The only straightforward measure of the amount of fossil-fuel-derived CO_2, ^{14}C (radiocarbon), is used in these calibration measurements, but is too expensive for wide use. Even more important, it cannot be monitored quasi continuously with high time resolution, while CO can be monitored online with a time resolution on the order of 5 min, for example, by gas chromatography. Fossil fuel combustion is, in Western Europe, the most important source of CO by far. Though there are other CO sources, and OH radicals act as an independent sink, on a short regional time scale the correlation of CO and fossil-fuel-derived CO_2 concentrations is normally very good. Regional differences are to be expected according to the respective fossil fuel mix; for example, in the Netherlands where there is a high percentage of (clean) natural gas burning, the CO production rate will be lower than in regions with a high percentage of solid fuel use. Thus, once the relationship of CO to fossil-fuel-derived CO_2 is established (and

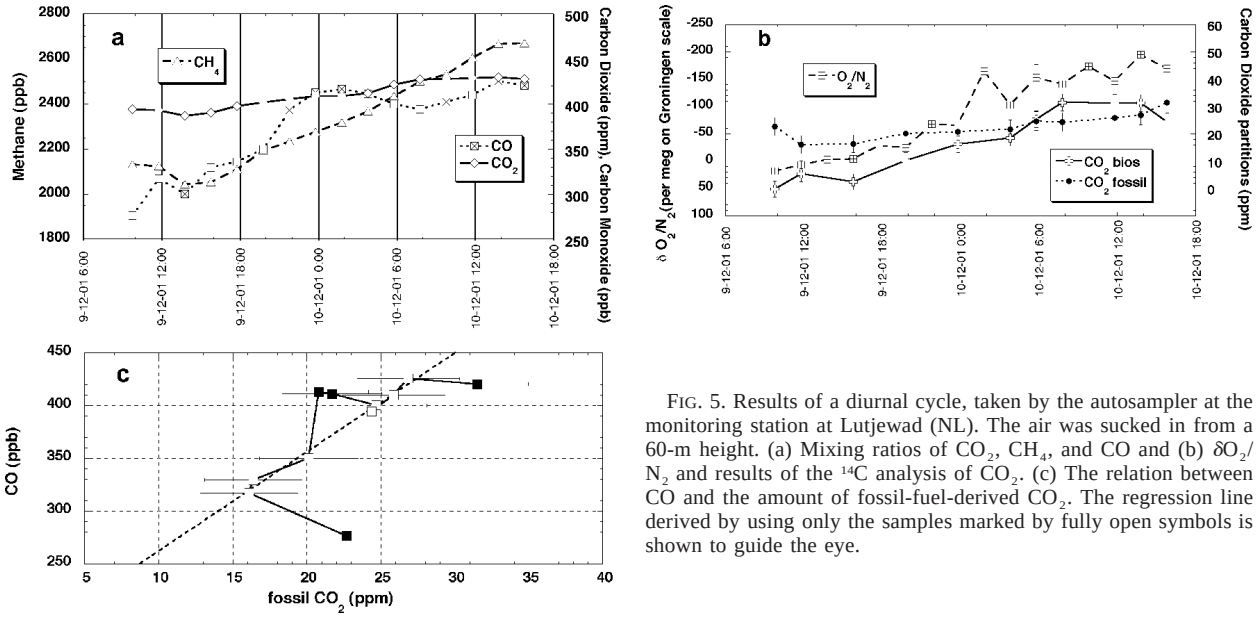

FIG. 5. Results of a diurnal cycle, taken by the autosampler at the monitoring station at Lutjewad (NL). The air was sucked in from a 60-m height. (a) Mixing ratios of CO_2, CH_4, and CO and (b) $\delta O_2/N_2$ and results of the ^{14}C analysis of CO_2. (c) The relation between CO and the amount of fossil-fuel-derived CO_2. The regression line derived by using only the samples marked by fully open symbols is shown to guide the eye.

monitored), CO can be effectively used as a proxy for the amount of fossil-fuel-derived CO_2 present in the total CO_2. Some first experiments of this kind have been performed by Zondervan and Meijer (1996) and Meijer et al. (1996), and it has been decided that during two years of the the Aerocarb project automated diurnal cycle flask sampling will get full attention, at at least four different locations. It was this type of application that the autosampler was developed for in the first place. Naturally, the sampling strategy can be adjusted to other needs by monitoring other tracers online, by choosing CO_2 events of purely biogenic origin, that is, a CO_2 peak without enhanced CO concentrations, to determine, for example, the $\delta^{13}C$ signature of CO_2 released by the biosphere, or for any other online–laboratory measured tracer combination.

