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- (19) Budzikiewicz, H.; Krüger, U.; Sasse, W. D.; Wiegand, W. *Liebigs Ann. Chem.* **1970**, 737, 119.
- (20) Windholz, M., Ed. "The Merck Index"; 9th ed.; Merck and Co.: Rahway, NJ, 1976; p 872.
- (21) Hultzer, H. J. *Forensic Sci.* **1983**, 28, 40.
- (22) Polonovski, M.; Polonovski, M. *Bull. Soc. Chim. Fr.* **1927**, 41, 1190.
- (23) Polonovski, M.; Polonovski, M. *C. R. Hebd. Seances Acad. Sci.* **1927**, 184, 331.
- (24) Polonovski, M.; Polonovski, M. *Bull. Soc. Chim. Fr.* **1927**, 1186.
- (25) Sunjic, V.; Kafetz, F.; Kolbah, D.; Hofman, H.; Stromer, M. *Tetrahedron Lett.* **1973**, 3209.
- (26) Hayashi, Y.; Nagano, Y.; Hongyo, S.; Teramuna, K. *Tetrahedron Lett.* **1974**, 1299.
- (27) Shamma, M. "The Isoquinoline Alkaloids"; Academic Press: New York, 1971; p 373.
- (28) Schneider, W.; Müller, B. *Liebigs Ann. Chem.* **1958**, 615, 34.
- (29) Santavy, F. *Alkaloids (N. Y.)* **1979**, 17, 399.
- (30) See reference 27, p 377.
- (31) *Top. Stereochem.* **1976**, 9, 87.
- (32) Safe, S.; Moir, R. Y. *Can. J. Chem.* **1964**, 42, 160.
- (33) Shamma, M.; Georgiev, V. S. *Tetrahedron Lett.* **1974**, 2339.
- (34) Snatzke, G.; Wollenberg, G.; Herbek, J., Jr.; Santavy, F.; Blaha, K.; Klyne, W.; Swan, R. J. *Tetrahedron* **1969**, 25, 5059.
- (35) Bertgen, C.; Fleischhacker, W.; Viebock, F. *Chem. Ber.* **1967**, 100, 3002.
- (36) Klein, M.; Moore, L. P.; Studier, M. H., unpublished work, Argonne National Laboratory, Argonne, IL, 1974.
- (37) Allen, A. C.; Cooper, D. A., unpublished work, Drug Enforcement Administration, McLean, VA, 1980.
- (38) Rice, K. C.; May, E. L. *J. Heterocyclic Chem.* **1977**, 14, 665.
- (39) Rice, K. C. *J. Org. Chem.* **1975**, 40, 1850.
- (40) Rice, K. C. *J. Org. Chem.* **1975**, 40, 1850.
- (41) Klein, M. In "Mass Spectrometry in Drug Metabolism"; Frigerio, A., Ghisalbetti, E. L., Eds.; Plenum Press: New York, 1977; p 449.
- (42) Holmes, H. L. *Alkaloids (N. Y.)* **1952**, 2, 109-112.

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Automated Cryogenic Preconcentration and Gas Chromatographic Determination of Volatile Organic Compounds in Air

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The methodology used in reduced temperature preconcentration of volatile organic compounds (VOCs) has been tested by using a specially designed system for automated sampling and analysis. The system design incorporates microprocessor-controlled trap temperature cycling and gas chromatographic valve sequencing. Stabilized trap temperature levels are electronically maintained by either controlled release of vaporized liquid N₂ during sampling or by intermittent resistive heating during thermal desorption. A unique trap design permits rapid cooling and heating. During methodology testing, VOC collection and recovery efficiencies were 100 ± 5% and the integrity of sample components was unaffected by the use of a Nafion tube dryer or by cocollection of ozone and nitrogen dioxide. Two nominally identical automated systems gave nearly identical results during simultaneous monitoring of the same laboratory air samples.

