

Theoretical Evaluation of Stability of
Volatile Organic Chemicals and
Polar Volatile Organic Chemicals in Canisters

by

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FOREWORD

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Whole air collection using passivated stainless steel canisters is rapidly becoming the method of choice for sampling of ambient volatile organic compounds. This methodology has been validated through previous laboratory and field experience for a limited subset of possible analytes. The current work provides a fundamental basis for development of guidelines for the application of canister sampling to the ever expanding list of volatile polar and non-polar organic compounds of importance to assessment of ambient air quality.

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ABSTRACT

The potential for physical adsorption as a mechanism for loss of volatile organic chemicals (VOC) and polar volatile organic chemicals (PVOC) from the vapor phase in canister samples was assessed using the principles embodied in the Dubinin-Radushkevich isotherm. This isotherm provides a specific relationship between the tendency for adsorption and compound/sample specific properties such as polarizability, vapor concentration, temperature, and equilibrium vapor pressure. In addition, the isotherm provides means for distinguishing between surfaces having different physical and chemical properties. A computer based model was developed for predicting adsorption behavior and vapor phase losses in multicomponent systems. At present, the data base for the model contains relevant physicochemical data for more than 60 compounds (42 VOC, 19 PVOC, and water), and provisions for inclusion of additional compounds are incorporated in the software.

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CONTENTS

FOREWORD	iii
ABSTRACT	iv
FIGURES	vi
TABLES	vii
ACKNOWLEDGEMENT	viii
1. INTRODUCTION	1
2. CONCLUSIONS	3
3. RECOMMENDATIONS	5
4. MODEL DESCRIPTION AND RESULTS	6
Background	6
Canister Stability Software	8
General Description of Software	8
Program Operation	9
Results	10
Qualitative Results	10
Comparison with Experimental Results	22
REFERENCES	30
APPENDIX A. SOURCE CODE FOR CANISTER STABILITY PROGRAM	31

FIGURES

<u>Number</u>	<u>Page</u>
1 Adsorption Potential for Water Vapor	11
2 Adsorption Potentials for VOC and PVOC at 5 ppbv	17
3 Calculated Recoveries of Toluene, o-Xylene, 1,2,4-Trichlorobenzene from a Canister as a Function of Relative Humidity at a Sample Pressure of 1 Atmosphere	18
4 Calculated Recoveries of Toluene, o-Xylene, 1,2,4-Trichlorobenzene from a Canister as a Function of Relative Humidity at a Sample Pressure of 5 Atmospheres	19
5 Effect of Temperature on Recovery of o-Xylene	21
6 Effect of Temperature on Recovery of 1,2,4-Trichlorobenzene	21

TABLES

<u>Number</u>	<u>Page</u>
Table 1. Physicochemical Properties of Target VOC and PVOC	12
Table 2. Experimental Results for RTI Canister Experiment	25
Table 3. Calculated Results for RTI Canister Experiment	26
Table 4. Experimental and Calculated Recoveries for VOC	27

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SECTION 1

INTRODUCTION

Physical adsorption of trace atmospheric constituents on the surfaces of sampling apparatus has long been recognized as a contributing factor to apparent losses of some organic compounds during sampling and sample storage. The use of passivated stainless steel canisters for sample collection, shipping, and storage prior to analysis has diminished this problem sufficiently that these devices are widely used for whole air sampling of non-polar volatile organic compounds (VOC). Nonetheless, it is recognized that not all VOC are equally stable in canisters under all possible sampling temperatures and relative humidities. The number of compounds that need to be accurately sampled and analyzed is expanding as the provisions of the Clean Air Act are implemented. These new compounds include polar volatile organic compounds (PVOC) and additional VOC, some of which have lower vapor pressures than VOC that are currently being sampled and analyzed using canisters.

Experimental investigation of the stability of all possible combinations of important VOC and PVOC at all concentration levels of interest and under all realistic sampling conditions is not practical particularly given the dynamic nature of the provisions of the Clean Air Act. A more sensible approach is to develop guidelines for future evaluation and application of canister sampling technology based on the implications of fundamental processes that govern the stability of whole air samples. Excluding compounds that are inherently unstable (*i.e.* reactive) in the atmosphere, such as ozone, these processes can be limited to (1) heterogeneous chemical reaction (including chemisorption) with surfaces within the sampling system, and (2) physical adsorption on surfaces within the sampling system. Passivation of a surface is generally performed to minimize the chemical reactivity of the surface by either altering the chemical nature of the surface or by masking the surface by

deposition of a less reactive coating. In the case of Summa™ polished stainless steel canisters, the surface area is reduced by the polishing process, and the surface is predominantly the relatively inert CrO_2 . However, examination of the Summa polished surface by ESCA, after exposure to air, shows the top 20 Å to be covered by oxygen and carbon species. This is a common observation for most metallic surfaces that have been exposed to air, and indicates that the main advantage of the Summa process may be in the reduction of the surface area.

The objective of this program was to evaluate the potential for physical adsorption for a broad range of VOC and PVOC with the goal of developing a fundamentally consistent model for assessing the stability of such compounds in canisters. A subsidiary goal was to collect and consolidate relevant experimental information for comparison with model predictions.

SECTION 2

CONCLUSIONS

The potential for physical adsorption as a mechanism for loss of VOC and PVOC from the vapor phase in canister samples was assessed using the principles embodied in the Dubinin-Radushkevich isotherm. This isotherm provides a specific relationship between the tendency for adsorption and compound/sample specific properties such as polarizability, vapor concentration, temperature, and equilibrium vapor pressure. In addition, the isotherm provides means for distinguishing between surfaces having different physical and chemical properties. A computer based model was developed for predicting adsorption behavior and vapor phase losses in multicomponent systems. At present, the data base for the model contains relevant physicochemical data for more than 60 compounds (42 VOC, 19 PVOC, and water), and provisions for inclusion of additional compounds are incorporated in the software.

Based solely on the physicochemical properties of the compounds (*i.e.* independent of surface considerations), the model predicts displacement of the more volatile VOC and PVOC from a canister surface by water vapor at relative humidities in the range of 1 to 20 percent. This is generally consistent with experimental observations, but in most cases, the experimental conditions are not sufficiently characterized to permit detailed quantitative comparison with the model. For example, relative humidities less than about 5 to 10 percent are generally not measured but rather are calculated based on the addition of a known amount of water to a "dry" system. A different kind of uncertainty arises when attempting to compare the model results with field samples. In this case, the analysis is usually conducted for a restricted set of analytes, whereas the model considers all components to be in competition for the surface.

Some conclusions inferred from this theoretical evaluation of canister sampling for VOC and PVOC result from this work:

- (1) Measurements of relative humidity and temperature should be made during the sampling process. Under conditions where the relative humidity is so low that the model predicts target compound loss, provision should be made to add water vapor to the canister prior to analysis.
- (2) The sample pressure should be as high as possible without causing precipitation of liquid water within the canister. However, pressure restrictions during shipment may apply. The pressure, P , for 100% RH occurs at: $P = (100/RH_s) \text{EXP}(-(\Delta H_v/R)(T_s^{-1} - T_a^{-1}))$, where RH_s is the relative humidity during sampling, ΔH_v is the heat of vaporization, R is the universal gas constant, and T_s and T_a are the analysis and sampling temperatures respectively.
- (3) When considering the suitability of the canister sampling method for new compounds, the first parameters to be evaluated should be chemical reactivity and the vapor pressure of that compound. Compounds with equilibrium vapor pressures less than about 1 torr at ambient temperatures may require heating of the canister to effect good recovery, but heating of canisters should be done only with recognition of all of the effects this process may have on the recovery of the analytes.
- (4) Inasmuch as all species present participate in the competitive adsorption process, retrospective considerations of the quality of data obtained from multiple canisters at the same site should include at least semi-quantitative specification (*e.g.* total FID response) of non-target species contained in the samples.

Pending experimental confirmation of these conclusions under known controlled conditions, a set of specific guidelines can be formulated for use in practical situations encountered by Regional, State and Local agencies as they implement canister-based monitoring programs.

SECTION 3

RECOMMENDATIONS

The model developed in this program shows considerable promise for qualitative and semi-quantitative explanation of physical adsorption phenomena associated with mixtures of trace VOC and PVOC in canisters. At this point, however, quantitative data are lacking with respect to characterization of canister surface properties. In particular, the surface roughness factors for both electropolished and unpolished canisters are unknown. At present, the model calibration depends on an assumed value for this parameter, and uncertainty in the calibration could be reduced by measurements of surface roughness. The model calibration also is currently dependent on incompletely characterized experimental measurements at low relative humidities. The accuracy of the calibration could be improved by a simple set of experiments conducted under very controlled conditions. It would be desirable, for example, to prepare a standard cylinder of VOC in very dry air that could be used to charge a well-cleaned and dried canister to various pressures. Analysis of the residual gas concentration at each pressure would yield a more reliable calibration of the model than is currently in place.

