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## PROBLEMS WITH A NAFION® MEMBRANE DRYER FOR DRYING CHROMATOGRAPHIC SAMPLES

WALTER F. BURNS\*

*Northrop Services, Inc., 200 S.W. 35th St., Corvallis, OR 97333 (U.S.A.)*

DAVID T. TINGEY

*USEPA, Corvallis Environmental Research Laboratory, 200 S.W. 35th St., Corvallis, OR 97333 (U.S.A.)*  
and

ROSEMARY C. EVANS and EMILY H. BATES

*Northrop Services, Inc., 200 S.W. 35th St., Corvallis, OR 97333 (U.S.A.)*

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### SUMMARY

A Nafion® membrane dryer was used to dry samples of organic gases emitted by vegetation before chromatographic separation to reduce water-related retention time variations on a fused-silica column. The dryer caused rearrangement of several monoterpenes and removed several important oxygenated compounds from the samples. Therefore, it was concluded the Nafion dryer was not suitable for this application.

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### INTRODUCTION

The ubiquitous presence of water vapor can cause problems when analyzing trace gases in the atmosphere. Water vapor can interfere with detector response<sup>1-3</sup>, condense and cause spurious absorption signals<sup>4</sup>, interfere with the concentration of samples<sup>5</sup>, and cause retention time variations on fused-silica open tubular columns<sup>6</sup>. The retention time variability complicates identification and quantification of compounds, particularly those which are closely eluting.

There are many desiccant materials available to dry gaseous samples, but most are not suitable for drying trace levels of a wide variety of organic compounds<sup>7</sup>. One method of drying samples for gas chromatographic (GC) separation is the permeation distillation technique<sup>8,9</sup>. This method uses a Nafion®\* tubular membrane through which water vapor permeates and then is either removed by a counterflow of dry air<sup>10</sup> or absorbed on molecular sieve<sup>8</sup>. The Nafion dryer has a low dead volume, a constant pressure drop compared to conventional bed desiccants<sup>8</sup> and most inorganic gases, hydrocarbons, chlorinated or fluorinated hydrocarbons, esters, aldehydes and some ethers were unaffected by the dryer<sup>1,8,11</sup>. However, NO<sub>2</sub> and most amines, ketones, alcohols and some ethers were removed by the Nafion dryer<sup>1,3</sup>.

\* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This report describes the use of a Nafion dryer to dry samples of organic gases emitted by vegetation to reduce retention time variations on a fused-silica column and problems encountered in this application.

## EXPERIMENTAL

### *Apparatus*

The Nafion dryer<sup>8</sup> was constructed of a 22 cm × 7 cm O.D. clear plastic cylinder with removable nylon end caps, contained approximately 1 m of 0.16-cm O.D. Nafion 815 tubular membrane and was filled with approximately 250 g molecular sieve 13X. The ends of the Nafion tube were connected to inlet and outlet ports (0.32 cm Swagelock bulkhead unions) in one of the end caps.

The analyses were performed on a Finnigan 9500 gas chromatograph interfaced to a Finnigan 3200 mass spectrometer or a Hewlett-Packard 5830 gas chromatograph with dual flame ionization detectors. Both gas chromatographs were modified with cryogenic concentration systems which contained a Carle 6-port valve inserted between the carrier gas pressure regulator and the column entrance, and an auxiliary flow system to transport the samples from the injection port to the cryogenic concentration loop on the 6-port valve<sup>6,12</sup>. Helium at 30 ml/min for 10 min and 20 ml/min for 4 min for the GC-mass spectrometry (MS) and GC-flame ionization detection (FID), respectively, was used to transport the samples from the injection port to the cryogenic concentration loop. The Nafion dryer was inserted between the injection port and the Carle 6-port valve on the auxiliary flow systems. The samples were cryogenically collected in the loop using liquid oxygen, revolatilized with boiling water and chromatographed on 60 m × 0.25 mm I.D. DB-1 (J & W Scientific, Rancho Cordova, CA, U.S.A.) fused-silica columns with 0.25- $\mu$ m and 1- $\mu$ m phase thicknesses for GC-MS and GC-FID, respectively. The gas chromatographs were initially maintained at 40°C for 3 min and 60°C for 1 min for GC-MS and GC-FID, respectively, and then temperature programmed at 12°C/min to 250°C.

