



JAPCA

ISSN: 0894-0630 (Print) (Online) Journal homepage: <http://www.tandfonline.com/loi/uawm17>

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To cite this article: Joachim D. Pleil , Karen D. Oliver & William A. McClenny (1987) Enhanced Performance of Nafion Dryers in Removing Water from Air Samples Prior to Gas Chromatographic Analysis, JAPCA, 37:3, 244-248, DOI: [10.1080/08940630.1987.10466219](https://doi.org/10.1080/08940630.1987.10466219)

To link to this article: <http://dx.doi.org/10.1080/08940630.1987.10466219>



Published online: 08 Mar 2012.



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Enhanced Performance of Nafion Dryers in Removing Water from Air Samples Prior to Gas Chromatographic Analysis

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Nafion tube dryers were tested for applications of sample preparation prior to gas chromatographic analysis. Steady-state and time-dependent drying efficiency were measured for four similar dryers using a 50-mL/min sample flow at 95 percent relative humidity at room temperature. A procedure was developed in which water removal efficiency was temporarily enhanced by a factor of 20 as compared with the steady state. This was accomplished by heating the dryer while purging it with a dry sample stream immediately prior to processing the gas sample of interest. The procedure was tested on an automated gas chromatographic system equipped with a cryogenic sample preconcentrator. Data for 15 volatile organic compounds of interest showed no effect of this procedure on sample integrity; some improvement in run-to-run precision was observed.

The accurate identification and quantitation of the many trace level volatile organic compounds (VOCs) in ambient air generally requires preconcentration of analytes to enhance instrument sensitivity. Analyses are typically performed with high-resolution chromatographs coupled to appropriate detectors.¹⁻⁵ In this laboratory, preconcentration is accomplished by passing whole air through a cryogenic trap. The sample is then thermally desorbed onto a capillary-column gas chromatograph (GC) using flame ionization detection (FID), electron capture detection (ECD), and/or mass selective detection (MSD). The methodology has been described elsewhere.⁶⁻⁸

Cryogenic trapping has been shown to be a preferred preconcentration technique, particularly for the lighter VOCs, i.e., C₁, C₂ and C₃ compounds.^{6,9-13} These compounds tend to have low breakthrough volumes on the solid sorbents (such as Tenax-GC) that are often used as preconcentration media. However, the co-collection of ambient water vapor in a cryogenic trap can cause a number of problems that are not encountered while using the hydrophobic Tenax-GC. Ice formation during sample collection can alter sample flow or clog the trap, the variability of ambient water vapor can cause detector baseline shifts, and co-collected water can cause blockage upon injection onto the capillary column in separation techniques that require subfreezing initial GC oven temperatures. In extreme cases, the excess water when eluted can even extinguish the hydrogen flame of an FID.

Water-related problems can be alleviated by various methods. The simplest method is to reduce sampling volume, but this also reduces sensitivity. Other techniques involve predrying the sample with various desiccants; however, these desiccants can affect sample integrity by adsorbing or outgassing some compounds. Also, desiccants are inconvenient to use because they require periodic replacement or reconditioning.

In this laboratory, a permeable membrane dryer is used to remove water vapor from a flowing sample stream. The permeable membrane consists of Nafion tubing (E. I. DuPont de Nemours, Inc., Wilmington, DL), a copolymer of tetrafluoroethylene and fluorosulfonyl monomer, that is coaxially mounted within larger tubing.¹⁷ The sample stream is passed through the interior of the Nafion tubing; this allows water (and other light, polar compounds) to permeate through the walls into a dry air purge stream flowing through the annular space between the Nafion and the outer tubing.^{18,19} This is a constant process that requires no maintenance. The Nafion dryer's water removal efficiency for particular applications and its transmission efficiency for specific compounds have been described in the literature.¹⁷⁻²¹ The use of these dryers has already been validated for our sampling conditions and compounds of interest, i.e., selected light, nonpolar hydrocarbons and halogenated hydrocarbons of environmental concern.⁶ For convenience, the dryers used in our laboratory were purchased pre-assembled with fittings and purge tubing from Perma-Pure Products, Inc. (Farmingdale, NJ).

This paper describes a novel dryer cleanup technique that can be implemented during the non-sampling portion of a GC analysis cycle. This technique temporarily increased the water vapor removal efficiency of the dryer by a factor of 20 over the steady-state efficiency and reduced system memory effects. Fifteen VOCs of environmental interest were tested at concentrations in the range of 8 to 12 ppbv to determine if this technique affects sample integrity.