The parameters included in the model suggest a complex dependence of analyte recovery on sample temperature. This aspect of canister analysis should be evaluated systematically.

SECTION 4

MODEL DESCRIPTION AND RESULTS

BACKGROUND

Physical adsorption is a widely studied phenomenon, and several excellent texts are available on this topic (*e.g.* Flood, 1967). In brief, physical adsorption is characterized by isosteric heats of adsorption that are no greater than a few kcal/mole (*i.e.* less than typical chemical bond energies). A wide variety of theoretical and empirical isotherms have been used to describe physical adsorption, but the most successful isotherm that is also thermodynamically sound is the Dubinin-Radushkevich (DR) isotherm (Flood, *op.cit.*). This isotherm has received wide use in the description and modeling of adsorption of multicomponent mixtures of VOC on activated carbons and in modeling the effect of relative humidity on such systems (Coutant, 1987; Werner and Winters, 1986). Unlike many empirical and other less well founded theoretical isotherms, the DR isotherm has been shown to correctly describe physical adsorption behavior over a very broad range of relative pressures, extending from near saturation to values of P/P_0 of the order of 10^{-12} (Hobson, 1961).

The general form of the DR isotherm is given by

$$\frac{W}{W_0} = \exp\left(-\frac{B}{\beta^2} \left(RT \ln\left(\frac{P}{P_0}\right)\right)^2\right) \quad (1)$$

where W is the number of moles of adsorbed gas; W_0 is the total number of moles of gas that could be adsorbed at saturation; B is a characteristic of the surface; β is the electronic

polarizability of the sorbate, which is equal to the molar refractivity; R is the gas constant; T is the absolute temperature; P is the experimental vapor pressure; and P_o is the equilibrium vapor pressure at T.

By invoking ideal solution theory, Equation 1 can readily be transformed for application to mixtures of sorbates, including water vapor. Then each component of the system is represented by an equation of the type

$$\frac{W_i}{W_o X_i} = \exp - \left(\frac{B}{\beta_i^2} (RT \ln \left(\frac{P_i}{X_i P_{oi}} \right))^2 \right) \quad (2)$$

where X_i is the mole fraction of the i th component in the adsorbed phase. The set of resulting equations can then be solved by requiring

- (1) Mass balance between starting vapor phase and final vapor phase plus adsorbed phase amounts for each component. Inasmuch as formation of the adsorbed layer takes place at the expense of the gas phase concentration, the decrease in gas phase pressure (ΔP) of each component is given by

$$\Delta P_i = - \frac{W_i RT}{V} \quad (3)$$

where V is the volume of the container.

- (2) The sum of the mole fractions in the adsorbed phase is unity, *i.e.*,

$$\sum X_i = 1 \quad (4)$$

- (3) The adsorption potentials for each component are equal at equilibrium (Grant and Manes, 1966), *i.e.*,

$$\frac{1}{\beta_i} (RT \ln(\frac{P_i}{X_i P_{oi}})) = \frac{1}{\beta_j} (RT \ln(\frac{P_j}{X_j P_{oj}})) \quad (5)$$

The latter requirement provides a mechanism for directly determining the relative amounts of each compound in the adsorbed and vapor phases. Note that the adsorption potential combines the effects of polarizability and vapor pressure and that these properties are the drivers for determining the composition of the adsorbed phase.

CANISTER STABILITY SOFTWARE

General Description of Software

A computer based model was developed to facilitate solution of the set of simultaneous equations represented by Equations 2-5. Code for this model was written in Microsoft Quick-Basic. The software package includes the main program that is used for all calculations, a Lotus-123 file that contains the listing of compounds and their physicochemical properties, and a .prn file that is generated from the Lotus-123 file. The .prn file serves as a data base for the main program, and provides a mechanism for expansion of the list of available compounds without requiring alteration of the program. A listing of the source code for the main program is given in Appendix A, and copies of the compiled program and associated Lotus-123 files have been supplied to the Project Officer and Work Assignment Manager under separate cover.

The program is menu driven, with all inputs necessary for a computation being specified through use of the menu. Certain default values are specified at startup, but these can be changed to suit the user's needs. The program should be run on a system capable of EGA graphics and it requires a math co-processor for completion of a calculation in a reasonable time.

The program assumes a spherical geometry for the canister, and the volume of the canister is used to determine the geometrical surface area. The surface roughness also is used to determine the available area, which is related to W_0 . The surface roughness is dependent on the extent of polishing -- a perfect mirror surface would have a roughness factor of 1, *i.e.*, a true surface area equal to the geometrical surface area. Electropolishing typically yields roughness factors of the order of 1.5-2, and we have calibrated the model using a default value of 2 for the surface roughness and experimental data derived using Summa polished canisters.

When trying to simulate experimental conditions, it is necessary to know the temperatures for sampling and analysis. The absolute pressure of the canister sample at the completion of sampling also is needed. The program adjusts the measured sampling humidity to the analysis temperature and canister pressure, and provides a warning when the sample properties are such as to lead to water condensation. The condensation of liquid water within the canister could have a significant effect on the recovery of compounds that are essentially miscible with water, *e.g.*, low molecular weight alcohols and acids.

Three output choices are available - screen, printer, and disk. The screen and printer outputs yield tables of compound names, adsorbed phase mole fractions (X_i), final gas phase pressure (P_{fn}), initial gas phase pressure (P_{in}), and the ratio of P_{fn}/P_{in} . The disk output yields a file that can be imported into Lotus-123 for tabulation and comparison with experimental data.

Program Operation

Default settings are provided for all variables except sample composition which must be supplied by the user. Listings of compounds currently included in the data base can be viewed either on screen by accessing the help feature or on hard copy by request from the main menu. Once a particular composition is selected, it is stored by the program so that

multiple computations involving changes in relative humidity, temperatures, etc. can be conducted without reentry of the composition data.

The program first uses the Newton-Raphson method to determine the values of X_i at the known initial values of P_i . Then Equations 2 and 3 are used to estimate the amounts of each component adsorbed and the corresponding residual gas phase pressures. This process of estimation of X_i and P_i is reiterated until the sum of the X_i converges to within 1 part-per-million of unity. Approximately the same precision is achieved with the P_i except for the case of very strongly adsorbed species. To minimize computation time, any species for which the estimated residual gas phase concentration is less than 1 percent of the starting concentration, is arbitrarily set at the 1 percent level.

RESULTS

Qualitative Results

The approach taken using the DR isotherm explicitly assumes that all species present in the gas phase are in competition with each other for adsorption sites on the surface of a canister, and that the ability for each species to compete is a function of (1) its concentration in the gas phase, (2) its equilibrium vapor pressure, and (3) its polarizability. Quantification of the combined effects of these variables on the total extent of adsorption depends on experimental determination of B in Equation 1. Inasmuch as B is a function solely of the surface, the usual approach is to measure W as a function of P using a single component system. For the current work, W_0 was estimated by assuming a saturation density of 10^{14} molecules/cm² and a surface area equal to the geometrical area times the roughness factor. The value of B was then obtained as 7.05×10^{-5} by trial and error comparison of model predictions with experimental data of Smith and Holdren (1989) on the recoveries for a 41 component VOC mixture.

In principle, it is possible to explore the qualitative and even semi-quantitative relationships embodied in the DR isotherm independent of consideration of the specific surface involved. For example, Figure 1 illustrates the dependence of the adsorption potential for water vapor at different temperatures and gas phase concentrations. This information is combined in Figure 2 with similar data for the target VOC and PVOC (calculated using physicochemical data shown in Table 1).

