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Efficiency and Temperature Dependence of Water Removal by Membrane Dryers

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The vapor pressure of water in equilibrium with sorption sites within a Nafion membrane is given by $\log P_{WN} = -3580/T + 10.01$, where P_{WN} is expressed in Torr and T is the membrane temperature, in kelvin. The efficiency of dryers based on selective permeation of water through Nafion can thus be enhanced by cooling the membrane. Residual water in effluents exceeds equilibrium levels if insufficient time is allowed for water to diffuse to the membrane surface as gas passes through the dryer. For tubular configurations, this limitation can be avoided if $L \geq F_c(10^{3.8}/120\pi D)$, where L is the length of the tubular membrane, in centimeters, F_c is the gas flow rate, in mL/min, and D is the diffusion coefficient for water in the carrier gas at the operating temperature of the dryer, in cm^2/s . An efficient dryer that at room temperature dries gas to a dew point of -61°C is described; the same dryer maintained at 0°C yields a dew point of -80°C and removes water as effectively as $\text{Mg}(\text{ClO}_4)_2$ or a dry ice/acetone slush. The use of Nafion membranes to construct devices capable of delivering gas streams with low but precisely controlled humidities is discussed.

Removal of water vapor from a carrier gas is required for gas chromatographic analyses of volatile organic compounds in aqueous samples, chromatographic or spectroscopic analyses of trace components in air, and continuous-flow combustion of organic samples for elemental or isotopic analysis. Tubular dryers based on the selectively permeable membrane Nafion are often useful in such applications. Attention to their optimization is, therefore, well justified.

As shown in Figure 1, Nafion is an ionic polymer with a tetrafluoroethylene backbone and perfluorinated ether side chains terminating in hydrophilic sulfonic acid sites.¹ Each sulfonic acid group can be hydrated by up to 13 water molecules,^{2,3} making the membrane both hygroscopic and selectively permeable to water. In Nafion-based tubular dryers (Figure 2), carrier gas is passed through one or more Nafion tubes mounted coaxially inside a second tube or sheath which is continuously purged with a countercurrent flow of dry gas. The resulting gradient in the vapor pressure of water across the membrane drives the transfer

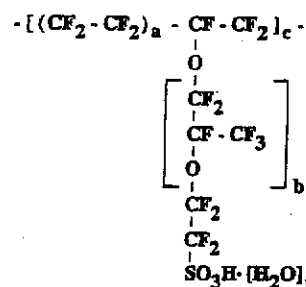


Figure 1. Chemical structure of Nafion, where $a = 5-11$, $b = 1-3$, $c \approx 1000$, and $n = 1-13$. The dry membrane has an equivalent weight of approximately 1100 g per sulfonic acid site and absorbs up to 22% by weight of water.

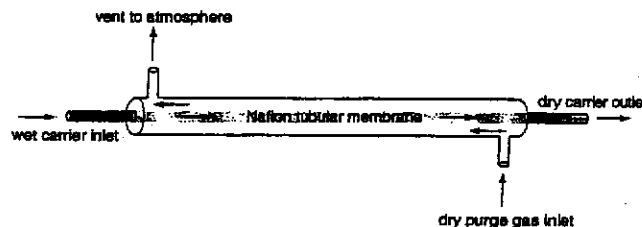


Figure 2. Diagram of a Nafion dryer. Wet gas flows through a Nafion tube, the outside of which is purged by a countercurrent flow of dry gas. A gradient in the vapor pressure of water across the membrane drives the transfer of water from carrier to purge.

of water from the carrier to the purge gas.^{4,5} In an alternative "static" arrangement, the Nafion tube can be enclosed in a container packed with desiccant,^{6,7} eliminating the need for purge gas but limiting the efficiency and lifetime of the dryer.⁷

Nafion dryers are highly selective for water, resistant to chemical degradation, and impermeable to many analytes, excepting low-molecular-weight, polar, oxygenated compounds including some ketones, alcohols, aldehydes, and water-soluble ethers.^{5,8,9} The dryers have low dead volume and low resistance to flow and (when purged with dry gas) are continuously self-regenerative. As a consequence, they have become increasingly popular in a wide variety of applications, including analysis of trace organic compounds in water by direct aqueous injection GC¹⁰ or purge-and-trap GC,^{9,11} atmospheric trace gas analyses of methane,¹² sulfur

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oxides,¹³ reduced sulfur gases,¹⁴⁻¹⁶ nitrogen oxides,¹⁷ and volatile organic compounds;¹⁸⁻²⁰ continuous-flow stable isotope ratio measurements;²¹⁻²³ and analysis of trace metals by vapor-generation atomic absorption spectroscopy.²⁴⁻²⁶

Despite these widespread applications of Nafion dryers, little quantitative information is available regarding their efficiency in terms of relative or absolute residual humidity, or in comparison to desiccants or cryogenic traps. Moreover, published information is fragmentary and often contradictory. Reports of efficiencies of Nafion dryers have varied from 59% to $\geq 98\%$.^{5,8,12,20,26} In terms of absolute humidity of the dried gas, dew points ranging from -5 to -40 °C^{9,14,19} have been observed. All reports of absolute humidity indicate dew points above -45 °C, the value cited by the manufacturer as the limit of performance under ambient conditions.²⁷