### *Methods*

To determine the effect of flow-rate and water content on the dryer efficiency, air was bubbled through water at various temperatures and an EG&G dew-point meter (EG&G, Waltham, MD, U.S.A.) was used to measure dew point before and after the dryer. Flow through the system was controlled with a needle valve and measured with a soap bubble flowmeter.

Samples of organics emission from eucalyptus (*Eucalyptus globulus*) volatiles were collected from live plants maintained in a dynamic gas exchange chamber<sup>13</sup>. Approximately 10 l of encapsulation air was evacuated through a portable sampler immersed in liquid oxygen for GC-MS analysis and 0.1 l of encapsulation air was collected in 100-ml Pressure-Lok<sup>®</sup> syringes for GC-FID analysis.

Monoterpene standards were obtained from SCM Glidden Organics (Jacksonville, FL, U.S.A.); oxygenated compounds and isoprene were obtained from Aldrich (Milwaukee, WI, U.S.A.). The standards were maintained in septum top bottles at room temperature (22°C). For GC-MS samples, 10  $\mu$ l of headspace vapor was collected, unless otherwise specified, and injected into the auxiliary flow system. To determine the effect of water on dryer reactivity, 50  $\mu$ l of  $\alpha$ -pinene headspace vapor

was injected into 100 ml of air which had been passed through a tube immersed in liquid oxygen (dry air), or bubbled through water maintained at 22°C (wet air). For GC-FID analyses, headspace vapor of the standards was collected in 1-ml disposable syringes and approximately 40- $\mu$ l samples were injected.

GC-MS identifications were made using the Battelle (Ribermag, Houston, TX, U.S.A.) and U.S. Environmental Protection Agency (EPA)-National Institutes of Health (NIH) minicomputer mass spectral libraries and by comparing the spectra to published spectra<sup>14,15</sup>. Standard compounds were used to confirm compound identity, using retention time and mass spectral data.

## RESULTS AND DISCUSSION

Initial studies were conducted to determine the water removal efficiency of the dryer under approximately ambient conditions. At dew points between 0 and 23°C, the Nafion dryer removed between 58 and 84% of the water from the incoming air, depending on flow-rate (Table I). At low flows (below 55 ml/min), the drying efficiency increased with dew point, but the absolute amount of water exiting the dryer also increased. At low dew points (0 or 8°C), dryer efficiency was not affected by air flow-rate while at higher dew points efficiency decreased with increasing air flow. Our drying efficiency was less than the previously reported 97 to 99% efficiencies<sup>8,10</sup>. The drying efficiency decreased with increasing flow, and when the desiccant surrounding the Nafion was exhausted, the efficiency rapidly decreased. This may account for the lower efficiency we measured compared to earlier reports.

Chromatographic profiles of vegetative emissions dried with the Nafion dryer showed more peaks than in undried samples (Fig. 1 and Table II). GC-MS analysis

TABLE I  
THE EFFECT OF AIR FLOW-RATE AND DEW POINT ON DRYING EFFICIENCY FOR THE NAFION DRYER

Dew point (°C)	Air flow-rate (ml/min)	Incoming* water content ( $\mu$ g/ml)	Exiting** water content ( $\mu$ g/ml)	Water removed (%)
0	20.7	4.80	1.74	64
	54.2	4.80	1.74	64
	97.0	4.80	1.87	61
8.3	20.7	8.45	2.18	74
	55.1	8.45	2.26	73
	98.4	8.45	2.26	73
17.5	19.9	15.0	3.55	76
	54.3	15.0	5.16	66
	96.9	15.0	6.25	58
	174.4	15.0	6.35	58
23.1	20.7	20.7	3.32	84
	57.0	20.7	4.80	77
	95.2	20.7	6.80	67
	171.4	20.7	8.54	59

\* Water content of air entering the dryer.

\*\* Water content of air leaving the dryer.