The reduced trapping technique for preconcentration of volatile organic compounds (VOCs) from ambient air has proven to be a viable approach to achieve optimum analytical sensitivity and selectivity for VOC monitoring. In most cases the samples are first collected by some convenient means such as on solid adsorbents, or in specially prepared canisters or polymeric bags, and transported to the appropriate analytical instrumentation. Sample is then pulled through a packed, coiled tubular trap immersed in a cryogenic fluid such as liquid nitrogen or liquid oxygen to "cryofocus" the sample prior to

thermal desorption (1-4). Some of the most recent applications include the determination of concentrations of 44 organics during on-site monitoring in 10 US cities (5), the monitoring of selected trace gas concentrations as indicators of the source of pollution (6), and the development of new analysis procedures for trace level organics in ambient air (7). In some instances, whole air samples are cryocondensed using liquid nitrogen or liquid helium. The required equipment can be made portable so that large sample volumes can be collected remotely and returned to the laboratory for analysis. This approach has been utilized in numerous tropospheric (8, 9) and stratospheric (10, 11) sampling programs.

Our application is for direct sampling from a manifold located at the sampling site, e.g., sampling from a stationary mobile van or fixed installation, or for sampling from canisters that have been returned to the fixed installation for analysis. A given sample volume is passed through a reduced temperature trap cooled to typically -150 °C. The trap is warm enough to allow the main components of air to pass completely through yet cold enough to collect trace organics efficiently. This procedure has several limitations which must be considered when designing a sampling and analytical system. A limiting factor of major importance is the trapping of water vapor from the ambient air sample. One liter of air at 50% relative humidity and 25 °C will contain approximately 10 mg of water that appears as ice in the collection trap. The possibility of ice plugging the trap and stopping or altering flow is of concern. Even when the trap is not plugged, carrier flow stoppage can still occur at the head of the capillary

column if oven temperature programming is started below 0 °C. Carrier flow variation or temporary stoppage will cause variability in retention times and may cause incomplete cryotrap desorption.

The purpose of this paper is to report the results of experiments designed to characterize the reduced temperature preconcentration technique for a given set of VOCs, mostly chlorinated hydrocarbons, when sampling directly from an ambient manifold. Considering the prospect of a large number of tests and repetitions, we have designed an automated sampling and analysis system, the main features of which are presented first. Following this, the technique characterization is presented and includes (1) the effect of Nafion tube dryers on sample integrity, (2) potential interference or artifact effects from cocollected ozone and nitrogen dioxide gases, and (3) collection and recovery efficiencies. Comparisons of monitoring sequences with two nominally identical systems are given as an example of the successful use of the information and procedures that were developed during the studies.

Some previous applications of Nafion tube dryers have helped to define the conditions under which they can be successfully used (7, 13–15). To our knowledge, no previous systematic tests have been reported on the effects of cocollected ozone and nitrogen dioxide on sample integrity with respect to VOCs. As part of a study on rural non-methane hydrocarbons, Ferman (12) describes a partially automated system using a cryogenic trap and injection system similar in function to ours; however, the system presented here incorporates unique features including (1) a Nafion tube dryer at the sample inlet, (2) adaptation of commercially available equipment, and (3) totally automated, repetitive performance.

EXPERIMENTAL SECTION

Preparation of Gas Mixtures. For most of the tests, liquid standards were made by diluting the neat reagents with methanol. The reagents were obtained from the Eastman Kodak Co. or the Baker Chemical Co. Compounds were at least 95% pure. Gas mixtures were prepared by injecting predetermined amounts of each test compound into a cylinder that had been partially evacuated, to ensure total vaporization of the standard. Once the mixture had equilibrated, the cylinder was pressurized to 1200 psig with nitrogen. FID response to benzene in the gas mixture was compared to the response of an NBS-certified propane standard to establish the absolute benzene concentration based on equal parts-per-billion carbon (ppbC) FID response of these two hydrocarbons. Accurate compound response factors relative to benzene were then established in a second set of experiments. Finally the response factors and the absolute benzene concentration were multiplied to establish the absolute concentration of other gases in the mix. A compressed gas mixture purchased from Scott Environmental Technology Inc. was also used at times. It contained several VOCs at nominal concentrations of 10 ppmv in N₂. Of the 16 compounds 5 were compared with NBS-prepared compressed gas standards and shown to agree within ±10%.