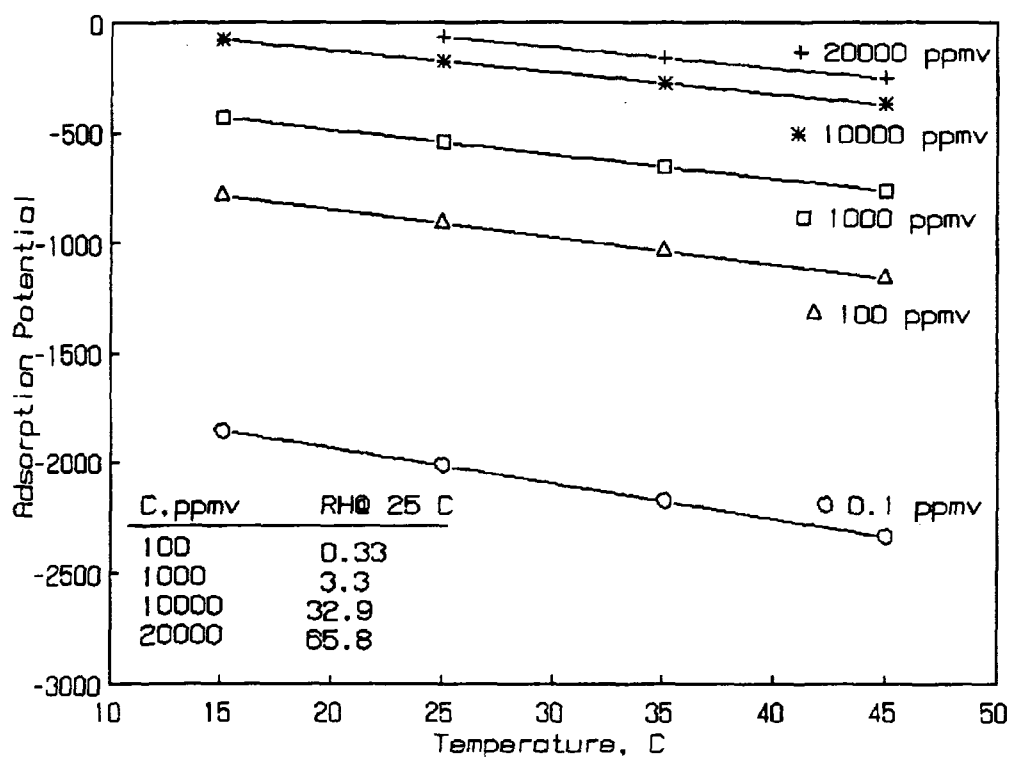


Figure 1. Adsorption Potential for Water Vapor.

Table 1. Physicochemical Properties of Target VOC and PVOC

Compound CA Index Name	Molecular Weight, M_w	Density, ρ	Refractive Index, n	Molar Refrac- tivity ²	Vapor Pressure Constants ¹		Vapor Pressure @25C, torr	Log(P) @25 C	Adsorption Potential @5ppbv
					A	B			
dichlorodifluoromethane	120.91	1.1834	NF ³	17.0	17.3	2598	5421.3	3.73	-733
methyl chloride	50.49	0.9159	1.3389	11.5	17.6	2719	4578.0	3.66	-1075
1,2-dichloro-1,1,2,2-tetrafluoroethane	170.93	1.5312	1.3092	21.5	17.8	3079	1697.2	3.23	-550
vinyl chloride	62.50	0.9106	1.3700	15.5	17.9	2933	3315.8	3.52	-785
methyl bromide	94.94	1.6755	1.4218	14.4	17.7	3048	1676.6	3.22	-819
ethyl chloride	64.52	0.8978	1.3676	16.2	17.7	3148	1216.3	3.09	-718
trichlorofluoromethane	137.38	1.4940	NF ³	21.7	17.5	3221	796.9	2.90	-522
1,1-dichloroethene	96.94	1.2180	1.4249	20.3	17.8	3414	590.8	2.77	-549
dichloromethane	84.93	1.3266	1.4242	16.3	18.1	3610	414.5	2.62	-671
3-chloropropene	76.53	0.9376	1.4157	20.5	17.7	3522	366.4	2.56	-532
1,1,2-trichloro-1,2,2-trifluoroethane	187.38	1.5635	1.3557	26.2	17.8	3578	326.0	2.51	-413
1,1-dichloroethane	98.96	1.1757	1.4164	21.1	18.0	3740	222.0	2.35	-501
cis-1,2-dichloroethene	96.94	1.4459	1.4490	18.0	18.2	3843	202.9	2.31	-586
trichloromethane	119.38	1.4832	1.4459	21.5	17.9	3775	192.1	2.28	-489
1,2-dichloroethane	98.96	1.2351	1.4448	21.3	18.2	4113	81.8	1.91	-469

Table 1. Physicochemical Properties of Target VOC and PVOC

Compound CA Index Name	Molecular Weight, M_w	Density, ρ	Refractive Index, n	Molar Refrac- tivity ²	Vapor Pressure Constants ¹	Vapor Pressure @25C, torr	Vapor Log(P) @25 C	Adsorption Potential @5ppbv		
									A	B
1,1,1-trichloroethane	133.41	1.3390	1.4379	26.1	17.6	3813	124.4	2.09	-392	
benzene	78.12	0.8787	1.5011	26.2	17.9	3967	95.2	1.98	-385	
carbon tetrachloride	153.82	1.5940	1.4601	26.4	17.8	3909	109.3	2.04	-385	
1,2-dichloropropane	112.99	1.1560	1.4394	25.7	17.7	4082	53.2	1.73	-379	
trichloroethene	131.39	1.4642	1.4773	25.4	17.8	4016	75.3	1.88	-392	
cis-1,3-dichloropropene	110.97	1.2170	1.4730	25.6	17.0	4356	10.9	1.04	-344	
trans-1,3-dichloropropene	110.97	1.2240	1.4682	25.2	17.0	4356	10.9	1.04	-349	
1,1,2-trichloroethane	133.41	1.4397	1.4714	25.9	18.1	4432	24.9	1.40	-359	
toluene	92.15	0.8669	1.4961	31.1	17.9	4306	30.2	1.48	-303	
1,2-dibromoethane	187.87	2.1792	1.5387	27.0	18.0	4611	12.9	1.11	-330	
tetrachloroethene	165.83	1.6227	1.5053	30.3	18.0	4487	19.5	1.29	-302	
chlorobenzene	112.56	1.1058	1.5241	31.1	18.0	4593	12.9	1.11	-286	
ethylbenzene	106.17	0.8670	1.4959	35.8	18.0	4639	11.1	1.04	-246	
m-xylene	106.17	0.8611	1.4958	36.0	18.2	4745	9.5	0.98	-242	
p-xylene	106.17	0.8642	1.4972	36.0	17.8	4614	10.4	1.02	-244	

Table 1. Physicochemical Properties of Target VOC and PVOC

Compound CA Index Name	Molecular Weight, M_w	Density, ρ	Refractive Index, n	Molar Refrac- tivity ²	Vapor Pressure Constants ¹		Vapor Pressure @25C, torr	Log(P) @25 C	Adsorption Potential @5ppbv
					A	B			
ethenylbenzene	104.16	0.9060	1.5468	36.4	18.0	4764	7.7	0.89	-236
1,1,2,2-tetrachloroethane	167.85	1.5953	1.4940	30.6	18.2	4827	7.1	0.85	-279
o-xylene	106.17	0.8802	1.5055	35.8	18.0	4753	7.9	0.90	-241
4-ethyl toluene	120.19	0.8620	1.4930	40.6	18.0	4959	4.0	0.60	-202
1,3,5-trimethylbenzene	120.20	0.8652	1.4994	40.8	18.1	5017	3.5	0.55	-199
1,2,4-trimethylbenzene	120.20	0.8758	1.5048	40.7	18.1	5076	2.9	0.47	-197
benzyl chloride	126.59	1.1002	1.5391	36.1	18.7	5449	1.5	0.17	-211
m-dichlorobenzene	147.01	1.2884	1.5459	36.1	17.9	5028	2.8	0.45	-222
p-dichlorobenzene	147.01	1.2473	1.5285	36.3	18.4	5278	2.1	0.32	-215
o-dichlorobenzene	147.01	1.3048	1.5515	36.0	18.5	5352	1.7	0.22	-214
1,2,4-trichlorobenzene	181.45	1.4542	1.5717	41.0	18.1	5577	0.5	-0.26	-171
hexachlorobutadiene	260.76	1.6820	1.5542	49.7	20.4	6625	0.2	-0.78	-127
oxirane	44.05	0.8824	1.3597	11.0	18.0	3239	1314.4	3.12	-1057
2-propenenitrile	53.06	0.8060	1.3911	15.6	17.4	3786	109.9	2.04	-650
methyloxirane	58.08	0.8590	1.3670	15.2	18.0	3501	528.7	2.72	-731

Table 1. Physicochemical Properties of Target VOC and PVOC

Compound CA Index Name	Molecular Weight, M_w	Density, ρ	Refractive Index, n	Molar Refrac- tivity ²	Vapor Pressure Constants ¹		Vapor Pressure @25C, torr	Log(P) @25 C	Adsorption Potential @5ppbv
					A	B			
2-propenoic acid, ethyl ester	100.11	0.9240	1.4050	26.6	18.3	4361	40.7	1.61	-361
1,3-butadiene	54.09	0.6211	1.4292	22.5	17.5	2912	2223.8	3.35	-532
acetonitrile	41.05	0.7857	1.3442	11.1	17.7	3939	91.6	1.96	-909
2-propanone	58.08	0.7899	1.3588	16.2	18.3	3844	221.4	2.35	-654
methanol	32.04	0.7914	1.3288	8.2	20.4	4632	122.2	2.09	-1243
ethanol	46.07	0.7893	1.3611	12.9	21.0	5045	58.0	1.76	-758
2-butanone	72.12	0.8054	1.3788	20.7	17.7	3903	100.0	2.00	-489
2-methoxy-2-methyl-propane	88.15	0.7405	1.3690	26.9	17.6	3526	311.4	2.49	-402
2-ethoxy-2-methyl-propane	102.18	0.7519	1.3794	31.4	17.7	3897	104.5	2.02	-323
2-propanol	60.11	0.7855	1.3776	17.6	21.4	5240	44.2	1.65	-547
n-butanol	74.12	0.8098	1.3993	22.2	21.3	5733	8.0	0.90	-389
acetic acid, ethenyl ester	86.09	0.9317	1.3959	22.2	18.8	4220	108.5	2.04	-458
acetic acid, ethyl ester	88.12	0.9003	1.3723	22.3	18.8	4252	90.9	1.96	-452
2-methyl-1,3-butadiene	68.13	0.6810	1.4219	25.4	17.4	3278	578.1	2.76	-439
2,6,6-trimethylbicyclo[3.1.1]hept-2-ene	136.24	0.8582	1.4658	44.0	18.0	4857	5.4	0.73	-191