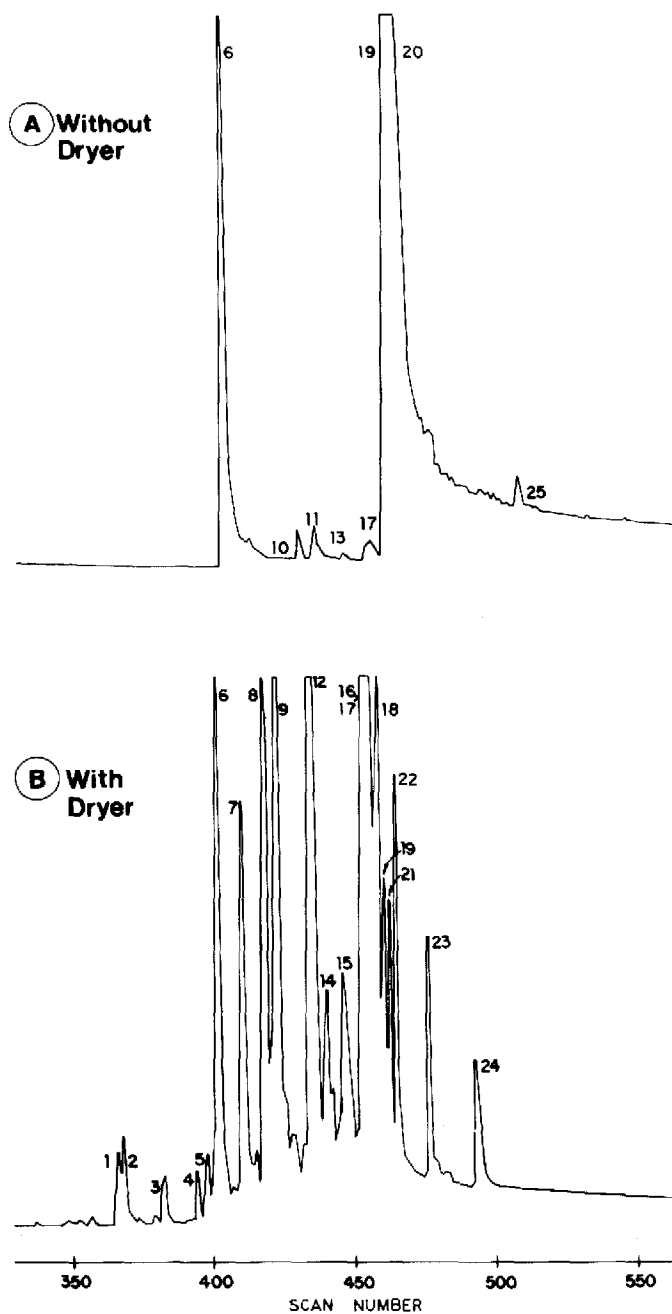


Fig. 1. The emission profiles of eucalyptus volatile emissions (A) without the Nafion dryer and (B) with the Nafion dryer. Both samples were collected under constant environmental conditions from the same plant within 1 h and analyzed under the same conditions. Eucalyptus emission profiles were found to be stable over several h under constant environmental conditions. Numbered peaks correspond to compounds in Table II.

TABLE II

COMPOUNDS IDENTIFIED FROM EUCALYPTUS VOLATILES WITHOUT AND WITH THE NAFION DRYER

Numbers correspond to numbered peaks in Fig. 1. CAS No. = Chemical Abstracts Registry Number.

Peak No.	Name	CAS. No.
<i>Without Nafion dryer</i>		
6**	$\alpha$ -Pinene	80-56-8
10**	$\beta$ -Pinene	127-91-3
11**	Myrcene	123-35-3
13**	$\alpha$ -Phellandrene	99-83-2
17**	<i>p</i> -Cymene	99-87-6
19**	Limonene	5689-27-5
20**	1,8-Cineole	470-82-6
25*	2-Methyl-6-methylene-1,7-octadiene-3-one	41702-60-7
<i>With Nafion dryer</i>		
1*	2,2,3-Trimethylbicyclo[2.2.1]heptane	20536-41-8
2	Unknown, mol.wt. 136 (C <sub>10</sub> H <sub>16</sub> )	
4*	Tricyclene	508-32-7
5	Unknown, mol.wt. 136 (C <sub>10</sub> H <sub>16</sub> )	
6**	$\alpha$ -Pinene	80-56-8
7**	Camphene	79-92-5
8	Unknown, mol.wt. 136 (C <sub>10</sub> H <sub>16</sub> )	
9	Unknown, mol.wt. 136 (C <sub>10</sub> H <sub>16</sub> )	
12*	1-Methyl-4-(1-methylethylidene)cyclohexane	1124-27-2
14	Unknown, mol.wt. 136 (C <sub>10</sub> H <sub>16</sub> )	
15**	$\Delta$ -3-Carene	13466-78-9
16**	$\alpha$ -Terpinene	99-86-5
17**	<i>p</i> -Cymene	99-87-6
18*	1-Methyl-4-(1-methylethyl)cyclohexene ( <i>p</i> -menth-1-ene)	1195-31-9
19**	Limonene	5989-27-5
21*	4-Methyl-1-(1-methylethyl)cyclohexene ( <i>p</i> -menth-3-ene)	500-00-5
22*	1-Ethyl-6-ethylidenecyclohexene	61141-57-9
23**	$\gamma$ -Terpinene	99-85-4
24**	Terpinolene	586-62-9