Details of construction and operation such as length and diameter of the Nafion tubing, carrier and purge gas flow rates, dryness of the purge gas, and operating temperature all affect the performance of Nafion dryers. Notably, little information is available on the effect of temperature on drying efficiency, although this paper will show that temperature is a major determinant of dryer performance. Sundin et al.²⁶ found lower drying efficiency when the dryer was maintained at 60 °C instead of room temperature. Both Baker⁵ and Thornton et al.¹³ improved performance by cooling the dryer with ice, and Pleil et al.²⁰ found that efficiency could be temporarily enhanced 20-fold if the dryer was heated to 100 °C, purged with dry carrier, and then cooled immediately prior to use. Product literature notes that residual humidity depends on temperature of the dryer but provides no quantitative information for other than ambient conditions.²⁷

This paper addresses the efficiency and temperature-dependence of water removal by Nafion dryers. (1) Residual humidity in the effluent of a Nafion dryer is quantified by mass spectrometry for a variety of dryer temperatures. (2) The thermodynamic relationship between temperature and water vapor pressure over Nafion is determined. This relationship both establishes limits of performance for Nafion dryers as a function of temperature and shows how devices based on Nafion membranes could serve

to establish and control low levels of humidity in gas streams (for example, when required for calibration of water-sensing devices). (3) General points relating to the construction and optimization of Nafion dryers are discussed. (4) The performance of a Nafion dryer at several temperatures is compared with that of common desiccants and cryogenic traps.

EXPERIMENTAL SECTION

Nafion Dryer. The Nafion dryer used in these experiments consisted of a 60-cm length of 0.51-mm-o.d. \times 0.33-mm-i.d. tubular Nafion membrane (Perma Pure, Inc., Toms River, NJ), with an internal volume of 50 μ L. The Nafion tubing was mounted coaxially inside a 60-cm \times 3.18-mm-o.d. \times 2.2-mm-i.d. stainless steel sheath and secured at each end with reducing-tee unions ($1/8$ in. \times $1/16$ in. \times $1/16$ in., SGE Inc., Austin, TX). A purge gas supply was connected to the arm of the downstream reducing union. Gas-tight seals between the Nafion tubing and the capillaries acting as carrier gas inlet and outlet were made by sliding 2-3 cm of the flexible Nafion tubing over each capillary and compressing with 0.6-mm graphitized vespel ferrules. An upstream segment (20 cm) of the Nafion trap was always maintained at ambient temperature (23 ± 2 °C), while the downstream (40 cm) segment was bent into a "U" shape, inserted into an insulated Dewar flask filled with thermostatic fluids, and maintained at temperatures ranging from 50 to -40 °C ($\pm 1^\circ$). The ambient upstream segment prevented the formation of ice during low-temperature experiments.¹³ Subsequent references to the dryer temperature refer to the second stage only.

Gas Flow Pathway. As shown in Figure 3, a single tank of zero-grade He provided carrier gas as well as purge gas to the Nafion dryer. A carrier gas flow of 5.38 mL/min (20 psi head pressure; 50-cm \times 0.11-mm-i.d. restrictor capillary) was humidified by bubbling through a vial of deionized water at ambient temperature and directed to an open split. At the split, 250 μ L of carrier/min was continuously directed through the Nafion dryer, through a capillary restrictor, and into the mass spectrometer via a set of changeover valves. In addition to providing a vent for excess carrier, the open split served as a spray trap to prevent mist from entering the Nafion and isolated the mass spectrometer from small pressure variations in the carrier stream introduced by the bubbler.

A purge gas flow of 3.24 mL/min (20 psi, 30-cm \times 0.11-mm i.d. restrictor capillary) was dried to a nominal dew point of -195 °C by passage through a liquid nitrogen trap. To monitor background water levels in the purge gas and associated plumbing, 250 μ L/min was continuously directed through a restrictor capillary and into the changeover valves of the mass spectrometer. The remainder of the dry helium purged the annular space of the Nafion dryer countercurrent to the flow of wet carrier gas.

Mass Spectrometer. Residual humidity in purge gas entering and in carrier gas exiting the dryer was measured using a Finnigan MAT 252 mass spectrometer. As shown in Figure 3, the MAT 252 is equipped with external changeover valves which alternately admit one of two gas streams to the ion source while directing the other to waste. Thus, the changeover valves facilitate comparison of water levels in carrier and purge. The optimum range of gas flows into the MAT 252 is 0.2-0.3 mL/min.²¹ The rates at which carrier and purge gases were admitted to the mass spectrometer were controlled with matched 2.5-m, 0.11-mm-i.d. restrictor capillaries, which restricted flows of carrier and purge