A gas-phase dynamic dilution system from Columbia Scientific Industries (Model 1750) was employed to generate ppbv and pptv VOC concentrations from the compressed gas mixtures. Zero air from an Aadco Inc. clean-air generator was used for sample dilution. Internal Tylan Model 260 mass flow controllers provided accurate gas flows, which were verified with a soap-film bubble meter. The CSI unit was also used to produce different concentration levels of O₃ and NO₂. To do this, modifications were made so that the target mixture would enter through one mass flow controller while NO gas simultaneously passed through the other controller. With the unit in the gas-phase titration mode various ozone concentrations were generated and served to oxidize the incoming NO to NO₂. The NO₂, excess O₃, and target compounds were then directed through a mixing chamber and exhausted to the gas chromatographic system for analysis. During tests on humid air streams, an impinger filled with distilled water was placed in the sample stream. An EG&G Model 911 hygrometer provided data on relative humidity. A sling psychrometer provided a calibration check of the hydrometer.

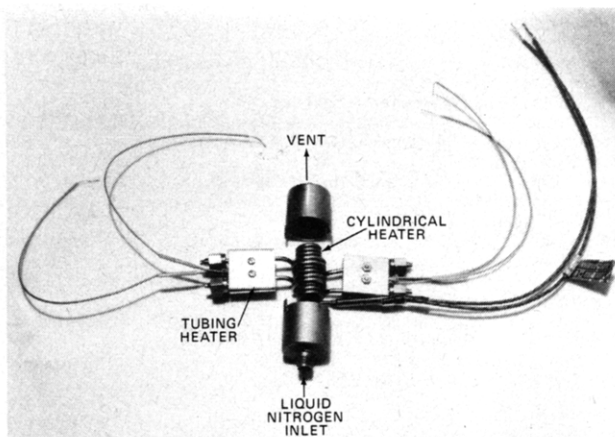


Figure 1. Photograph of a disassembled trap enclosure.

Instrumentation. The prototype system incorporates a Hewlett-Packard Model 5880A-Level 4 gas chromatograph and a Nutech Model 320-01 cryogenic sampling unit. A 50 m × 0.32 mm i.d., OV-1 fused silica column (Hewlett-Packard) was used to resolve the target compounds. The column flow was maintained at a linear velocity of 30 cm/s by using a Tylan Model 260 flow controller. Zero-grade helium served as the carrier gas, and zero-grade nitrogen was used as the make-up gas to provide proper electron capture operation. Optimum analytical results were achieved by temperature programming the gas chromatographic column from -50 to 150 °C at 8 °C/min. All transfer components (tubing, valves) were heated to minimize sample losses by physical adsorption.

The packed metal tubing used for reduced temperature trapping of VOCs is shown in Figure 1. It consists of a double loop of 0.32 cm o.d. nickel tubing packed with 60–80-mesh Pyrex beads. Two of these loops are shown wound onto a cylindrically formed tubing heater (250 W). Cartridge heaters (25 W) are sandwiched between pieces of aluminum plate at the trap inlet and outlet to provide additional heat to eliminate cold spots in the transfer tubing. During operation, the traps are inside the two-section stainless steel shell which is well insulated from its surroundings. Direct thermal contact between the heater and the trap tubing assures rapid heating (-150 to +100 °C in 55 s), and the shell facilitates efficient cooling (+120 to -150 °C in 225 s) by confining the vaporized cryogen to the small open volume surrounding the trap assembly.

Flow routing is controlled by operation of a Seiscor Model VIII six-port air-actuated vacuum-assisted valve. Electronic mass flow control (Tylan Model 260, 1–50 mL/min) downstream of the trap assures a constant sample flow and provides an analogue output to detect flow anomalies. The carrier gas flow is held constant at 4 mL/min by a second controller (0–10 mL/min of helium). Flow is normally split in equal amounts to a FID and an ECD.

The trap assembly and Seiscor valve are mounted on a base-plate fitted into the injection and auxiliary zones of the GC on an insulated pad directly above the column oven. The carrier gas line is connected to the injection end of the analytic column with a zero-dead-volume fitting that is usually held in the heated zone above the GC oven. At 15 cm × 15 cm × 24 cm aluminum box is fitted over the sample handling elements to complete the package. Trap coolant is vented through the top of the box.