\* Identified by comparison of mass spectrum to published spectra.

\*\* Identified by comparison of mass spectrum and retention time to standard.

of undried eucalyptus volatiles (Fig. 1a) contained large amounts of  $\alpha$ -pinene, limonene, and 1,8-cineole and smaller amounts of  $\beta$ -pinene, myrcene,  $\alpha$ -phellandrene, *p*-cymene, and 2-methyl-6-methylene-1,7-octadien-3-one. This agrees closely with the compounds identified in eucalyptus oil<sup>16</sup>. The Nafion-dried samples of eucalyptus volatiles (Fig. 1b) contained only  $\alpha$ -pinene, *p*-cymene and limonene in common with the non-dried samples. In addition, other compounds identified in the dried sample included: 1-methyl-4-(1-methylethylidene)cyclohexane,  $\alpha$ -terpinene, *p*-cymene, *p*-menth-1-ene, limonene, *p*-menth-3-ene, 1-ethyl-6-ethylidenecyclohexene,  $\gamma$ -terpinene, terpinolene and several compounds which appeared to be C<sub>10</sub>H<sub>16</sub> terpenes (mol.wt. 136). Several compounds, 1,8-cineole,  $\beta$ -pinene, myrcene,  $\alpha$ -phellandrene and 2-methyl-6-methylene-1,7-octadien-3-one previously identified in the wet samples were not

TABLE III  
 THE COMPOUNDS FOUND AND THEIR PERCENT RECOVERY AFTER THE INJECTION OF INDIVIDUAL DRY STANDARDS THROUGH THE  
 NAFION DRYER  
 CAS No. = Chemical Abstracts Registry Number.

Standards studied		<i>Isoprene</i> ***	<i>Camphene</i> ***	<i>Myrcene</i> ***	<i>p-Cymene</i>	<i>Limonene</i> ***	<i>Δ-3-Carene</i> ***
<i>Compounds found</i>	<i>CAS. No.</i>						
<i>Isoprene</i> **	78-79-5	100					
2,2,3-Trimethyl-bicyclo[2.2.1]-heptane*	20536-40-7	28 9	22 7				
Unknown C <sub>10</sub> H <sub>18</sub> , mol.wt. 138							
1,4-Dimethyl-5-(1-methylethyl)-cyclopentene*	61142-33-4			22 14 9 11		7 7	7 4
Unknown C <sub>10</sub> H <sub>18</sub> , mol.wt. 138							
Unknown C <sub>10</sub> H <sub>16</sub> , mol.wt. 136		19	29				
Unknown C <sub>10</sub> H <sub>18</sub> , mol.wt. 138							
Unknown C <sub>10</sub> H <sub>16</sub> , mol.wt. 136			18				
Unknown C <sub>10</sub> H <sub>16</sub> , mol.wt. 136						5	
Unknown C <sub>10</sub> H <sub>18</sub> , mol.wt. 138		11	18				
2,3,4,5-Tetramethyl-1,4-hexadiene*	51504-54-2			20			
1-Methyl-4-(1-methyl-ethylidene)cyclohexane*	1124-27-2	12				20	18
1-Methyl-3-(1-methyl-ethyl)cyclohexene*	13828-31-4						3
<i>p</i> -Cymene**	99-87-6	21	6	24	100	59	62
3-Methyl-6-(1-methyl-ethyl)cyclohexene*	1124-26-1					9	6
Total		100	100	100	100	100	100

\* Identified by comparison of mass spectrum to published spectra.