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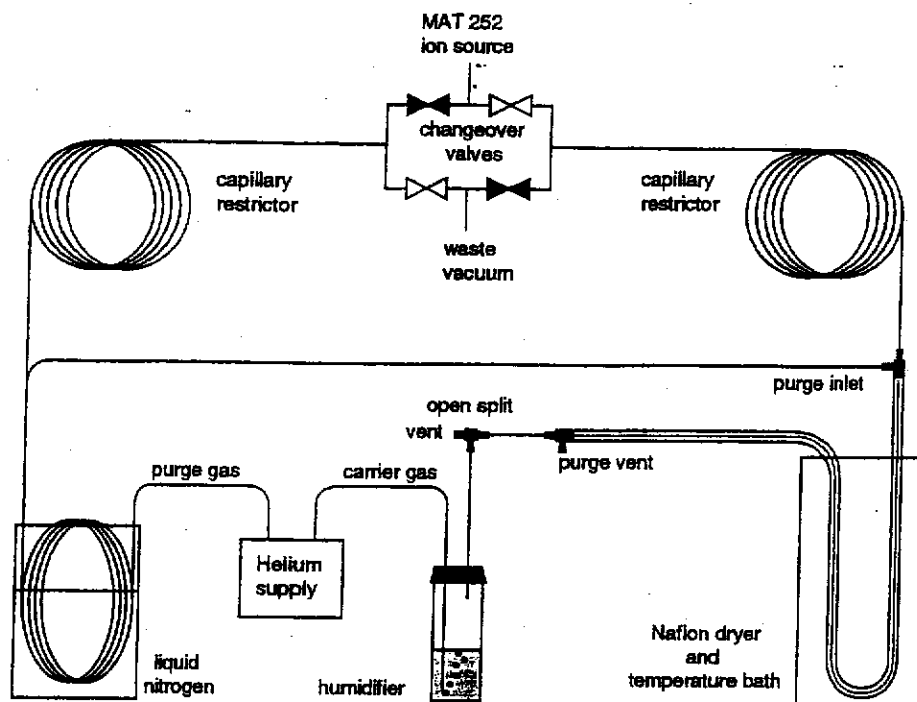


Figure 3. Experimental setup for measuring the efficiency and temperature dependence of water removal by Nafion dryers.

to $250 \pm 20 \mu\text{L}/\text{min}$, resulting in indicated source pressures of 7×10^{-6} – 8×10^{-6} Torr.

Although the MAT 252 is ordinarily used for isotope ratio measurements, in these experiments it was used only to quantify water. Ions were generated by electron impact at 70 eV and accelerated using a potential of 10 kV. The resulting m/z 18 ion currents were collected in Faraday cups, converted to voltages via feedback electrometers, and recorded on a strip-chart recorder. The efficiency of the mass spectrometer for water was 3000 ± 400 molecules per collected ion based on measurements of CO_2 ionization efficiency according to the methods of Merritt and Hayes²⁸ and on published ionization cross sections of CO_2 and H_2O at 70 and 75 eV.^{29,30}

Procedures. For each temperature–humidity measurement, the m/z 18 ion current of the purge gas was recorded while the carrier was pumped to waste. The changeover valves were reversed, and, after stabilization of the signal, the m/z 18 ion current of the dried carrier was recorded. The changeover valves were again reversed, the signal was again allowed to stabilize, and the water background of the purge was remeasured while the temperature of the Nafion dryer was changed in preparation for the next measurement. Residual humidity was measured for eight dryer temperatures ranging from -40 to 50 °C. The temperature of the dryer was continuously monitored and was stable to ± 1 °. Temperatures from 0 to 50 °C were maintained by hot or cold water baths; -20 and -40 °C baths consisted of 20% NaCl and 32% CaCl_2 freezing mixtures.

RESULTS AND DISCUSSION

Residual Humidity Measurements. Typical results are illustrated in Figure 4, a schematic diagram of m/z 18 ion current (I_{18} ; in picoamperes) over the course of a measurement.

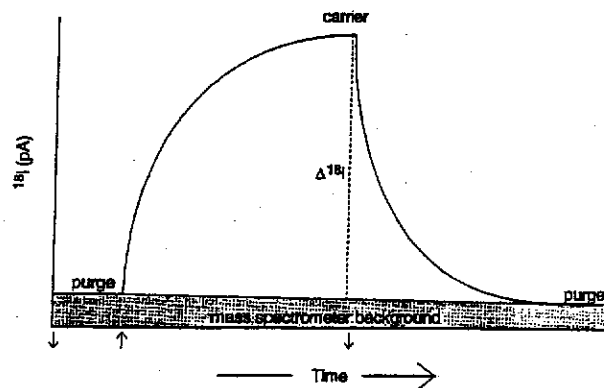


Figure 4. Schematic diagram of a residual humidity measurement (not to scale). Solid lines represent measured m/z 18 ion currents (I_{18}). Arrows mark alternate admission of purge or carrier gas to the ion source. The shaded zone represents background levels of water in the mass spectrometer, and ΔI_{18} gives the background-corrected m/z 18 ion current, which is proportional to the residual humidity of carrier exiting the Nafion dryer.