To illustrate the main aims of the autosampler, Fig. 5 shows the results of one such event, captured at the Lutjewad station (53.38°N, 6.37°E, 1 m above sea level). A diurnal cycle was sampled, filling a flask every 90 min from an intake at 60-m height, covering the period from 0950 LT 9 December 2001 until 1550 LT 10 December 2001. Figure 5a shows the mixing ratios of CO_2, CH_4, and CO. During stable meteorological conditions, all concentrations were already enhanced at the beginning of the experiment, and they increased until the end; the CO_2 concentration varying in the range from 387 ppm up to 427 ppm. This is not a classical event, including background conditions before and afterward. Figure 5b shows the results of the ^{14}C analysis on CO_2. According to Meijer et al. (1996), the total CO_2 was separated into background, biospheric, and fossil contributions, assuming constant background values and a biospheric ^{14}C content that is equal to the atmospheric background. Fossil fuel, however, no longer contains any ^{14}C, as the radioactive half-life period is only about 5730 yr. The biospheric and fossil-fuel-derived CO_2 contributions both increase to a maximum of 31.5 ppm (right-hand side of the *y* axis), though at slightly different times. Also shown in Fig. 5b is the $\delta O_2/N_2$ value, which has also been analyzed in the samples. Analogous to stable isotope measurements, it is given in per meg [1 per meg = 0.001‰; cf. Keeling and Shertz (1992)], as the deviation of the sample O_2/N_2 ratio from a reference gas O_2/N_2 ratio. The results are given on the local Groningen scale, defined by cylinder 2534, as there is no international transferable scale yet. This cylinder had been filled with clean air at Lutjewad station, and its O_2/N_2 ratio established the scale zero point that is propagated to all O_2/N_2 (working) reference cylinders at our institute. Note that the axis is inverted in order to show the anticorrelation between CO_2 concentration and $\delta O_2/N_2$. The linear regression of $\delta O_2/N_2$ versus CO_2 yields an oxidative ratio of (-0.96 ± 0.06) mol O_2 being used per mol CO_2 added to the air (correlation coefficient $R = 0.97$). Here, a lower value might have been expected, as biospheric processes yield a mean of (-1.1 ± 0.05) mol mol^{-1} (Severinghaus 1995) and CH_4 burning (which is always prominently present in the fossil fuel use of the Netherlands) has an oxidative ratio of -2 mol mol^{-1}. However, depending on the soil conditions, variations of the biospheric oxidative ratio between -1.0 and -1.2 have been observed by Severinghaus (1995). On short time scales the ratios might deviate considerably from the mean value as induced by local transport processes. Finally, Fig. 5c shows the relation between the CO concentration and the amount of fossil CO_2. As one can see, there is a good correlation, with a slope of (9.4 ± 0.5) ppb CO per ppm fossil CO_2 for the majority of samples (open symbols),

a value that is quite typical for this relation in winter in the Netherlands (Meijer et al. 1996). However, there are also four samples clearly deviating from this mean value. They have been intentionally left out of the fit to show the nice correlation of the other samples, but there is no known reason to reject these data! A back-trajectory analysis of the respective air masses could not yet be performed on this diurnal cycle but such an analysis might also contribute important information toward explaining, for example, the strong deviations from the mean CO/fossil CO_2 ratio in these data, which might arise from the significantly differing travel times and trajectories of the air parcels. In order to use CO as a surrogate for fossil-fuel-derived CO_2 determination, this CO/fossil CO_2 ratio has to be known on a regional and temporal basis and of course has to be constant to a certain extent. The example shows that there is considerable variation that needs to be further assessed and taken into account. A flask autosampler is a very valuable option for taking series of samples in selected periods of time to get a broad database and to finally find out if the envisaged surrogate methodology is feasible.

The diurnal cycles contain much more detailed process information. The ^{14}C signal, together with background air information, and combined with the detailed (^{13}C and ^{18}O) isotopic analysis of CO_2, the $\delta O_2/N_2$ signal, and possible other tracers, deliver a very detailed ''fingerprint'' of the air parcel (Zondervan and Meijer 1996; Meijer et al. 1996), including, for example, the $\delta^{13}C$ signature of the fossil fuel and its oxidative ratio, that is, the ratio O_2/CO_2 when burnt. These kinds of results will be reported in forthcoming papers by the Aerocarb project members. The other type of application of the system, that is, weekly sampling at a remote place, is about to commence at the Hegyhatsal station in Hungary and will start at the 213-m-high research tower of the Royal Netherlands Meteorological Service (KNMI) at Cabauw, Netherlands, in early 2004.

4. Conclusions

We have developed an apparatus for the continuous automatic flushing and filling of up to 20 sample flasks with dry air. This dry airstream can be used for other instrumentation packages (e.g., a gas chromatograph) as well. The instrument has proven to work reliably in the four field situations in which it is currently being put to use operating in a continuous diurnal sampling mode. The flexibility of the system makes it useful for other settings as well, most notably that of periodic (e.g., once a week) flask sampling in a remote, unmanned station. In this latter situation one could even take several (pairs of) samples in a row on a certain day, and decide later, for example, based on meteorological circumstances or measured concentrations, which of these flasks are going to be preserved. In this way, flask sampling at such a station can be performed under better-defined, and more representative, conditions. This would reduce the scatter on the time series and thus also increase its value for simulation study verification purposes.

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