Experimental Methods

Equipment

A number of different dryer configurations are available from the manufacturer for drying air streams at flow rates of a few milliliters per minute to more than 30 L/min. The single-stranded models that cover the flow range up to approximately 200 mL/min were chosen for our application of

GC sample drying. Five models were initially tested for steady-state and time-dependent drying performance (for details see reference 22). The configuration that proved most effective for this work was a tubular Nafion membrane with a 0.12 cm O.D., 0.065 cm I.D., and a 112 cm length mounted in 0.32 cm O.D. purge tubing. These dryers can accommodate up to a 200-mL/min sample flow with a corresponding purge flow of 250 to 2000 mL/min.

Most dryer performance data were obtained with an optical water vapor monitor. This instrument is a prototype developed under contract for the U.S. Environmental Protection Agency by Ford Aerospace and Communications Corporation, Newport Beach, CA.²³ Water vapor concentration in a flowing gas stream is determined by differential infrared absorption using bandpass filters centered at 2.51 and 2.59 μm . Sample cell volume is 56 cm^3 and the detection limit is 10 ppmv at 1 atm. Calibration curves cover ranges of up to 5 percent water vapor concentration. The monitor was spot checked periodically with known samples near 100 percent relative humidity, and measurements were compared to measurements of room air made by a sling psychrometer and a calibrated hygrometer. The monitor was extremely stable when sampling zero gas and at the span settings. For the various experiments in which the water vapor monitor was used, individual data points consisted of three concentration measurements: dry zero air (Z), humidified sample at dryer inlet (H), and dried sample at dryer outlet (S). Percent drying efficiency, E , was defined as $E = 100[1-(S/H)]$. Because Z , the baseline response, was always two or three orders of magnitude less than S , it was only used as a qualitative check on the water vapor monitor's stability. Normalizing with H removed the effect of laboratory temperature drifts that slightly affected the water vapor concentration at the dryer inlet.

The analytical instrumentation consisted of a fully automated sampling and analysis system that included an HP-5880 Level 4 GC (Hewlett-Packard, Avondale, PA) equipped with both FID and ECD detectors and a modified Nutech 320-1 cryogenic trapping and desorption unit (Nutech Corp., Durham, NC). All critical gas flows were regulated by Tylan mass flow controllers (Tylan Corp., Carson, CA). For some tests, a quadrupole mass spectrometer (HP-5970 MSD, Hewlett-Packard) was used as a GC detector for water to alleviate the FID and ECD insensitivity. Dryer purge gas was zero-grade air passed through a drierite-molecular sieve scrubber. Humidified samples were zero-grade air passed through a partially filled 500-mL water impinger flask. When appropriate, this air could be mixed with a second flow containing various compounds of interest. Purge and sample flows were maintained with mass flow controllers and were periodically audited.

Dryer Performance Experiments

The water vapor monitor was used in a set of initial experiments on four dryers (two new and two used) to determine

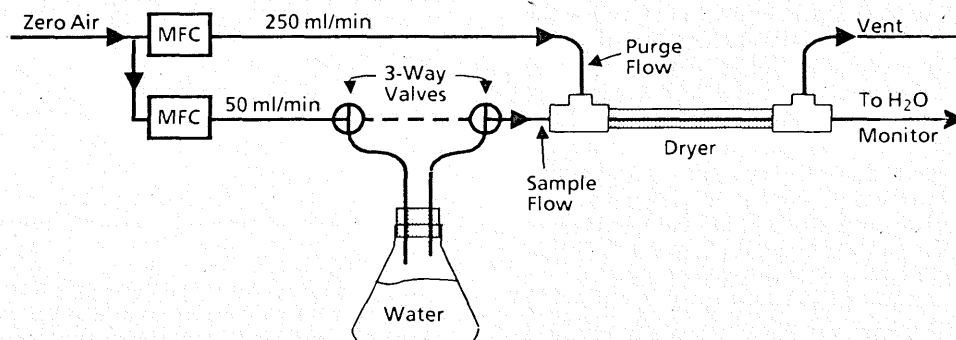


Figure 1. Flow diagram for testing dryer performance. Note that the valves allow decoupling of humidity from the sample stream. MFC denotes mass flow controller.

typical drying efficiencies. The time dependence of drying efficiency was measured in response to a step function of sample stream humidity (from 0 to 95 percent relative humidity). The time needed for the dryer outlet humidity to increase from the originally established zero level to 10 percent of the eventual steady-state value was recorded. Steady-state drying efficiency was independently measured for each dryer at various times throughout a one-month testing period during which room temperatures ranging from 19 to 24°C were encountered. These temperature changes caused some variation in the absolute water content of the sample at the dryer inlet. Humidified sample flow and dry purge flow were maintained at 50 and 250 mL/min, respectively. Flows were periodically audited with a bubble flow meter to ensure consistency over this extended testing period. A diagram of the experimental arrangement is given in Figure 1.