(i) **Corrections for Background Water and Memory Effects.** During introduction of purge gas to the ion source, m/z 18 ion currents decreased slowly but continuously as long as the purge gas was observed, averaging 12 ± 3 pA over the duration of the experiment. This is equivalent to a dew point of -74 ± 4 °C (for conversion from ion currents to dew points, see below) and is significantly more water than expected at the nominal dew point of -195 °C. Additional experiments in which purge gas was passed through a liquid nitrogen trap immediately prior to entering the changeover valves or in which the valve block and ion source were closed to all flows of incoming gas demonstrated that $>90\%$ of the water signal measured during admission of the purge gas was actually background water associated with the mass spectrometer. This background water was sustained by desorption of water from surfaces including the changeover valves, internal transfer lines, and the interior walls of the ion source. It could be reduced to <3 pA by baking the changeover valves and ion

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Table 1. Temperature Dependence of Residual Humidity in Nafion-Dried Gas^a

T (°C)	$\Delta^{18}i$ (pA)	P_{WN} (mTorr) ^b
49.8 ± 0.4	635 ± 19	90 ± 10
40.2 ± 0.8	286 ± 9	41 ± 6
29.7 ± 0.3	112.5 ± 4	16 ± 2
20.1 ± 0.1	44.3 ± 1.8	6.3 ± 0.9
19.8 ± 0.0	40.8 ± 1.7	5.8 ± 0.8
9.9 ± 0.1	13.1 ± 0.9	1.9 ± 0.3
0.2 ± 0.1	3.7 ± 0.7	0.52 ± 0.12
-18.9 ± 1.1	0.8 ± 0.6	0.11 ± 0.09
-42 ± 0.3	0.7 ± 0.6	0.10 ± 0.08

^a T and $\Delta^{18}i$ are means of 2–4 replicate observations. Uncertainties are the standard deviations of the populations. ^b Calculated according to eqs 2–4. Uncertainties were obtained by propagation of errors and incorporate uncertainties in T and $\Delta^{18}i$ as well as in collection efficiency and flow rate measurements.

source at 80 °C for 2–3 h, but it returned when humid gases were reintroduced to the mass spectrometer. Rather than repeatedly baking the source between measurements, background water levels were treated as equal to the purge gas water signal and were subtracted from measurements of carrier gas water prior to further calculations.

As illustrated in Figure 4, residual humidity of carrier exiting the Nafion dryer was measured as $\Delta^{18}i$, the difference between carrier and background ion currents. Quantitation of water was complicated by slow (20–30 min) response of the m/z 18 ion current after switching gas streams, which resulted in skewed rising edges and tailing falling edges of the peaks related to residual water in the gas stream. These effects were probably due to sorption and desorption of water in the mass spectrometer and/or transfer lines. To minimize the impact of such memory effects without dramatically increasing analysis times, ^{18}i was recorded after its slope dropped to 1–3% of its initial slope. This procedure underestimated $\Delta^{18}i$ by 5–10% and thus overstates drying. Corrections for this systematic error are considered below.

(ii) **Residual Humidity vs Nafion Temperature.** Results of residual humidity measurements for $-40 \leq T \leq 50$ °C are summarized in Table 1. Residual humidity increased strongly with increasing dryer temperature. This observation is consistent with Baker's⁵ and Thornton et al.'s¹³ observations of increased efficiency of drying by ice-cooled Nafion dryers. It is also qualitatively supported by Sundin et al.'s²⁶ report of decreased efficiency at 60 °C, although the magnitude of the effect observed here is greater than that previously reported.

The temperature dependence of dryer efficiency can be understood by considering in detail the mechanism. So long as the partial pressure of water in the carrier gas exceeds the vapor pressure of water bound to sulfonic acid sites in the Nafion (P_{WN}), water is continually absorbed at the inner Nafion surface, transported across the membrane, and lost at the outer surface, which is maintained in a state of disequilibrium at a near-zero partial pressure by the countercurrent flow of dry purge gas. The carrier, however, is not necessarily dried to the humidity of the purge; in fact, it will be as dry as the purge gas only if P_{WN} is less than or equal to the vapor pressure of water in the purge. In a reversed mode of operation, introduction of dry gas together with control of membrane temperature and supply of water by means of a humidified purge stream would yield an output gas stream in which the concentration of water was controlled by P_{WN} .

Thermodynamics of Water Removal by Nafion. (i) Theory.

If thermodynamic equilibrium between the carrier gas and water in the Nafion membrane is the primary control on residual humidity of Nafion-dried streams, then residual water in the carrier should plot against Nafion temperature according to the Clausius–Clapeyron equation for equilibrium between a gas and a condensed phase:

$$\ln P_{WN} = -\Delta H/R(1/T - 1/T_0) \quad (1)$$

where ΔH is the molar enthalpy of vaporization of the substance in J/mol, R is the ideal gas constant in J/(K mol), and T_0 is the normal boiling point of the liquid or sublimation point of the solid.³¹ To determine whether Nafion dryers follow this relationship or whether kinetic factors such as rate of transport of water through the membrane cause deviations from linearity, the thermodynamic relationship between residual vapor pressure of water in the carrier and temperature of the dryer was determined from $\Delta^{18}i$ measurements as follows.