Perma-Pure dryers (16) with a tubular hygroscopic ion-exchange membrane (Nafion) were used to remove water vapor selectively from mixed gas streams. The dryers were purchased in a shell and tube configuration. The tube was 0.1 cm i.d. and was imbedded within a shell of tubing with 0.25 cm i.d. of either Teflon or poly(propylene), depending on the particular dryer used. Tube lengths of both 30 and 120 cm were evaluated as noted in the text. Sample flow through the tube was set within the range of 15–60 mL/min during the tests. A countercurrent flow of dry zero air (approximately 200 mL/min) was used to purge the shell. Literature data on the drying performance of this unit under our experimental conditions show a product dew point of less than -5 °C when the incoming wet stream has a dew point of 24 °C (16). Experiments in our laboratories have confirmed this.

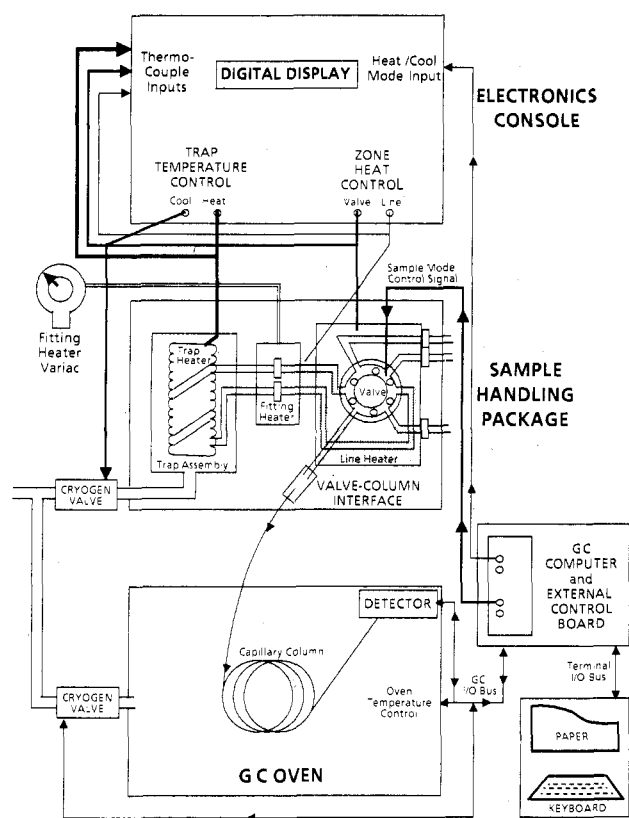


Figure 2. Block diagram of the fully integrated and automated sampling system.

The valve-column interface is placed in the heated enclosure of the sample handling package to optimize chromatographic resolution. Optimization occurs since the VOCs are recondensed in the capillary column. Alternative placement of the interface in the GC oven increases the volume in which condensation occurs and decreases resolution. Base-line separation of 1,2-dichloroethane and methylchloroform which have retention times of 14.63 and 14.77 min can be achieved.

Automation. Repetitive, unattended operation of sampling and analysis is achieved by adding communication links between the GC and both the Nutech and the air-assist valve that switches the Seiscor valve. A schematic of the overall system is shown in Figure 2. The communication link is established by using the external event control board of the HP 5880A. One 24-V dc output signal from the board is used to choose between the heating and cooling mode of the Nutech. During heating, current is supplied to the trap heater. Trap temperature is monitored by a thermocouple attached to the trap surface, and the signal is used to control the trap temperature at a preselected set point by turning the heater current off or on. During cooling, the Nutech is used to supply an actuation current to a cryogen valve so as to regulate the rate of release and thereby achieve a preselected set point. A second circuit on the external event control board is used to change the Seiscor valve configuration so as to either bypass the trap or not. Table I gives the listing of programs to implement automated repetitive operation. As noted from the table, valve 1 is used to select the position of the Seiscor valve and valve 3 is used to select the heat/cool mode. When this program is implemented, the temperature cycling for the trap and oven, as monitored by type K thermocouples is shown in Figure 3 along with the valve and GC status modes.