Table 1. Physicochemical Properties of Target VOC and PVOC									
Compound CA Index Name	Molecular Weight, M_w	Density, ρ	Refractive Index, n	Molar Refrac- tivity ²	Vapor Pressure Constants ¹		Vapor Pressure @25C, torr	Log(P) @25 C	Adsorption Potential @5ppbv
					A	B			
water	18.02	1.0000	1.3330	3.7	20.5	5178	23.1	1.36	-2498
ethanoic acid	60.05	1.0490	1.3718	13.0	33.1	10345	0.2	-0.71	-494

1. $\ln (P, \text{torr}) = A - B/T$

2. $Molar Refractivity = \left(\frac{M_w}{\rho}\right)\left(\frac{n^2-1}{n^2+2}\right)$ (estimated by group contributions when refractive index not given)

3. Refractive index not found

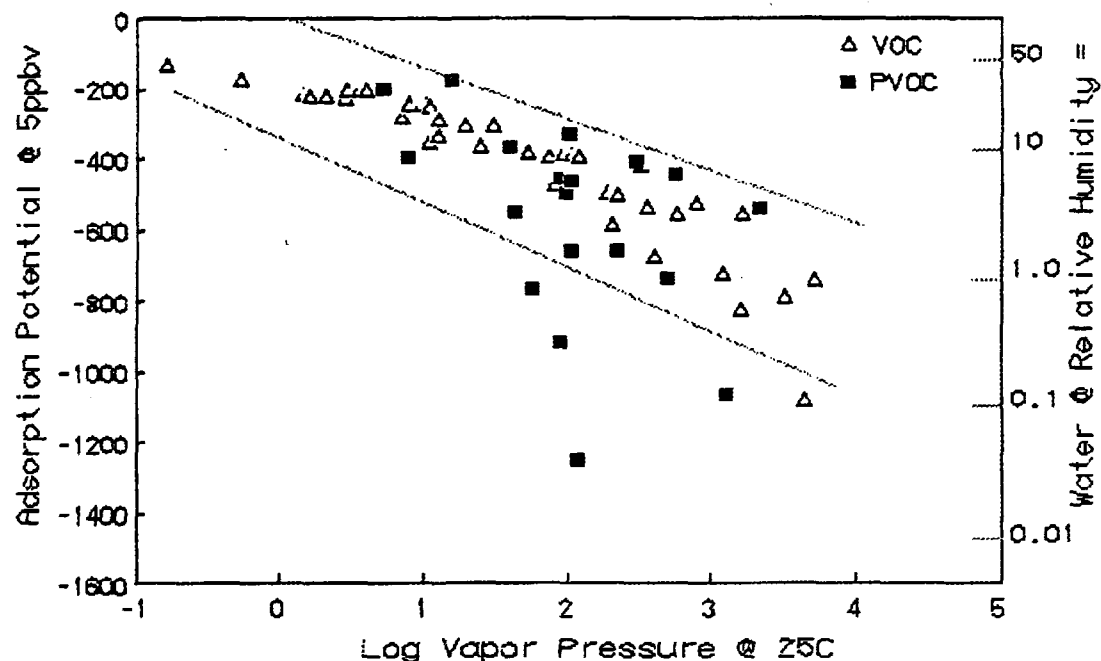


Figure 2. Adsorption Potentials for VOC and PVOC at 5 ppbv.

Figure 2 shows the adsorption potentials of VOC and PVOC (at 5 ppbv) plotted as a function of the logarithm of the pure compound vapor pressures at 25 C. The right-hand scale of Figure 2 shows the position of the adsorption potential for water at various relative humidities (at 25 C). Several observations and conclusions can be made from this plot:

- (1) All but one of the VOC (methyl chloride) and most of the PVOC (excepting ethanol, methanol, acetonitrile, and ethylene oxide) fall within a fairly narrow band that is linear with $\log(P_0)$. Therefore, for compounds that lie within this band, the equilibrium vapor pressure is the most significant factor in determining their relative adsorption potential. This plot also serves as a means for distinguishing those PVOC that can be expected to have physical adsorption behaviors that differ significantly from the majority of the compounds considered.

- (2) Superposition of the information from Figure 1 on the VOC/PVOC data shows the relative position of water vapor at various relative humidities. In the sense of the adsorption potential as used here, the more positive the adsorption potential, the greater the tendency for adsorption. Therefore, water vapor at 1-20 percent RH is expected to inhibit adsorption of many of the VOC and PVOC considered. It should be noted, however, that the adsorption potentials of the organics also are functions of their gas phase concentration and that increased concentrations will enhance their ability to compete with water vapor.

One further aspect of the information contained in Figure 2 is made more obvious in Figure 3, which shows the results of application of the model to a three-component mixture of aromatic compounds at various relative humidities.

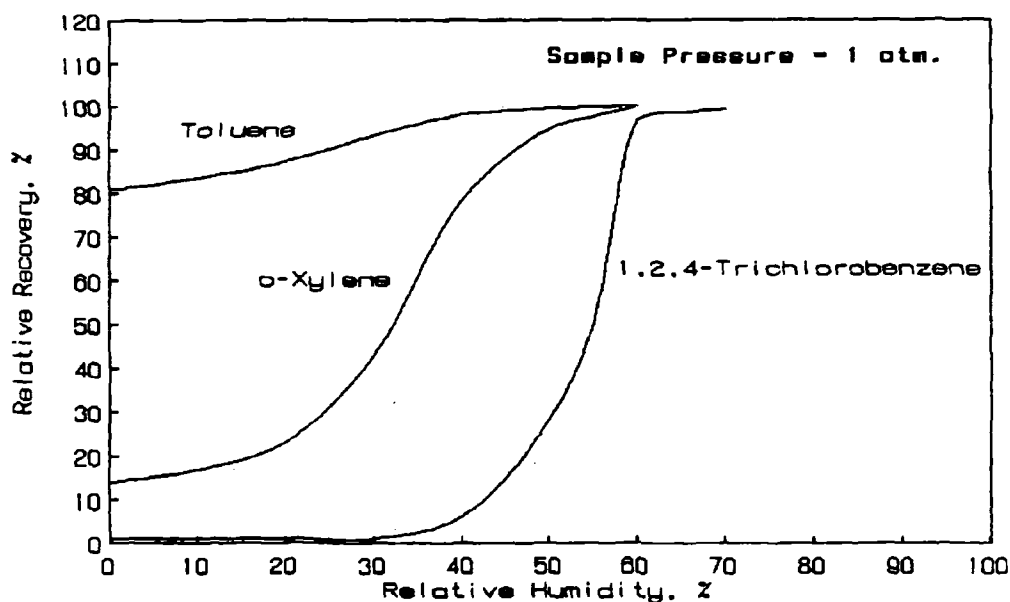


Figure 3. Calculated Recoveries of Toluene, o-Xylene, 1,2,4-Trichlorobenzene from a Canister as a Function of Relative Humidity at a Sample Pressure of 1 atm.

Figure 3 clearly illustrates the fact that compounds with lower vapor pressures require higher relative humidities to effect good recoveries. It also illustrates the effect of having more than two components in the system. In this regard, the recoveries of toluene and o-xylene are enhanced at low relative humidities by the presence of the trichlorobenzene.

The effect of yet another variable, total sample pressure, is implicit in the model. Sample concentrations are customarily expressed as ppbv with the tacit assumption that the sample is at a total pressure of 1 atmosphere. In the model, the important variable is P_i , the partial pressure of each component. In the sampling process, canister samples are usually pumped to pressures greater than 1 atmosphere to facilitate recovery of the gas during analysis. Under these conditions, the partial pressures of all components including water vapor are greater than they were at 1 atmosphere. The effect of this increase in pressure can be seen by comparing Figure 4 with Figure 3.