(ii) **Calculations.** At each temperature, the flux of water entering the mass spectrometer was calculated from $\Delta^{18}i$ according to

$$F_w = \Delta^{18}i/Eq_e N_A \quad (2)$$

where F_w is the flux of water in mol/s, $\Delta^{18}i$ is the background-corrected ion current measured for the carrier gas, E is the efficiency of the MAT 252 for water in ions/molecule, q_e is the electronic charge, and N_A is Avogadro's number.

The mole fraction of water in the carrier was calculated as the ratio of fluxes of water to carrier gas into the mass spectrometer:

$$X_w = (60 \times 10^6) V_m F_w / f_c \quad (3)$$

where X_w is the mole fraction of water in the carrier, F_w is the water flux in mol/s, f_c is the volumetric flow of carrier into the mass spectrometer in $\mu\text{L}/\text{min}$, and V_m is the molar volume in liters of an ideal gas at ambient temperature and pressure.

The partial pressure of water in the carrier gas was then calculated according to Dalton's law of partial pressures:

$$p_w = X_w P \quad (4)$$

where p_w is the partial pressure of water in the carrier, in Torr, and P is ambient pressure, 760 Torr. The dew point of the carrier gas was calculated from its partial pressure according to the relation

$$\log p_w^\circ = -2466/T + 9.65 \quad (5)$$

where p_w° is the saturation vapor pressure of water, in Torr, and T is the temperature, in kelvin. The coefficients -2466 ± 29 and 9.65 ± 0.11 were obtained by least-squares regression of vapor pressure and temperature data obtained from the *CRC Handbook*³² over the temperature interval used in the experiment.

(iii) **Vapor Pressure–Temperature Relationship.** The experimentally determined vapor pressure–temperature relationship for water in Nafion-dried carrier gas is shown in Figure 5. For comparison, a line corresponding to the saturation vapor

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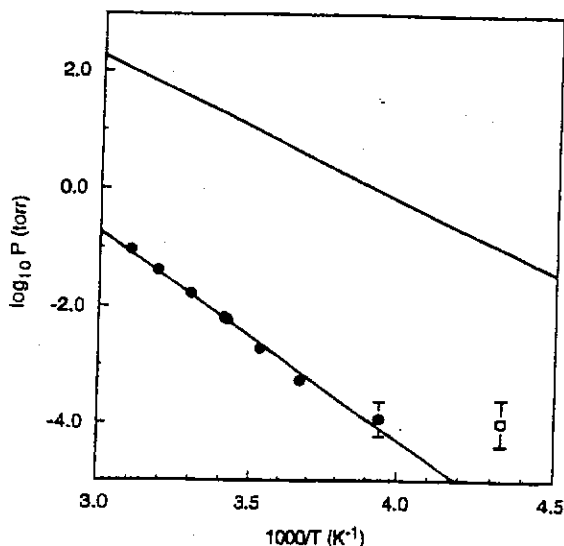


Figure 5. Log pressure vs inverse temperature relationship for water vapor (upper) and for water vapor in equilibrium with sorption sites within a Nafion membrane. Least-squares regression of Nafion data (excepting one outlier, see text) yields a slope of -3.58 ± 0.14 and an intercept of 10.02 ± 0.47 . Corresponding values for water are -2.467 and 9.654 .

pressures of pure water over the same temperature interval is also shown.³² At any given temperature, the vapor pressure of water in equilibrium with a Nafion membrane is 3–4 orders of magnitude lower than that of pure water.

For temperatures from -20 to 50 °C, the relationship between P_{WN} and $1/T$ is described by the linear equation

$$\log P_{WN} = -3580/T + 10.01 \quad (6)$$

where P_{WN} is in Torr and T is in kelvin. The standard deviations of the slope and intercept, determined from linear regression, are 140 and 0.47, respectively, and the coefficient of determination is $r^2 = 0.991$. This relationship confirms that thermodynamic equilibrium between water in the carrier gas and water in the Nafion membrane determines the residual humidity of Nafion-dried streams, and it establishes the minimum residual water content of Nafion-dried gas as a function of temperature for Nafion dryers operated within this temperature range.

(iv) **Enthalpy and Entropy of Vaporization.** Substituting the experimentally determined slope from eq 6 into the Clausius–Clapeyron equation and solving for ΔH yields a molar enthalpy of vaporization of water from Nafion of 69 ± 3 kJ/mol. This value is reasonable when considered in the context of related thermodynamic data for Nafion and for pure water:

(1) The enthalpy (ΔH) and free energy (ΔG) of vaporization of water from Nafion are related according to $\Delta G = \Delta H - T\Delta S$. For any transition from condensed phase to vapor, entropy (ΔS) is necessarily positive; therefore, the enthalpy of vaporization must be larger than the free energy of vaporization. The observed enthalpy of vaporization significantly exceeds the free energy of vaporization reported by Pushpa et al.³

$$\Delta H_{\text{vap, naf}} (69 \pm 3 \text{ kJ/mol}) > \Delta G_{\text{vap, naf}} (33.4 \pm 1.0 \text{ kJ/mol})$$

(2) More quantitatively, the difference between enthalpy and free energy of vaporization corresponds (at 298 K) to an entropy of 120 ± 11 J/(K mol). While no prior literature reports of $\Delta S_{\text{vap, naf}}$

are available for comparison, the entropy of vaporization of water from Nafion calculated here is quite similar to the entropy of vaporization of water:

$$\Delta S_{\text{vap, naf}} (120 \pm 11 \text{ J/(K mol)}) \approx \Delta S_{\text{vap, H}_2\text{O}} (118 \text{ J/(K mol)})$$

This fits with observations, based on NMR,³³ IR,³⁴ and X-ray³⁵ and neutron³⁶ scattering experiments, that sulfonic acid sites and associated water in Nafion cluster to form “encapsulated micro-solutions”³³ with intermolecular structure and properties closely resembling those of aqueous solutions.