Trap temperature stability during a run was measured for trapping temperature set points ranging from 50 down to -180°C . From $+50$ to -70°C , the trap temperature stayed at the preset value, but temperature variation about the nominal value increased monotonically to a maximum of $\pm 4^{\circ}\text{C}$ at a set point of -180°C . Close examination of the thermocouple trace shows fluctuations of $\pm 3^{\circ}\text{C}$ at the normal set point for trapping of -150°C .

Overall system precision for sampling and analysis of VOCs at the 1–10 ppbv level is 2–5% based on statistical analyses of

Table I. Programs to Implement Automated Repetitive Operation

Oven Temperature Program	
initial value	-50°C
initial time	3 min
program rate	$8^{\circ}\text{C}/\text{min}$
final value	150°C
final time	7 min
post value	-50°C
post time	10 min

Run Table Program (Concurrent with Oven Temperature Program)

run time, min	command	comments
0.50	valve 1 on	sampling valve to inject mode
1.00	valve 3 off	trap temp control to heat mode
5.00	valve 3 on	trap temp control to cool mode
10.00	valve 1 off	sampling valve to collect mode
35.00	start valve 4 on	dummy command to recycle program

Table II. Average Retention Times (RT) and Standard Deviations (SD) for Several Compounds Cryogenically Collected and Analyzed under Dry and Humidified Conditions^a

compound	dry ^b		humidified ^c	
	RT	SD	RT	SD
chloroform	11.61	0.01	11.82	0.28
methylchloroform	12.50	0.01	12.66	0.22
carbon tetrachloride	13.09	0.00	13.22	0.18
trichloroethylene	14.12	0.01	14.21	0.12
tetrachloroethylene	17.27	0.00	17.30	0.04

^a 200-cm³ air samples analyzed via electron capture detection.

^b Average of three runs at <100 ppm H₂O vapor. ^c Average of four runs at 27% RH and 27°C .

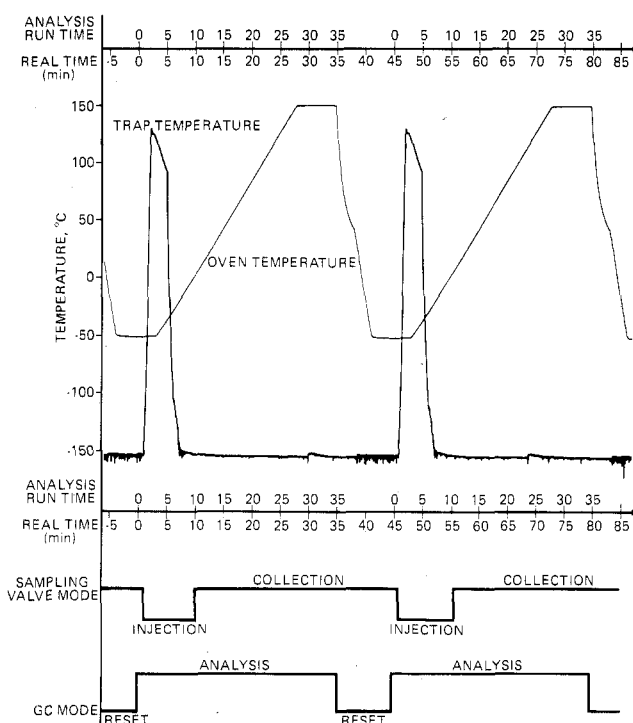


Figure 3. Event sequencing and temperature profiles for typical repetitive operations using programs given in Table I.

replicate sampling when collecting a 150–200-mL sample. Retention time variability of ≈ 0.01 -min variation occurs for retention times in the range of 11–18 min, although humidified samples taken without drying the sample show a marked increase in