Dryer Cleanup Procedure Experiments

Previous work had demonstrated that the permeable membrane of the dryers, Nafion tubing, could be successfully cleaned by applying heat and substituting dry zero-air for the sample flow.⁶ A set of experiments was performed to determine the effects of such treatment on dryer performance under actual sampling conditions.

Typically, an ambient air analysis in our laboratory consists of three distinct phases: sample collection using a cryogenic trap (15 min); GC analysis using a capillary column (30 min); and instrument resetting, report printing, etc. (15 min). This procedure is fully automated and repetitive; run-to-run precision is determined primarily by the sample. Because sample drying is only necessary for 15 min out of the total analysis time of 60 min, a procedure was devised to automatically clean up the dryer during its idle time. This procedure involved flushing the inner dryer tubing with dry zero-grade air while the dryer was heated to 100°C. It was then allowed to cool to room temperature before the next sample collection.

The dryer currently in use on the instrument was wrapped with aluminum foil, heating tape, and insulation. The heating tape was wired through a solid state relay to a variable transformer (used to set a maximum temperature). A solenoid gas switching valve, also wired through a relay, was installed at the dryer inlet to select either sample or dry air. Both relays were connected to the GC to allow computer-controlled activation. A diagram of this arrangement is shown in Figure 2. The appropriate programming was installed to allow automated repetitive analysis with or without the cleanup procedure. A number of experiments were then performed to evaluate the new method.

In the first experiment, the mass spectrometer was used as the GC detector. The system was set up to display the elution of 18 atomic mass unit (amu) fragments, the parent ion for water. A humidified zero air stream at a flow rate of 2 L/min introduced into a glass manifold was the sample. Four

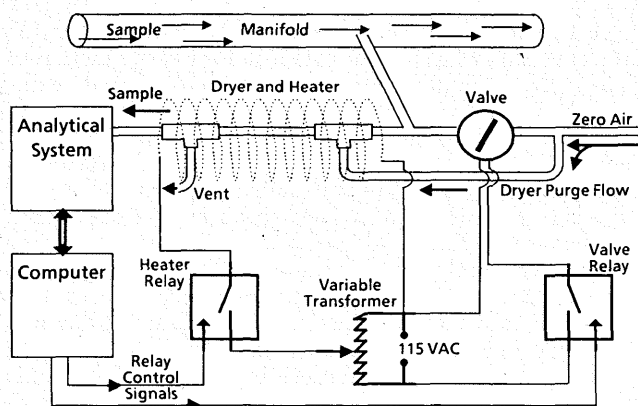


Figure 2. Schematic diagram of automated dryer cleanup procedure. When valve relay is off, valve is closed and sample is pulled from manifold. When valve relay is activated, valve is open and zero air overfills dryer inlet and displaces manifold sample. Heater relay can then be activated to apply pre-set voltage from variable transformer to heat the dryer.

consecutive analyses were then performed using the described cleanup procedure; these were followed by four analyses without the procedure. Before each set of four analyses the dryer was heated and thoroughly purged of all residual water by supplying dry zero-air to the inner tubing.

A second experiment was performed to determine the dependence of drying efficiency on time during such cleanup cycles. The water vapor monitor was inserted into the sample stream between the dryer and the analytical system (see Figure 2). The analytical procedure used in the first experiment was repeated while the water content at the dryer outlet was monitored.

Finally, the effect of the cleanup procedure on sample integrity was tested. The water vapor monitor and the mass spectrometer were removed from the system. Simultaneous FID and ECD were used. A calibration mixture of 15 compounds of interest, all within the concentration range of 8 to 12 ppbv in humid zero air, was established in the glass manifold at a flow rate of 2 L/min. Seven consecutive analyses were performed with the cleanup procedure, and seven were performed without the procedure. These two sets of runs were performed on consecutive days under identical conditions. After each set, humidified zero air was sampled to determine residual contamination.

Results and Discussion

The first performance experiment, in which time dependence of drying efficiency as a response to a step function in sample humidity was measured, indicated that approximately 4 h was required for humidity to reach a steady-state value, E_s , when the dryer was initially dehydrated. The time required to reach 10 percent of E_s was consistently measured at 23 ± 1 min and was designated the useful time of enhanced performance for these dryers.