\*\* Identified by comparison of mass spectrum and retention time to standard.

\*\*\* None of the injected standard was recovered.

found. From these data it appeared that one or more of the compounds in the eucalyptus volatiles were reacting or rearranging in the dryer, yielding new compounds.

To determine if standards of the monoterpenes would react or rearrange in the dryer and form similar products, six monoterpenes which represent five common skeletal structures as defined by Devlon and Scott<sup>17</sup> were selected for analysis by GC-MS with and without the dryer. The monoterpene skeletal types included: menthanes, represented by limonene and *p*-cymene; the linear group by myrcene; pines by  $\alpha$ -pinene; camphanes by camphene, and caranes by delta-3-carene. Isoprene, a hemiterpene, was also studied.

Isoprene and *p*-cymene were unaffected in the Nafion dryer; the other monoterpenes studied rearranged into several products (Table III). Except for *p*-cymene and isoprene, none of the injected compounds were detected. The monoterpenes each yielded slightly different products. Ten of the new products appeared to have a molecular weight of 138 ( $C_{10}H_{18}$ ), three appeared to have a molecular weight of 136 ( $C_{10}H_{16}$ ) and *p*-cymene which has a molecular weight of 134 ( $C_{10}H_{14}$ ). *p*-Cymene was the largest product from the rearrangement of the monoterpene standards except from the  $\alpha$ -pinene and camphene standard, where it ranked 2nd and 6th, respectively. The same standards were analyzed before the Nafion dryer was installed in the injection system and each had a purity of greater than 75%. From these data it appeared that the dryer was more reactive to the monoterpene standards than to similar compounds from the eucalyptus sample. In the dried eucalyptus sample (Fig. 1b),  $\alpha$ -pinene and limonene were present, while these were completely rearranged and not detected when these standards were injected. When the dryer was removed from the injection system, it was found that the injection system had become contaminated and was still reactive to the standards.

To document the injection system contamination and determine if water in the samples could decrease the reactivity of the Nafion dryer,  $\alpha$ -pinene standard in dry air was analyzed by GC-MS without the dryer (Fig. 2a), in dry air with the dryer (Fig. 2b), in wet air with the dryer (Fig. 2c), and in dry air immediately after the dryer was removed (Fig. 2d). Figure 2a shows the purity of the  $\alpha$ -pinene standard and that rearrangement did not occur under normal operating conditions without the dryer. When an identical sample was injected through the dryer (Fig. 2b),  $\alpha$ -pinene was not found, but camphene, *p*-cymene, tricyclene, and a  $C_{10}H_{18}$  compound were the major components. The products from the wet  $\alpha$ -pinene standard (Fig. 2c) were similar to the dry standard (Fig. 2b), indicating that the water in the sample did not change the reactivity of the Nafion dryer to the  $\alpha$ -pinene standard. After the dryer was removed, camphene was still found as the major component when a dry sample of  $\alpha$ -pinene was injected (Fig. 2d), indicating that a product from the dryer had contaminated the stainless-steel lines, the 6-port valve, and/or the cryogenic loop on the injection system. It is not known if the rearrangements of the monoterpenes occurred in the dryer as well as in the contaminated injection system. The reactivity of the injection system lasted for several days after the dryer was removed, even when helium continuously purged the system. A solution of 0.5 ml Liqui-NOX<sup>®</sup> detergent in 100 ml distilled water, all of which was forced through the injection system, eliminated the reactivity. Over the course of this study, it was found that the reaction products changed each time the dryer was removed, the injection system cleaned, and the dryer reinstalled. However, in all cases except for isoprene and *p*-cymene, the