Table III. Ozone and Nitrogen Dioxide Interference Results Using Flame Ionization Detection (200-cm³ Samples; Concentrations in ppbv)

compound, ppb	test 1	test 2	test 3	test 4
O ₃	0	100	200	300
NO ₂	0	250	250	250
vinylidene chloride	8.7	8.8	8.8	9.1
trichlorotrifluoroethane	17.3	17.0	17.0	16.8
chloroform	4.8	5.1	5.1	5.2
1,2-dichloroethane	3.1	3.2	3.1	3.2
methylchloroform	3.8	3.8	3.8	4.0
benzene	5.7	5.7	5.7	5.9
carbon tetrachloride	7.8	7.9	8.0	7.9
trichloroethylene	4.8	5.0	5.0	5.2
1,3-dichloropropene	9.7	9.4	9.7	8.7
toluene	14.2	14.1	14.5	14.2
1,2-dibromoethane	6.7	6.9	7.1	7.2
tetrachloroethylene	4.2	4.1	4.1	4.3
chlorobenzene	2.9	3.0	3.1	3.2
o-xylene	7.2	7.5	7.8	7.5
benzyl chloride	1.3	1.3	1.4	1.4
hexachlorobutadiene	0.9	0.9	1.0	1.1

^a 200-cm³ samples analyzed via flame ionization detection.**Table IV. Sample Integrity Results with a Perma-Pure Dryer for Compounds Responding to an Electron Capture Detector (5-cm³ Sample Loop; Concentrations in pptv)^a**

compound, ppt	dry sample ^b		humidified sample ^c	
	thru dryer	bypass dryer	thru dryer	bypass dryer
trichlorotrifluoroethane	375	345	376 ± 60	378 ± 40
chloroform	213	213	215 ± 3	219 ± 3
methylchloroform	290	287	251 ± 13	274 ± 9
carbon tetrachloride	660	660	630 ± 21	655 ± 28
trichloroethylene ^d				
1,3-dichloropropene (cis)	900	900	933 ± 35	950 ± 35
1,2-dibromoethane	640	659	640 ± 13	653 ± 6
tetrachloroethylene	318	318	316 ± 7	313 ± 14
hexachlorobutadiene	130	145	140 ± 3	138 ± 7

^a A single analysis was made during the dry sample experiment; duplicate analyses were performed during the humidified experiments. ^b <100 ppm H₂O vapor. ^c 80% RH at 25 °C.^d Contamination in stream-selecting valve.

retention time variability. This behavior is shown in Table II. The trend of increased variability with decreasing retention time in Table II is typical when cryogenically trapped compounds including water are transferred from the trap to a capillary column held at reduced temperature. The column is blocked temporarily by ice until the column temperature is increased. The time delay

interval is a smaller fraction of the retention time for compounds eluting last.

Collection and Release Efficiency. Cryogenic collection and recovery efficiency studies of the target compounds were carried out by comparing the peak area response values obtained by direct sample loop injections to the values found by cryogenic preconcentration of dilute sample streams. When the dilution stream and concentration effects from the cryogenic collection procedure (200-mL samples) were taken into account, recovery efficiencies of 100 ± 5% were obtained for all the compounds. This recovery is within the estimated experimental error of ± 10% and consisted primarily of errors in determining gas dilution and sample volumes. It should be noted that cryogenic trapping of trace species has also been tested in the presence of high ppmv levels (100 ppmv) of compounds such as methanol and water. In these studies low recovery efficiencies were initially obtained due to low trap desorption temperatures (90 °C) that resulted in partial transfer of the collected trace species. When the desorption temperature was increased to 120 °C, recovery efficiencies of 100 ± 5% were realized.

Interference from Collected Compounds. The results from four ozone and nitrogen dioxide interference tests are depicted in Table III. Sample air was dry and no dryer was used. Test 1 was conducted without the addition of O₃ and NO₂. During tests 2, 3, and 4, ozone concentrations were 100, 200, or 300 ppbv and the nitrogen dioxide level was maintained at 250 ppbv. Target compound concentrations ranged from 0.9 ppbv for hexachlorobutadiene to 17.3 ppbv for trichlorotrifluoroethane. None of the target compounds was effected by the presence of O₃ or NO₂. Furthermore, no artifact peaks or deleterious column effects were observed during or subsequent to these tests. Although these experiments were certainly not exhaustive, the generated concentrations were construed to be realistic atmospheric levels.