(v) **Low-Temperature Operation of Nafion Dryers.** Provided that eq 6 is valid at low temperatures, operating dryers at subfreezing temperatures would allow drying of the carrier gas to levels currently obtainable only using cryogenic traps. This approach would provide active removal rather than simple freezing of water, thereby reducing problems of sorption of analyte, plugging, and water release during trap defrosting^{21,37,38} which limit the applicability of cryogenic trapping. While the value of $\log P_{WN}$ predicted by eq 6 fits with observed values at -20 °C, the data at -42 °C plot above the line defining thermodynamic control of drying. At this temperature, however, ion currents for the carrier were virtually indistinguishable from background levels of water in the mass spectrometer. The -42 °C outlier probably represents the lower limit of water measurable in the analytical system, and it is likely that the $1/T$ relationship applies at temperatures below -20 °C.

Even though carrier gas saturated with water at 23 °C was introduced to the dryer, no problems with icing or peak broadening were evident at temperatures down to -42 °C. This trouble-free performance is attributed to the arrangement indicated in Figure 3, in which the first third of the overall length of the dryer was not cooled but, instead, kept at room temperature. The equilibrium dew point for gas dried by Nafion at 25 °C is -62 ° (eqs 5 and 6), and experience with short dryers (see also discussion of design optima, below), indicates that approximately 90% of the water is removed in this initial segment at temperatures above the freezing point of water.

Construction and Optimization of Nafion Dryers. (i) **Dimensions of the Dryer and Carrier Gas Flow Rate.** For efficient drying, the residence time of gas in a dryer must be greater than the time required for diffusion of water through the carrier gas and through the Nafion membrane. In a rigorous analysis, Wang et al.³⁹ report that, for dryers constructed of a material which is structurally similar to Nafion, mass transport of water through the membrane is sufficiently high that overall mass transport in the dryer is controlled by diffusion of water in the

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Table 2. Coefficient of Diffusion^a of Water at 1 atm

<i>T</i> (°C)	<i>D</i> , cm ² /s			
	H ₂ O in He	H ₂ O in air	H ₂ O in N ₂	H ₂ O in Ar
50	0.977	0.297	0.309	0.291
23	0.908 ^b	0.260 ^b	0.265	0.259
0	0.728	0.221	0.230	0.224
-40	0.552	0.168	0.175	0.170

^a Calculated according to methods in ref. 41. ^b Experimentally determined value reported in ref. 40.

gas phase. Consequently, in this analysis, only mass transport in the gas phase will be considered.

The residence time of gas in the dryer can be calculated from the dimensions of the dryer and flow rate of the carrier according to

$$t_R = 60\pi Lr^2/F_c \quad (7)$$

where t_R is the residence time, in seconds, L and r are the length and internal radius of the Nafion tube, in centimeters, and F_c is the flow rate of carrier gas in mL/min. The maximum time required for diffusion in the gas phase (i.e., that required for diffusion from the axis of the tube to the wall) can be approximated by

$$t_D = r^2/2D \quad (8)$$

where t_D is the diffusion time, in seconds, r is the internal radius of the Nafion tube, in centimeters, and D is the coefficient of diffusion of water, in cm²/s.⁴⁰ Specific values of D , given in Table 2, depend on temperature and carrier gas composition.^{40,41} Combining eqs 7 and 8 results in the ratio t_R/t_D , which relates the length of Nafion tubing, carrier gas flow rate, and diffusion coefficient according to

$$t_R/t_D = 120\pi LD/F_c \quad (9)$$

Since both t_R and t_D increase with the square of the radius, this ratio is independent of tubing diameter.

Figure 6 summarizes the efficiency of water removal for Nafion dryers of widely varying length, inside diameter, carrier gas type, and carrier gas flow rate. Data are taken from this work and from Merritt et al.,²¹ Burns et al.,⁸ and McClenny et al.¹⁹ Efficiency is plotted against residence time (t_R) and against residence time normalized to gas diffusion time (t_R/t_D). Efficiency correlates only roughly with t_R ; for example, air dried for ~1 s in 1.0–1.3-mm-i.d. dryers was wetter than helium dried for 0.6 s in a 0.5-mm-i.d. dryer. In contrast, efficiency increases smoothly and monotonically with t_R/t_D and is maximized at $t_R/t_D \geq 10^{3.8}$.