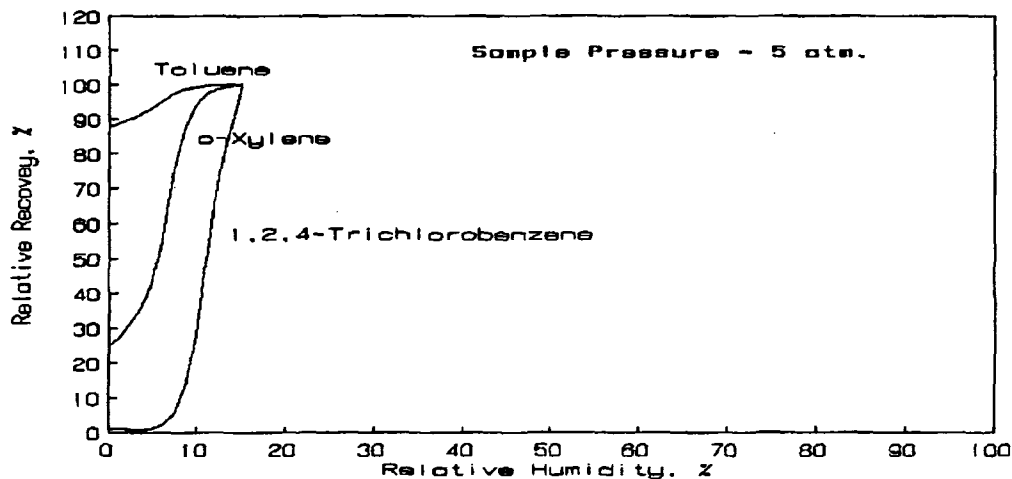


Figure 4. Calculated Recoveries of Toluene, o-Xylene, and 1,2,4-Trichlorobenzene from a Canister as a Function of Relative Humidity at a Sample Pressure of 5 Atmospheres.

The curves shown in Figure 4 were derived using the model and the same overall composition as that used for Figure 3, but with the sample pressure being increased to 5 atmospheres. Although canister pressures are usually considerably less than 5 atmospheres, Figure 4 shows that there is a significant effect of total pressure on sample recovery. To a first approximation, the data in Figure 3 are compressed to the left by a factor of 5 because of the increase in total pressure.

Another effect that is sometimes ignored is the effect of temperature on the competitive adsorption of water vapor. Increasing the temperature of the canister decreases the adsorption potential of water in just the same way as it decreases the adsorption potentials of the organic components. However, because of the different heats of vaporization for different compounds, the adsorption potentials will not change at the same rate with increasing temperature. For some sample situations, where the water adsorption potential decreases more rapidly than does that of a particular VOC, the result of increased temperature can be decreased recovery of the VOC. This is illustrated in Figures 5 and 6.

Figure 5 shows the calculated recovery of o-xylene with increasing temperature at two different relative humidities. At 10 percent RH, o-xylene is relatively unaffected by the water vapor and the recovery increases with temperature as expected. However, at 30 percent RH good recovery of o-xylene is predicted at room temperature, and the effect of increasing the temperature is dominated initially by the effect of lowering of the water adsorption potential, resulting in poorer recovery of the xylene. As the temperature is raised more, the effect of raising the vapor pressure of the o-xylene begins to dominate, and the recovery curve becomes coincident with that of the low humidity case. At higher humidities, the minimum in the response curve becomes progressively less pronounced. Figure 6 shows the results of a similar calculation for 1,2,4-trichlorobenzene. The lower vapor pressure of this compound causes the temperature/humidity effect to be even more pronounced than with o-xylene, and even slight increases in temperature cause dramatic initial drops in the

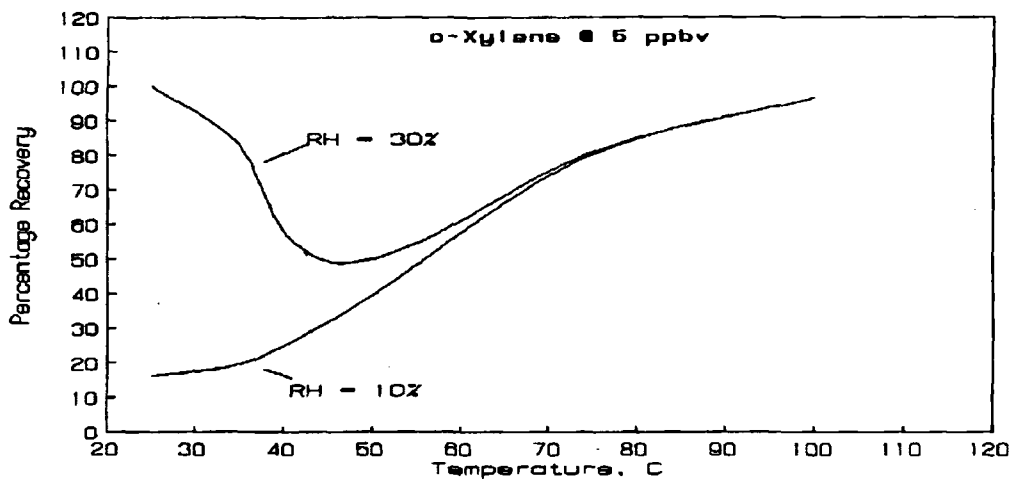


Figure 5. Effect of Temperature on Recovery of o-Xylene.

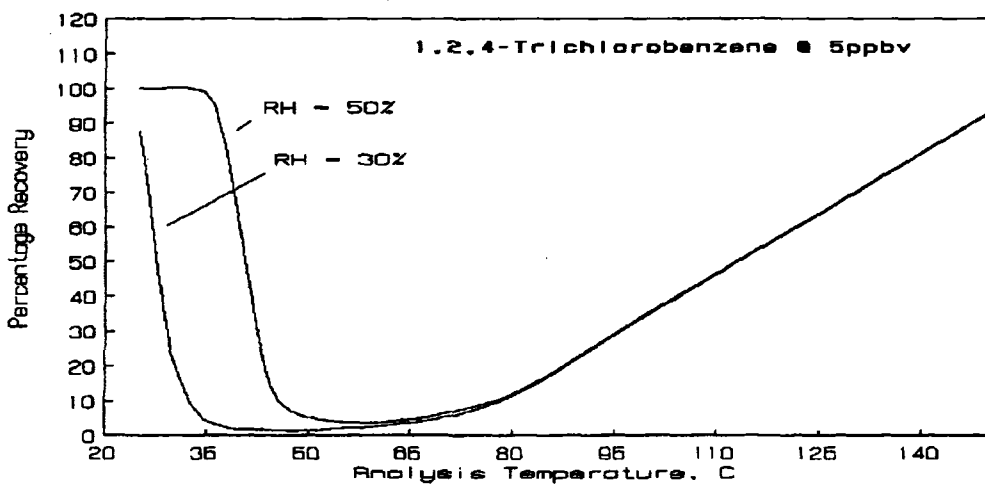


Figure 6. Effect of Temperature on Recovery of 1,2,4-Trichlorobenzene.

predicted recovery efficiency. Note that in both Figures 5 and 6, the minimum recovery occurs at temperatures in the vicinity of 50 C, which is comparable to temperatures used in some current laboratory analyses. Although heating of canisters to improve recovery of low vapor pressure analytes is a common practice, to the best of our knowledge, no systematic investigation of the effect of temperature on recovery has been conducted.

Comparison with Experimental Results

Experiments to evaluate the stability of simulated or real ambient air samples in canisters have been conducted by several laboratories. However, many of these experiments have been conducted without recognition of the potential importance of several variables and, therefore, experimental conditions have not always been adequately defined. As examples, neither the sample pressure nor the relative humidity (especially at low RH) are specified accurately in many cases. These experiments may provide valuable information for specific sampling applications, but they do not serve the broader goal of development of understanding and generalization of conclusions. Two sets of data that come close to having complete identification of conditions were obtained for use in this report. The general experimental procedures were similar for these works and consisted of the following:

- (1) A pressurized source cylinder of target compounds was prepared in "dry" gas and this cylinder was analyzed for the target compounds.
- (2) Canister samples were prepared from the source cylinder with addition of measured amounts of water to the canisters.
- (3) The canister samples were stored for various time periods prior to analysis.

The first set of data was received from Research Triangle Institute (RTI) (Jayanty, 1990). Jayanty's canister samples were prepared at a total pressure of 3 atmospheres

(absolute) and the samples were analyzed periodically over a 30-day period. Jayanty included both polished and unpolished canisters in his experiments, but inasmuch as no quantitative measures of the total surface areas (or surface roughness) of the two types of canisters were given, only the results obtained with polished cylinders are cited here. Furthermore, only the final analyses for the wet (RH ~ 100% with excess water present) and "dry" canisters are considered. Table 2 shows the experimental results obtained by Jayanty, and Table 3 shows the calculated results. Because of the uncertainty concerning the actual moisture content in Jayanty's "dry" experiment, the computations included several relative humidities. In general, the calculated recoveries are somewhat higher than the experimental results, with the calculated humidity effect stronger than the experimentally measured effect. Quite possibly, the low experimental recoveries of some compounds from the "wet" canisters could be due to dissolution in the excess liquid water that was present in these canisters. Problems with the analysis of methanol are acknowledged, and the most notable discrepancies between the experimental and calculated results occur with the three esters and n-butanol.