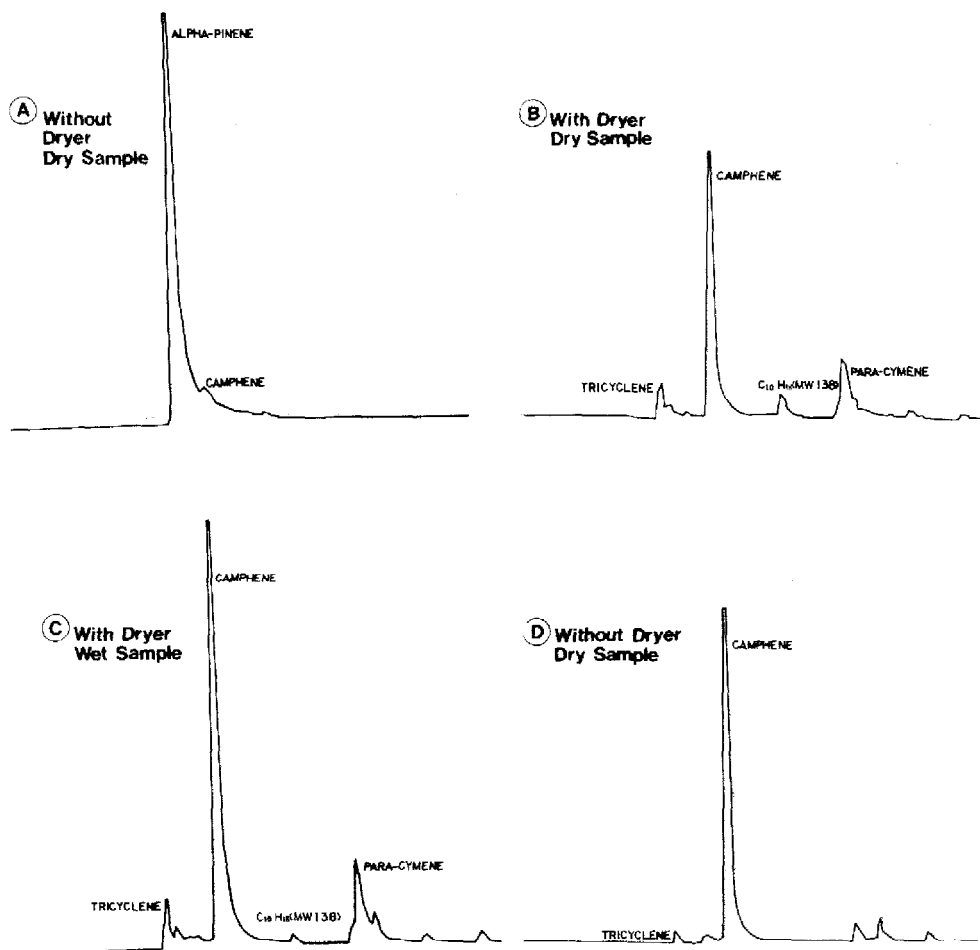


Fig. 2. Total ion current profiles of an  $\alpha$ -pinene standard (A) without the dryer and a dry sample, before the dryer was installed, (B) with the dryer and a dry sample, (C) with the dryer and a wet sample, and (D) after dryer was removed and a dry sample. Wet or dry samples were prepared by injecting 50  $\mu$ l of  $\alpha$ -pinene headspace vapor into 100 cc of air which had been bubbled through water at 22°C or drawn through a tube immersed in liquid oxygen, respectively. MW = Molecular weight.

TABLE IV

THE REMOVAL OF OXYGENATED COMPOUNDS FROM THE SAMPLE BY THE NAFION DRYER

CAS No. = Chemical Abstracts Registry Number.

Oxygenate standard	CAS No.	Amount removed
Cyclopentanone	120-92-3	All
Cyclopentanol	96-41-3	All
1-Penten-3-ol	616-25-1	All
3-Pentanone	96-22-0	All
<i>n</i> -Hexanal	66-25-1	Partial
<i>trans</i> -2-Hexenal	6728-26-3	Partial
3-Hexen-1-ol	544-12-7	All



injected standards were altered by the dryer, and/or by the dryer-contaminated injection system.

Several oxygenated compounds which have been identified in vegetative emissions<sup>18-21</sup> were studied to determine if these compounds also reacted or were removed by the dryer (Table IV). Three alcohols, two ketones and two aldehydes, either C<sub>5</sub> or C<sub>6</sub>, were tested by injecting 50  $\mu$ l of the standards through the dryer and analyzing by GC-MS. The alcohols and ketones were completely removed and the aldehydes were partially removed or held up in the dryer and appeared in the next several runs.

## CONCLUSION

We found the Nafion dryer unsuitable for drying hydrocarbons and oxygenated compounds emitted from vegetative sources because it caused rearrangement of the monoterpenes and removed several important oxygenated compounds from the sample.

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