These data confirm that diffusion in the gas phase can limit the efficiency of Nafion dryers, especially for applications involving a carrier gas (air, N₂, Ar) in which the coefficient for diffusion of water is small. Lowering the temperature of the dryer also slows diffusion in the gas phase, but in this study the effect was insignificant. Substituting $t_R/t_D \geq 10^{3.8}$ into eq 9 and rearranging produces a convenient scaling law that relates the Nafion length

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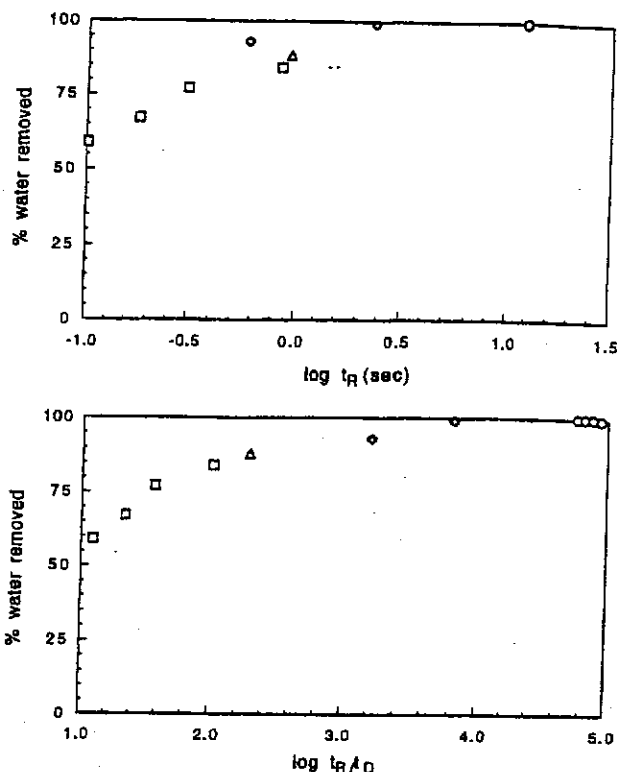


Figure 6. Efficiency of water removal as a function of $\log t_R$ and $\log t_R/t_D$ (eqs 7 and 9). Symbols represent dryers of varying length, internal diameter, carrier gas flow rate, carrier gas composition, and temperature of operation. \square :⁸ dryer, 22 cm \times 1.3 mm i.d.; saturated air flowing at 21, 57, 95, or 171 mL/min; $T = 23^\circ\text{C}$. Δ :¹⁹ 30 cm \times 1.0 mm i.d.; saturated air at 15 mL/min; $T = 23^\circ\text{C}$. \diamond :²¹ dryers, 10 cm \times 0.5 mm i.d. or 40 cm \times 0.5 mm i.d.; 2 mL He/min, $p_w \approx 1$ mTorr; $T = 23^\circ\text{C}$. \circ (this work): dryer, 60 cm \times 0.32 mm i.d., operated at 50, 23, 0, or -20°C ; carrier, 0.26 mL He/min saturated at 23°C .

necessary for efficient drying to the carrier gas flow rate:

$$L \geq F_c(10^{3.8}/120\pi D) \quad (10)$$

where L is in cm, D is in cm²/s, and F_c is in mL/min. The parenthesized scaling factor takes on values of 18–23 for drying a helium carrier at 23–0 °C; and 65–75 for drying air, N₂, or Ar over the same temperature range. As discussed for eq 9 above, this guide is independent of the diameter of the Nafion. For most analytical applications, r should be chosen to restrict broadening of analyte peaks in the dryer.

(ii) **Purge Gas Humidity and Flow Rate.** The humidity of the purge gas must be lower than the vapor pressure of water in Nafion at the operating temperature of the dryer, but strenuous efforts to dry the purge gas rigorously will lead to improvements in performance only if the Nafion membrane is also cooled. Since humidity in the purge gas rises as it absorbs water from the carrier, the annulus of the dryer should be purged countercurrent to the flow of carrier, and the flow rate of purge gas should be sufficient to prevent buildup of humidity within the annulus. Product literature recommends a purge gas flow rate at least twice the carrier flow rate.²⁷ However, for applications in which the carrier was saturated or nearly saturated with water, purge gas flows up to 8-fold higher than the carrier flow have been required in order to maintain efficient drying.^{24,25} For the measurements

Table 3. Comparison of Residual Water Levels Obtainable with Desiccants, Cryogenic Traps, and Nafion Dryers