The second data set was developed at Battelle (Smith and Holdren, 1989). In this case, the canisters were pressurized to 19.1 psia and analyses were conducted after a holding period of 1-2 days. As with Jayanty, Smith and Holdren did not measure the relative humidity of the pure air that was used for preparation of the "dry" source cylinder. Recent work conducted with the same air supply by this author suggests that the relative humidity of this air is currently at least 2 percent and possibly as high as 7 percent. It is possible, therefore, that the relative humidity values specified by Smith and Holdren are lower than the true values. Nonetheless, the model predictions are in at least qualitative agreement with the experimental recoveries for most of the compounds shown in Table 4. If the assumption is made that the reported relative humidities are low by 7 percent, the agreement with the model is better except for the lowest vapor pressure compounds such as hexachlorobenzene

and 1,2,4-trichlorobenzene. As shown in Figure 3, the latter compound is predicted to require relative humidities in the neighborhood of 50 percent to achieve the recoveries shown in the experimental data, and even higher relative humidities are predicted to be required for hexachlorobenzene recovery. It should be emphasized that this aspect of the model does not depend on the calibration and is a function only of the properties of the compounds. In this regard, the vapor pressure constants for hexachlorobenzene (see Table 1) appear to be inconsistent with those of similar compounds in Table 1, and this could be the cause of the lack of agreement for this compound.

Jayanty (private communication) reported that after completion of his 30-day experiment, he added water to his dry canisters and reanalyzed with the result that good recoveries were obtained. With both the RTI and Battelle work, it would have been desirable to investigate the effect of elevated temperatures on the recovery of analytes from the canisters.

Table 2. Experimental Results for RTI Canister Experiment					
Compound	C ₀ ,ppbv	Percentage Recovery			
		Dry		Wet ¹	
		Day 0	Day 31	Day 0	Day 31
1,1,1-trichloroethane	5.3	96.2%	95.9%	103.8%	104.7%
toluene	5.0	60.0%	53.7%	100.0%	100.4%
2-propenenitrile	13.9	42.4%	10.9%	89.9%	87.9%
2-propenoic acid, ethyl ester	4.9	0.0%	0.0%	55.1%	56.0%
2-propanone	7.2	20.8%	17.2%	84.7%	86.2%
methanol	13.1	188.5%	99.2%	99.2%	141.4%
n-butanol	5.8	0.0%	0.0%	29.3%	26.1%
acetic acid, ethenyl ester	5.7	0.0%	0.0%	129.8%	129.8%
acetic acid, ethyl ester	5.4	0.0%	0.0%	66.7%	68.0%

1. Estimated relative humidity = 100% (excess liquid water present).

Table 3. Calculated Results for RTI Canister Experiment*							
Compound	C ₀ ,ppbv	Recovery @ RH =					
		0.01 %	1.5 %	5 %	7.5 %	10 %	100 %
1,1,1-trichloroethane	5.3	98.8 %	98.8 %	99.0 %	99.3 %	99.9 %	100 %
toluene	5.0	66.8 %	68.5 %	75.1 %	83.9 %	98.3 %	100 %
2-propenenitrile	13.9	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100 %
2-propenoic acid, ethyl ester	4.9	95.7 %	95.8 %	96.4 %	97.4 %	99.7 %	100 %
2-propanone	7.2	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100 %
methanol	13.1	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100 %
n-butanol	5.8	97.4 %	97.3 %	97.3 %	97.6 %	99.6 %	100 %
acetic acid, ethenyl ester	5.7	99.8 %	99.8 %	99.8 %	99.8 %	100.0 %	100 %
acetic acid, ethyl ester	5.4	99.8 %	99.8 %	99.8 %	99.8 %	100.0 %	100 %

* Polished canister; sample pressure = 45 psia.

Table 4. Experimental¹ and Calculated Recoveries for VOC

Compound Name	C ₀ ² , ppbv	RH = 0 %		RH = 1.2%		RH = 2.9%		RH = 5.8%		RH = 8.7%		RH = 11.6%	
		exp	cal	exp	cal	exp	cal	exp	cal	exp	cal	exp	cal
dichlorodifluoromethane	2.60	ND ³	100	ND	100	ND	100	ND	100	ND	100	ND	100
methyl chloride	2.64	101	100	102	100	108	100	100	100	102	100	98	100
1,2-dichloro-1,1,2,2-tetrafluoroethane	2.68	106	100	106	100	110	100	108	100	109	100	100	100
vinyl chloride	4.61	96	100	100	100	100	100	94	100	94	100	106	100
methylbromide	3.06	96	100	97	100	101	100	97	100	96	100	97	100
ethyl chloride	2.58	95	100	98	100	99	100	96	100	97	100	98	100
trichlorofluoromethane	2.74	ND	100	ND	100	ND	100	ND	100	ND	100	ND	100
1,1-dichloroethene	3.22	96	100	97	100	98	100	96	100	97	100	97	100
dichloromethane	4.11	103	100	106	100	115	100	97	100	97	100	99	100
3-chloropropene	3.22	96	100	98	100	100	100	96	100	97	100	97	100
1,1,2-trichloro-1,2,2-trifluoroethane	2.72	99	99.8	98	99.8	99	99.8	97	99.8		99.9	98	99.8
1,1-dichloroethane	3.07	95	100	96	100	99	100	96	100	97	100	96	100
cis-1,2-dichloroethene	3.48	95	100	97	100	99	100	96	100	97	100	96	100
trichloromethane	3.45	93	99.9	94	99.9	96	99.9	94	99.9	91	99.9	91	99.9
1,2-dichloroethane	3.34	89	99.9	96	99.9	97	99.9	96	99.9	96	99.9	96	99.9
1,1,1-trichloroethane	1.86	101	99.5	97	99.5	100	99.5	97	99.6	98	99.6	96	99.6

Table 4. Experimental ¹ and Calculated Recoveries for VOC													
Compound	C ₀ ²	RH = 0 %		RH = 1.2%		RH = 2.2%		RH = 5.8%		RH = 8.7%		RH = 11.6%	
Name	ppbv	exp	cal	exp	cal	exp	cal	exp	cal	exp	cal	exp	cal
benzene	2.83	95	99.4	97	99.4	100	99.4	97	99.4	98	99.5	98	99.5
carbon tetrachloride	2.96	96	99.4	97	99.4	109	99.4	97	99.5	99	99.5	96	99.5
1,2-dichloropropane	2.69	90	99.1	96	99.1	98	99.1	96	99.1	96	99.2	98	99.2
trichloroethene	2.93	92	99.4	94	99.4	98	99.4	95	99.4	92	99.5	93	99.5
cis-1,3-dichloropropene	2.93	82	95.8	98	95.8	109	95.9	97	96.0	98	96.2	98	96.3
trans-1,3-dichloropropene	2.93	63	96.3	94	96.3	98	96.3	93	96.5	93	96.6	93	96.7
1,1,2-trichloroethane	2.83	79	97.9	95	98.0	100	98.0	97	98.1	96	98.1	100	98.2
toluene	2.45	88	91.8	95	92.0	96	92.1	95	92.5	97	92.9	97	93.3
1,2-dibromoethane	3.06	69	94.3	94	94.4	96	94.5	96	94.7	95	94.9	95	95.1
tetrachloroethene	2.51	91	89.6	95	89.7	96	89.9	94	90.4	95	90.8	95	91.4
chlorobenzene	2.54	81	82.1	95	82.4	95	82.8	95	83.5	94	84.3	98	85.2
ethylbenzene	2.16	75	46.9	95	47.4	96	48.3	98	49.9	97	51.8	96	54.0
m-xylene	1.07	72	41.1	93	41.7	94	42.5	97	44.1	97	46.0	97	48.3
p-xylene	1.07		42.4		43.0		43.8		45.5		47.4		49.6
styrene	2.25	33	31.7	82	32.2	84	33.0	83	34.5	89	36.3	94	38.5
1,1,2,2-tetrachloroethane	1.18		75.2		75.5		76.0		76.8		77.8		79.0