The second experiment was performed to determine the overall stability in performance of these dryers. Results of 17 independent tests to measure steady state drying efficiency showed a mean of 80.8 percent and a standard deviation of 0.84. All four dryers were treated identically in this test even though two had been used in our laboratory for about two years and the other two had just been purchased. Individual dryers showed no appreciable bias in drying efficiency. These encouraging results indicate that individual dryers of the same model can be considered interchangeable and that prolonged use does not appear to degrade performance.

As noted earlier, a fully dehydrated dryer exhibited a temporary increase in drying efficiency when a humidified sample was first introduced. Our sampling time of 15 min is well within the useful time window of a dehydrated dryer.

Because our sampling requirements allowed about 45 min of down time between sample collections, we used this time to recondition the dryer. Results of experiments to test the automated cleanup system (see Figure 2) showed that it greatly reduced the water introduced into the analytical system as compared to using the dryer under steady state conditions. Qualitative results (using the mass spectrometer as the GC detector) are presented in Figure 3, in which the eluting water vapor peak is shown for three consecutive GC runs with and without the cleanup cycle. The amount of eluting water was constant from run to run when the cleanup procedure was used, but increased dramatically when the cleanup procedure was not used. This experiment could not be used to quantify water removal improvements because steady-state dryer use (as reached after the fourth run) allowed so much water into the analytical system that the detector overloaded.

The drying improvement caused by the automated cleanup system was quantified with the water vapor monitor. The water content of the sample stream as it entered the analytical system is presented in Figure 4 as two overlapping graphs of water monitor response versus time that are annotated to indicate the sampling periods. These curves correspond to four complete sampling cycles for both drying procedures, i.e., with and without interim cleanup. When the dryer is at room temperature, the area under the curves is proportional to the total amount of water passing through the monitor. Careful study has shown a typical twentyfold improvement in water removal for our analytical conditions when the cleanup procedure is used. This is illustrated in Figure 4 by an expanded view of one sample collection portion of these curves.

Results for the final experiment, in which the cleanup procedure was used on well-characterized calibration samples, are presented in Table I. The individual compounds in the following calibration mixture, particularly those eluting late, tended to equilibrate throughout the day. This sample concentration drift during the tests was unavoidable because time and resource constraints did not permit overnight equilibration prior to each experiment. Thus, the data were compared based on linear regressions of peak area versus run number for each compound. The calculated regression slope is a combination of overall sample concentration drift and any run-to-run memory effects in the system. For the FID data, the cleanup procedure exhibited a consistently lower area/run number drift. The ECD data showed no consistent differences.

To determine the effect of the dryer cleanup on system precision, the root mean square difference between the regression curve and the individual data points was calculated for each compound. These values are expressed as a percentage of the mean peak area to facilitate comparisons among

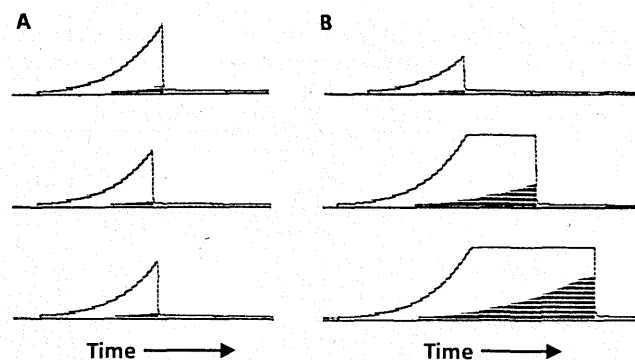


Figure 3. Two sequences of three consecutive GC runs showing the elution of the 18 amu fragment (parent ion of water) as measured by the mass spectrometric detector: (A) with interim dryer cleanup procedure and (B) without interim dryer cleanup procedure. In each case, the dryer was initially dehydrated.