drying method	T (°C)	residual H ₂ O			dew point (°C)
		mg/L ^c	ppmv	P _w (Torr)	
desiccants^a					
P ₂ O ₅	25	0.00003	0.04	3.1 × 10 ⁻⁵	-99
Mg(ClO ₄) ₂	25	0.00048	0.7	5.0 × 10 ⁻⁴	-83
CaO	25	0.003	4.1	3.1 × 10 ⁻³	-70
CaSO ₄	25	0.005	6.9	5.2 × 10 ⁻³	-66
Al ₂ O ₃	25	0.005	6.9	5.2 × 10 ⁻³	-66
cryogenic traps^a					
liquid N ₂	-196	4.0 × 10 ⁻²³	5.5 × 10 ⁻²⁰	4.2 × 10 ⁻²³	-196
pentane slush	-130	2.4 × 10 ⁻⁸	3.3 × 10 ⁻⁵	2.5 × 10 ⁻⁸	-130
ethanol slush	-117	6.6 × 10 ⁻⁷	9.2 × 10 ⁻⁴	7.0 × 10 ⁻⁷	-117
dry ice/acetone	-79	0.00083	1.1	8.7 × 10 ⁻⁴	-79
Nafion dryer^b					
	-40	4.2 × 10 ⁻⁶	0.0058	4.4 × 10 ⁻⁶	-109
	-20	0.00007	0.095	7.2 × 10 ⁻⁵	-94
	0	0.00075	1.0	7.9 × 10 ⁻⁴	-80
	25	0.0095	13.1	9.9 × 10 ⁻³	-61
	50	0.081	111.1	8.4 × 10 ⁻²	-43

^a Residual water data for desiccants and cryogenic traps are taken from ref 32. ^b Residual water data for Nafion dryers are calculated from eq 6. ^c For gas at 25 °C and 1 atm.

reported here, a purge gas flow rate 10 times that of the (saturated) carrier was used.

(iii) **Nafion Humidistats.** If regulation of the water content of a gas stream at some fixed level is required, this should be possible by capitalizing on the temperature dependence of P_{WN} , using an arrangement in which there is a net transfer of water from the purge gas to a carrier flow. The initial humidity of the conditioned gas would have to be below the desired set point, and the rate at which water was supplied by the (presumably humidified) purge gas would have to be higher than that required to condition the effluent, for which the humidity would be controlled by varying the temperature of the Nafion membrane. A heat exchanger could be used downstream to bring the gas to any desired temperature. For membrane temperatures between 25 and 141 °C, the water contents introduced would correspond (at 25 °C) to relative humidities between 0.04 and 100%.

Comparison of Nafion Dryers with Desiccants and Cryogenic Traps. To facilitate comparison among drying methods, Table 3 lists residual humidities obtained with a Nafion dryer in this study together, with values previously reported for commonly used desiccants and cryogenic traps. At 25 °C, a Nafion dryer can remove 99.96% of the water from a saturated carrier, resulting in a dew point of -61 °C. This result exceeds the -45 °C minimum value reported in the Nafion product literature²⁷ by 16 °C. Correction for the systematic 5–10% underestimation of Δ^{18} ; raises the dew point only to -59 °C. Random uncertainties associated with mass spectrometric measurements of m/z 18 ion currents, measurements of ionization efficiencies and gas flow rates, and regression coefficients for eqs 5 and 6, when carried through the dew point calculations, produce uncertainties of ± 11 °C. Based on the residual humidities measured in this study, Nafion dryers operated at ambient conditions are slightly less effective than CaSO₄ as a means of dehumidifying gas. A Nafion dryer operated at 0 °C removes water from (ambient) saturated carrier with 99.997% efficiency, or about as well as Mg(ClO₄)₂ or a dry ice/acetone cryogenic trap. It is possible that Nafion dryers at -50 to -70 °C may decrease residual humidity to levels otherwise attainable only with liquid nitrogen-cooled ethanol or pentane slushes while maintaining active removal of water;

however, limitations in the experimental approach taken here precluded the investigation of such low-temperature applications.

SUMMARY AND CONCLUSIONS

Humidity in Nafion-dried carrier gas initially saturated with water at 23 °C has been measured as a function of temperature of the Nafion dryer. The partial pressure of residual water in the dried gas increased by more than 3 orders of magnitude as the temperature of the dryer was increased from -20 to 50 °C.

The thermodynamic relationship between temperature and vapor pressure of water over Nafion was determined experimentally to be

$$\log P_{WN} = -3580/T + 10.02$$

The slope of this relationship was used to calculate the molar enthalpy and entropy of vaporization of water from Nafion, which are 69 ± 3 kJ/mol and 120 ± 11 J/(K mol), respectively. These values agree well with existing thermodynamic data and physical models of Nafion.

The efficiency of water removal was compared for Nafion dryers incorporating a variety of lengths, internal diameters, carrier gas compositions, and carrier gas flow rates. Insufficient time for mass transport in the gas phase can limit dryer efficiency. This problem can be avoided by choosing the length of the dryer such that

$$L \geq F_c(10^{3.8}/120\pi D)$$

A dry, countercurrent purge gas with a flow rate 8–10-fold greater than that of the carrier gas is sufficient for removing water from a saturated carrier gas without buildup of humidity in the purge.

A Nafion dryer operated at ambient temperature can remove water from a saturated stream with up to 99.96% efficiency, produces a dew point as low as -62 °C, and is about as effective a drying agent as CaSO₄. Nafion dryers operated at 0 °C remove water with 99.997% efficiency and yield a dew point of -80 °C, which allows avoidance of protonation artifacts in CO₂ isotope-ratio mass spectrometry and which is comparable to results obtainable using Mg(ClO₄)₂ or a dry ice/acetone cryogenic trap.

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