Table 4. Experimental ¹ and Calculated Recoveries for VOC													
Compound	C ₀ ²	RH = 0 %		RH = 1.2 %		RH = 2.9 %		RH = 5.8 %		RH = 8.7 %		RH = 11.6 %	
Name	ppbv	exp	cal	exp	cal	exp	cal	exp	cal	exp	cal	exp	cal
o-xylene	1.18	62	37.2	90	37.8	93	38.6	97	40.2	94	42.0	96	44.2
4-ethyl toluene	1.83	37	5.9	87	6.0	90	6.3	99	6.8	94	7.4	95	8.2
1,3,5-trimethylbenzene	1.83	37	5.1	87	5.2	88	5.4	91	5.8	93	6.4	95	7.1
1,2,4-trimethylbenzene	1.88	28	4.3	84	4.5	87	4.7	94	5.0	92	5.5	94	6.1
benzylchloride	1.10		9.7		9.9		10.2		10.8		11.6		12.5
m-dichlorobenzene	1.10	40	16.1	80	16.5	85	16.9	91	17.9	88	19.1	89	20.5
p-dichlorobenzene	1.78	37	11.4	78	11.6	87	12.0	94	12.7	85	13.6	87	14.7
o-dichlorobenzene	2.16	35	11.0	78	11.3	83	11.6	92	12.3	88	13.2	90	14.2
1,2,4-trichlorobenzene	1.64	5	1.0	45	1.0	55	1.0	66	1.0	64	1.0	69	1.1
hexachlorobutadiene	1.37	19	1.0	63	1.0	70	1.0	81	1.0	79	1.0	85	1.0

1. Temperature = 25 C; sample pressure = 19.1 psia; concentrations measured by GC/FID; (Smith and Holdren, 1989).
2. Concentrations measured in master cylinder by GC/MSD.
3. ND = not detected by FID.

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APPENDIX A. SOURCE CODE FOR CANISTER STABILITY PROGRAM

```
DECLARE SUB comp ()
DECLARE SUB menu ()
DECLARE SUB cmpdlist ()
DECLARE SUB help ()
DECLARE SUB molefrac ()
DECLARE SUB warn ()
DECLARE SUB done ()
DECLARE SUB putout ()
DIM SHARED fl(1 TO 3), name$(1 TO 100), i, mt, RHo, RH, P, Ps, R, B, Ts, Ta, V,
Wo, beta(1 TO 100)
DIM SHARED Pin(1 TO 100) AS DOUBLE, Pfn(1 TO 100) AS DOUBLE, Po(1 TO 100)
DIM SHARED X(1 TO 100) AS DOUBLE, n, AP(1 TO 100), BP(1 TO 100), ofile$, y AS
DOUBLE
REM ' Default values'
    mt = 0: B = .0000705: Ta = 298: Ts = 298: V = 6
    Wo = 2.66E-06: R = 2: Ps = 1: RHo = .01
FOR i = 1 TO 3: fl(i) = 2: NEXT
me: menu
molefrac
putout
GOTO me

SUB cmpdlist
CLS
SCREEN 9: COLOR 11, 11
    OPEN "R", #1, "cancal.prm", 69
    FIELD #1, 40 AS namf$, 9 AS fbet$, 9 AS fAP$, 9 AS fBP$, 2 AS ex$
    WHILE NOT EOF(1): j = j + 2
        GET #1, j: a$ = namf$: GET #1, j + 1: B$ = namf$
        PRINT a$; TAB(40); B$
        IF (j / 20 - INT(j / 20)) = 0 THEN
            COLOR 12
            PRINT "More -- press any key to continue"
            SLEEP
            COLOR 11
        END IF
    WEND
```

```

        CLOSE #1
    END SUB

    SUB comp
        CLS : i = 1: j = 0
        IF RH > 0 THEN
            name$(1) = "water vapor"
            beta(1) = 3.7025
            AP(1) = 20.514
            BP(1) = 5178
            i = 2
        END IF

        COLOR 12: INPUT "Number of Compounds including water = "; nc: COLOR 11
        OPEN "R", #1, "cancel.prn", 69: j = 0
        FIELD #1, 40 AS namf$, 9 AS fbet$, 9 AS fAP$, 9 AS fBP$, 2 AS ex$
        WHILE NOT EOF(1): j = j + 1
            GET #1, j
            PRINT namf$; : INPUT " Concentration, ppbv = "; Pin(i): Pin(i) = 1E-09 *
Pin(i)
            IF Pin(i) > 0 THEN
                name$(i) = namf$: beta(i) = VAL(fbet$)
                AP(i) = VAL(fAP$): BP(i) = VAL(fBP$)
                i = i + 1
            END IF
            n = i - 1
            IF n = nc THEN GOTO fin
        WEND
    fin:   CLOSE #1
        FOR i = 1 TO n: Pfn(i) = Pin(i): mt = mt + Pin(i): NEXT
        X(1) = Pin(1) / mt: X(2) = Pin(2) / mt
        FOR i = 1 TO n: Po(i) = (1 / 760) * EXP(AP(i) - BP(i) / Ta): NEXT

    END SUB

    SUB done
    STATIC xpo
    STATIC xpn
        IF (ABS(y) < 1) THEN

```

```

xpn = 10 + ABS(550 * (LOG(ABS(y)) / LOG(n * .000001)))
IF xpn < xpo THEN LINE (10, 260)-(559, 270), 0, BF
IF xpn >= 549 THEN xpn = 559
LINE (10, 260)-(xpn, 270), 11, BF
IF xpn > 285 THEN
    COLOR 14
    CIRCLE (20, 20), 20
    CIRCLE (20, 20), 10, , 3.93, 5.5
    CIRCLE (15, 15), 2
    CIRCLE (25, 15), 2
    COLOR 11
END IF
xpo = xpn
END IF
END SUB

SUB help
CLS
SCREEN 9: COLOR 15, 11
LINE (0, 0)-(639, 349), 12, B
LINE (2, 2)-(637, 347), 12, B
LOCATE 2, 2: PRINT "This program uses the Dubinin-Radushkevich isotherm and
assumes"
LOCATE 3, 2: PRINT "ideal solution behavior in the adsorbed phase to calculate losses by "
LOCATE 4, 2: PRINT "adsorption on the canister wall. Canister and sample parameters
are"
LOCATE 5, 2: PRINT "changed from the default values by selection from the menu. The "
LOCATE 6, 2: PRINT "initial composition of the sample is specified by selecting 'C' or 'c'."
LOCATE 7, 2: PRINT "The latter action will cause compound names to be displayed
sequentially,"
LOCATE 8, 2: PRINT "and requires that you enter the concentrations in ppbv. Any
compound for"
LOCATE 9, 2: PRINT "which you enter zero or no concentration will be excluded from the
computation."
LOCATE 10, 2: PRINT "The data file 'CANCAL.prn' must be under the same directory as
this program"
LOCATE 11, 2: PRINT "before you can run this program. To change that file, use
'CANCAL.wk1' and"

```

```

LOCATE 12, 2: PRINT "Lotus-123. Data output choices can be toggled on/off by repeating
the choice."
LOCATE 13, 2: PRINT "The disk output will generate a file that can be imported into
Lotus-123."
LOCATE 14, 2: PRINT "After each calculation the program will return to the menu so that
the effects"
LOCATE 15, 2: PRINT "of changes in either sample or canister parameters can be explored
with the"
LOCATE 16, 2: PRINT "same starting composition. To review list of available compounds,
press 'c'."
LOCATE 17, 2: PRINT "Note that the RH at analysis time is calculated based on the
sampling RH,"
LOCATE 18, 2: PRINT "the sample pressure, and the temperatures of sampling and
analysis, "
LOCATE 19, 2: PRINT "but only the analysis time conditions show."
LOCATE 20, 2: COLOR 4: PRINT "Any comments or suggestions should be directed to
Bob Coutant (614)424-5247."
LOCATE 23, 2: COLOR 9: PRINT "To return to the menu, press any key."
ret: BS = LCASE$(INKEY$): IF BS = "" THEN GOTO ret
    IF BS = "c" THEN cmpdlist

```

END SUB

SUB menu

```

menu: CLS : a$ = INKEY$
SCREEN 9: COLOR 7, 0
COLOR 9: LOCATE 1, 28: PRINT "Canister Sample Integrity"
COLOR 3: LOCATE 1, 70: PRINT "He(l)p"
COLOR 14: LOCATE 3, 31: PRINT "Canister Properties"
COLOR 2: LOCATE 4, 15: PRINT "(V)olume - "; V; "L"
LOCATE 4, 50: PRINT "(R)oughness - "; R
COLOR 14: LOCATE 6, 32: PRINT "Sample Properties"
COLOR 2: LOCATE 7, 15: PRINT "(T)emperature - "; Ta - 273; "C"
P = Ps * Ta / Ts: RH = P * RHo * EXP(5178 * (Ta ^ -1 - Ts ^ -1))
LOCATE 7, 50: PRINT "Relative (H)umidity - "; : IF RH > 100 THEN COLOR 12
LOCATE 7, 72: PRINT USING "###.###"; RH; : PRINT "%": COLOR 2
LOCATE 8, 15
    IF X(2) = 0 THEN
        COLOR 12