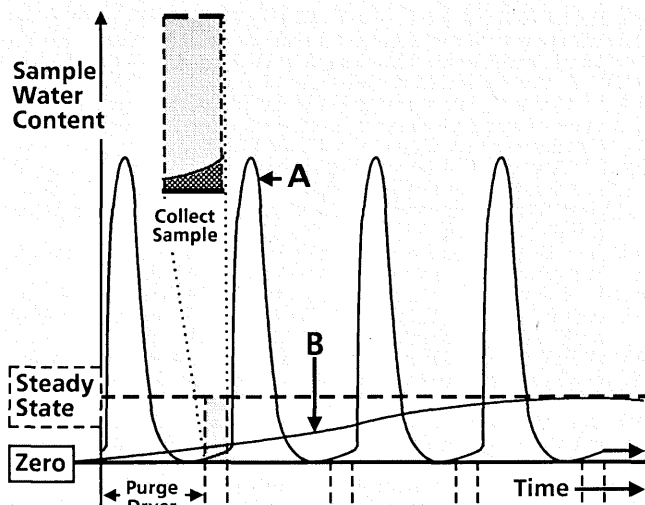


Figure 4. Sequence of four consecutive GC runs showing water monitor response versus time as measured at the dryer outlet just prior to entering the GC: (A) with interim dryer cleanup procedure and (B) without interim dryer cleanup procedure. Expanded view of the sample collection portion of the analytical cycle depicts reduction in injected water vapor. The heavily shaded region is proportional to the amount of water collected with the sample when the dryer is pretreated; the lighter shaded area beneath the steady state line is proportional to water collected without dryer pretreatment. Sample content at dryer inlet (95 percent relative humidity at room temperature) would be far off the scale in this graph.

compounds and among detectors. Data from the FID showed consistently lower scatter when the cleanup procedure was used. The ECD data showed either lower or equivalent residuals. In addition, when the procedure was not used, one instance of temporary column blockage and another instance in which the FID flame was extinguished were encountered. These occurrences were attributed to excess accumulated water; this was confirmed in similar tests using the mass spectrometer.

Finally, the zero air run performed after the set of seven calibration runs showed little or no contamination when the cleanup procedure was used. Residual peaks of about 0.1 to 0.3 ppbv each for carbon tetrachloride, tetrachloroethylene, benzyl chloride, and hexachlorobutadiene were observed when the interim cleanup procedure was not used.

Conclusion

In our restricted sample set, essentially no variation in performance among dryers of the same type and no degradation in performance of dryers used daily over a period of two years were observed. Drying efficiency can be greatly improved for a short time by first processing the dryer with a dry sample flow and heating it. In our experiments, water removal could be increased by a factor of 20 over steady state operation. Such a procedure does not affect sample integrity, at least for all 15 compounds tested here, and tends to reduce memory effects from previous samples. This cleanup

Table I. Comparison statistics for seven analysis runs with and without the interim dryer cleanup procedure.^a

Compound	Regression slope ^b average change/run no. (percent)		RMS residual ^c (percent)	
	Cleanup	No cleanup	Cleanup	No cleanup
FID				
Vinyl chloride	0.73	-0.26	1.52	2.16
Vinylidene chloride	-0.54	-0.56	1.48	2.95
1,1,2-Trichloro-1,2,2-trifluoroethane	0.22	-0.85	1.87	1.20
Chloroform	0.46	1.70	1.45	3.79
1,2-Dichloroethane	0.43	1.35	0.84	1.40
Methyl chloroform	0.35	0.23	0.77	1.16
Carbon tetrachloride	-0.06	1.53	1.34	6.53
Trichloroethylene	0.54	1.51	0.83	1.28
1,3-Dichloropropene				
-cis	0.52	1.97	0.81	1.54
-trans	0.65	2.43	0.93	5.53
1,2-Dibromoethane	0.22	0.36	1.06	1.49
Tetrachloroethylene	0.53	1.81	0.73	2.26
Chlorobenzene	0.68	2.42	1.06	3.50
Benzyl chloride	1.96	6.70	1.49	6.36
Hexachlorobutadiene	2.32	6.41	1.12	2.92
ECD				
1,1,2-Trichloro-1,2,2-trifluoroethane	0.12	-0.17	0.23	1.30
Chloroform	0.25	0.10	0.35	1.46
Methyl chloroform	0.25	-1.05	0.13	4.17
Carbon tetrachloride	2.02	0.29	0.27	1.20
Trichloroethylene	0.31	0.41	0.51	2.83
1,2-Dibromoethane	3.36	0.25	4.78	4.31
Tetrachloroethylene	1.22	0.09	3.06	5.26
Hexachlorobutadiene	0.80	2.07	2.40	2.24

^a Target compounds ranged from 8 to 12 ppbv in humidified zero-grade air. Samples were collected at 34 mL/min for 14 min into a cryotrap maintained at -155°C.

^b Least squares linear regression slope of percent normalized peak area vs. run no. for seven consecutive analyses either with or without the dryer cleanup procedure.

^c Root mean square difference between calculated linear regression curve and individual data points; normalized to a percentage of the mean peak area for the particular compound.

procedure is particularly useful for our application, cryogenic preconcentration of VOCs from ambient air for subsequent GC analysis, because excess accumulated water can cause trap and column blockage and also adversely affect detector precision. In addition, the improvement in water removal will allow sampling of much larger volumes of ambient air in the event that greater system sensitivities to compounds of interest are required.

Disclaimer

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through Contract 68-02-4035 to Northrop Services, Inc.—Environmental Sciences, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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