Testing of Perma-Pure Dryers. The Perma-Pure Dryers were tested by comparing results obtained while bypassing or sampling through the dryers. Results are shown for pptv level concentrations in Table IV using an electron capture detector and a 30-cm dryer (Model MD-125-12F). There is essentially no sample loss when the Perma-Pure dryer is in line. Additional tests for all VOCs listed in Table III (except for vinylidene chloride) using the FID, for concentration levels in the range 25–250 ppbv, gave similar results after inlet line sample conditioning effects were taken into account. Tests were later repeated with the 120-cm dryer (Model MD-125-48F) with the same results.

In separate tests two automated, nominally identical systems of the type used in the preceding tests were used to sample ambient and synthetic air mixtures through a common inlet port. In one test, Nafion tube dryers were switched between systems during successive sampling and analysis runs using a 16-component Scott compressed gas mixture diluted to approximately 20 ppbv concentrations in humidified zero air. Figure 4 shows the results of comparing electron capture detector (ECD) response ratios before (R1) and after (R2) the switch, where, for example, R1 denotes the ratio of ECD 1 to ECD 2 responses. Since response factors of the two ECDs were different, ECD 1 response ECD 2 response and R1, R2 ≠ 1.0. However, R2 should be equal to R1 if the Nafion tube dryers are equivalent. Figure 4 shows this to be the case where compounds 1–8 correspond to the list

Table V. Comparison of Two Automated GC Units Sampling Simultaneously from a Common Manifold^a

compound	run 1 GC			run 2 GC			run 3 GC		
	1	2	% D ^b	1	2	% D	1	2	% D
trichlorotrifluoroethane	0.157	0.176	5.7	0.236	0.240	0.8	0.229	0.235	1.3
chloroform	0.145	0.199	15.7	0.426	0.481	6.0	0.567	0.604	3.2
methylchloroform	0.489	0.559	6.7	0.712	0.747	2.4	0.644	0.663	1.4
carbon tetrachloride	0.154	0.155	0.3	0.208	0.194	3.5	0.202	0.184	4.6
trichloroethylene	0.288	0.439	20.8	0.639	0.753	8.4	0.762	0.678	5.8
tetrachloroethylene	1.252	1.467	7.9	4.786	5.368	5.8	4.632	4.988	3.7
benzene	0.720	c		0.77	c		0.91	c	
toluene	3.40	3.49	1.3	7.17	7.56	2.6	9.290	9.520	1.3
o-xylene	1.39	1.15	5.5	4.16	3.68	6.1	4.300	3.410	11.5

^a 0.3 L of laboratory air collected with cryogenic preconcentration techniques (23 °C, 40% RH). ^b Percent deviation from the mean.

c Indicates a coeluting interferant.

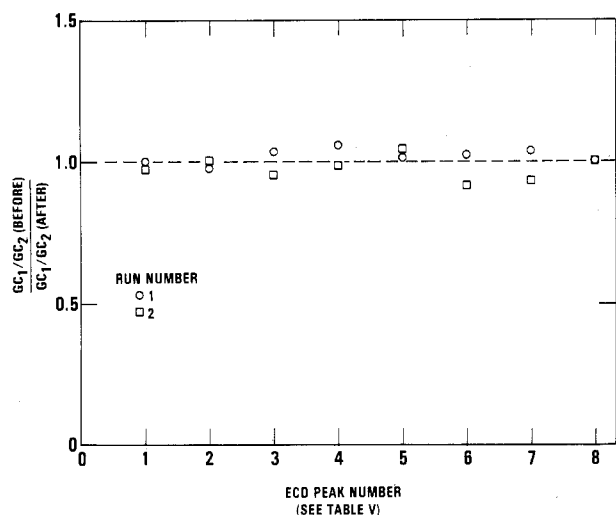


Figure 4. Ratio of response ratios from two nominally identical systems before and after switching Perma-Pure dryer units.

given in Table IV. The range of values for these ratios is from 0.92 to 1.06. The full set of 16 compounds gave similar results using the FID.