```

```

    END IF
PRINT "(C)omposition"
COLOR 2: LOCATE 8, 50: PRINT "(P)ressure - "; : PRINT USING "##.##"; P; : PRINT
"atm"
COLOR 14: LOCATE 10, 33: PRINT "Output Choices"
COLOR fl(1): LOCATE 11, 15: PRINT "(1) Screen"
COLOR fl(2): LOCATE 11, 33: PRINT "(2) Printer"
COLOR fl(3): LOCATE 11, 50: PRINT "(3) Disk"
    IF (X(2) = 0) OR fl(1) + fl(2) + fl(3) < 7 THEN
        LOCATE 13, 35
        COLOR 12
        PRINT "Not Ready"

    ELSE
        LOCATE 13, 37
        COLOR 10
        PRINT "Ready"
    END IF
LOCATE 15, 37: COLOR 9: PRINT "(S)tart"
COLOR 3: LOCATE 17, 1: PRINT "To change any of the above, press key corresponding
to letter or number"
PRINT "in parentheses - - or Q to exit program. For a printed list of available"
PRINT "compounds, press 4."
PRINT
COLOR 11
user: a$ = LCASE$(INKEY$): IF a$ = "" THEN GOTO user
    IF a$ = "t" THEN
        INPUT "Analysis Temperature, C = "; Ta
        Ta = Ta + 273
        INPUT "Sampling Temperature, C = "; Ts
        Ts = Ts + 273
    END IF
    IF a$ = "1" THEN fl(1) = 12 - fl(1)
    IF a$ = "2" THEN fl(2) = 12 - fl(2)
    IF a$ = "3" THEN
        fl(3) = 12 - fl(3)
        INPUT "Name of output file = "; ofile$
        ofile$ = ofile$ + ".pm"
    END IF

```

```

IF a$ = "4" THEN
    OPEN "R", #1, "cancal.prn", 69: j = 0
    FIELD #1, 40 AS namf$, 9 AS fbet$, 9 AS fAP$, 9 AS fBP$, 2 AS ex$
    WHILE NOT EOF(1): j = j + 1
    GET #1, j
    LPRINT j; " "; namf$
    WEND
    CLOSE #1: LPRINT CHR$(12)
END IF
IF a$ = "q" THEN END
IF a$ = "v" THEN
    INPUT "Canister volume, L = "; V
END IF
IF a$ = "h" THEN
    INPUT "Relative humidity (at sampling temperature), % = "; RHo
    IF RHo = 0 THEN
        COLOR 12
        PRINT "Warning -- Zero RH is unrealistic, try again using some small number"
        INPUT "Relative humidity (at sampling temperature), % = "; RHo
    END IF
END IF
IF a$ = "r" THEN
    INPUT "Roughness factor = "; R
END IF
IF a$ = "p" THEN INPUT "Pressure at sampling temperature, atm. = "; Ps
IF a$ = "c" THEN comp
IF a$ = "l" THEN help
IF a$ = "s" THEN
    IF (X(2) = 0) OR fl(1) + fl(2) + fl(3) < 7 THEN
        LOCATE 23, 5: COLOR 12: PRINT "Please select output mode or
composition -- press any key to continue"
        SLEEP
    ELSE
        CLS
        LOCATE 15, 35: COLOR 12: PRINT "Working"
        LOCATE 18, 70: COLOR 11: PRINT "Done"
        LINE (8, 257)-(561, 272), 12, B
    END IF
END IF

```



```

        LOCATE 18, 1: PRINT "0%"
        LOCATE 18, 35: PRINT "50%"
        GOTO es
    END IF
END IF

GOTO menu

es: END SUB

SUB molefrac
STATIC dy AS DOUBLE
STATIC dx AS DOUBLE
STATIC dP AS DOUBLE
STATIC w AS DOUBLE
    j = 0: Wo = R * 1.67E-08 * (12.57 * (V / 4.19) ^ .666)
    Po(1) = (1 / 760) * EXP(AP(1) - BP(1) / Ta): Pin(1) = .01 * RH * Po(1)
    mt = Pin(1): Pfn(1) = Pin(1)
    FOR i = 2 TO n: Pin(i) = P * Pin(i): Pfn(i) = Pin(i): mt = mt + Pin(i): NEXT
    X(1) = Pin(1) / mt: X(2) = Pin(2) / mt
    FOR i = 1 TO n: Po(i) = (1 / 760) * EXP(AP(i) - BP(i) / Ta): NEXT

repeat: FOR k = 1 TO 5
    y = 1 - X(1): dy = 1: j = j + 1
    FOR i = 2 TO n
        X(i) = (Pfn(i) / Po(i)) * (X(1) * Po(1) / Pfn(1)) ^ (beta(i) / beta(1))
        y = y - X(i)
        dx = (Pfn(i) / Po(i)) * (beta(i) / beta(1)) * (Po(1) / Pfn(1)) * (X(1) * Po(1) /
Pfn(1)) ^ ((beta(i) / beta(1)) - 1)
        dy = dy + dx
    NEXT i
    WHILE (X(1) + y / (dy)) < 0: dy = dy * 2: WEND
    IF ABS(y) > 1 THEN X(1) = X(1) + y / dy ELSE X(1) = X(1) + y / (n * dy)
    NEXT k
done
    IF ABS(y) > n * .000001 THEN
        w = Wo * EXP(-(B / beta(1) ^ 2) * (2 * Ta * LOG(X(1) * Po(1) / Pfn(1)))) ^
2)
        FOR i = 1 TO n

```

```

        dP = 0
        IF X(i) < 1 THEN
            dP = (.082055 * Ta / V) * w * X(i)
            IF dP > Pin(i) THEN dP = .99 * Pin(i)
            Pfn(i) = ((49) * Pfn(i) + (Pin(i) - dP)) / 50
        END IF
    NEXT i

    GOTO repeat
END IF
IF j < 50 THEN GOTO repeat
CLS
FOR i = 1 TO n: Pin(i) = Pin(i) / P: Pfn(i) = Pfn(i) / P: NEXT

END SUB

SUB putout
IF fl(1) = 10 THEN
    PRINT STRING$(79, 205)
    PRINT "Compound"; TAB(40); "mole frac"; TAB(55); "Cfin"; TAB(62); "Cinit";
    TAB(70); "%Recovery"
    PRINT STRING$(79, 205)
    FOR i = 2 TO n
        PRINT RTRIM$(name$(i)); TAB(40); : PRINT USING "##.##^" X(i); :
    PRINT USING "##.## "; Pfn(i) * 1E+09, Pin(i) * 1E+09; : PRINT USING "####.##"; 100
    * Pfn(i) / Pin(i)
    NEXT
    PRINT STRING$(79, 205)
    LOCATE 23, 2: COLOR 12: PRINT "Press any key to continue --"
    SLEEP
END IF
IF fl(2) = 10 THEN
    WIDTH LPRINT 80
    LPRINT STRING$(79, 61)
    LPRINT "Compound"; TAB(40); "mole frac"; TAB(55); "Cfin"; TAB(62); "Cinit";
    TAB(70); "%Recovery"
    LPRINT STRING$(79, 61)
    FOR i = 2 TO n

```

```

        LPRINT RTRIM$(name$(i)); TAB(40); : LPRINT USING "###.##^" " "; X(i); :
LPRINT USING "###.## " ; Pfn(i) * 1E+09, Pin(i) * 1E+09; : LPRINT USING "####.##";
100 * Pfn(i) / Pin(i)
    NEXT
    LPRINT STRING$(79, 61)
    LPRINT "Relative humidity = "; RHo; "% at sampling temperature = "; Ts - 273;
"C"
    LPRINT "Analysis temperature = "; Ta - 273; "C"; " and canister pressure = "; P *
14.7; "psia"
    LPRINT CHR$(12)
END IF
IF fl(3) = 10 THEN
    OPEN "O", #2, ofile$
    FOR i = 1 TO n
        mt = Pin(i)
        PRINT #2, name$(i); : PRINT #2, USING " ###.##^" " "; mt; : PRINT #2, USING "
###.##"; Pfn(i) / Pin(i)
    NEXT
    CLOSE #2
    fl(3) = 2
END IF

END SUB

SUB warn
CLS
SCREEN 9: COLOR 12, 11
LINE (0, 0)-(639, 349), 12, B
LINE (2, 2)-(637, 347), 12, B
LOCATE 10, 10
PRINT "WARNING -- You have selected a combination of pressure and relative"
LOCATE 12, 10: PRINT "humidity that will cause liquid water condensation! Try again."
LOCATE 20, 10: COLOR 9: PRINT "Press any key to continue --"
SLEEP
Ps = 1: RHo = .01
END SUB

```