The Nafion dryers used in this test were both the 120-cm model. Prior testing showed that the dryers must be cleaned to ensure low blank value, zero air runs. Our cleaning procedure consisted of outgassing the dryers at 70 °C while passing humidified helium through the Nafion tube and using a dry zero air purge gas for a period of approximately 10 h. The cleaning procedure is repeated after 40–100 h of operation, as needed.

Comparisons of Two Normally Identical Systems. A second comparison was performed by sampling ambient air in a laboratory environment. Again samples were taken through the 120-cm dryers from a common manifold over the same collection time interval. Total collection volume was 150 mL. Results are shown in Table V. The aromatic compounds were measured by the two FIDs while the remaining six compounds were measured by the ECDs. In general, comparisons of the two systems have shown exceptionally good agreement at the low ppbv concentrations. Deviations from the mean for the 24 comparisons ranged from 0.3% to 20.8%.

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Lonneman, V. L. Thompson, and L. E. High of the EPA for helpful discussions concerning their own related work.

Registry No. Vinylidene chloride, 75-35-4; trichlorotrifluoroethane, 26523-64-8; chloroform, 67-66-3; 1,2-dichloroethane, 107-06-2; methylchloroform, 71-55-6; benzene, 71-43-2; carbon tetrachloride, 56-23-5; trichloroethylene, 79-01-6; 1,3-dichloropropene, 542-75-6; toluene, 108-88-3; 1,2-dibromoethane, 106-93-4; tetrachloroethylene, 127-18-4; chlorobenzene, 108-90-7; *o*-xylene, 95-47-6; benzyl chloride, 100-44-7; hexachlorobutadiene, 87-68-3.

LITERATURE CITED

- (1) Westberg, H. M.; Holdren, M. W.; Hill, H. H. Final Report Project No. CAPA-11-71; Coordinating Research Council: New York, 1981.
- (2) Lonneman, W. A.; Kopczynski, S. L.; Darley, P. E.; Sutterfield, F. D. *Environ. Sci. Technol.* **1974**, *8*, 229.
- (3) Seila, R. L. U.S. EPA Report No. 600/3-79-010; EPA: Research Triangle Park, NC, 1979.
- (4) Pellizzari, E. D.; Bunch, J. E.; Burkley, R. E.; McRae, J. *Anal. Chem.* **1976**, *48*, 803.
- (5) Singh, H. B.; Salas, L. J.; Stiles, R.; Shigeishi, H. U.S. EPA Final Report on Cooperative Agreement 805990 to SRI International; EPA: Research Triangle Park, NC, 1982.
- (6) Rasmussen, R. A.; Khalil, M. S. K. *Geophys. Res. Lett.* **1983**, *10*, 144.
- (7) Cox, R. D.; Earp, R. F. *Anal. Chem.* **1982**, *54*, 2265.
- (8) Rasmussen, R. A. *Am. Lab. (Fairfield, Conn.)* **1972**, *4*, 19.
- (9) Hanst, P. L.; Spiller, L. L.; Watts, D. M.; Spence, J. W.; Miller, M. F. *JAPCA* **1975**, *25*, 1220.
- (10) Lueb, R. A.; Ehalt, D. H.; Heidt, L. E. *Rev. Sci. Instrum.* **1975**, *46*, 702.
- (11) Gallagher, C. C.; Forsberg, C. A.; Pieri, R. V. J. *Geophys. Res.* **1983**, *88*, 3798.
- (12) Ferman, M. A. In "Atmospheric Biogenic Hydrocarbons"; Bufalini, J. J.; Arnts, R. R., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI.
- (13) Baker, B. B., Jr. *Am. Ind. Hyg. Assoc. J.* **1974**, Nov. 735.
- (14) Foulger, B. E.; Simmonds, P. G. *Anal. Chem.* **1979**, *51*, 1089.
- (15) Burns, W. F.; Tingey, D. T.; Evans, R. C.; Bates, E. H. J. *Chromatogr.* **1983**, *269*, 1.
- (16) Perma-Pure Products, Inc., Bulletin 105, Farmingdale, NJ.

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