



Project Summary

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

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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 the 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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This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate

report of the same title (see Project Report ordering information at back).

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 (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 CrO₂. 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.

Objective

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.

Results

A computer-based model was developed to facilitate solution of the set of simultaneous equations representing multicomponent adsorption equilibria. 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.

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 available surface area. The surface roughness also is used to determine the available area. This factor 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 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 analysis condition is also 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.

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_m), initial gas phase pressure (P_i), and the ratio of P_m/P_i . The disk output yields a file that can be imported into Lotus-123 for tabulation and comparison with experimental data.

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 "remembered" by the program so that multiple computations involving changes in relative humidity, temperatures, etc. can be conducted without re-entry 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 the amounts of each component adsorbed and the corresponding residual gas phase pressures are estimated. This process of estimation of X_i and P_i is reiterated until convergence is achieved to less than 1 ppm.

The model was calibrated by comparison of model predictions with a single set of experimental results for recovery of VOC from "dry" canisters. Application of the

model to other experimental conditions yields predictions that are qualitatively in agreement with the experimental data. In some cases, the agreement between predictions and experimental results is nearly quantitative, suggesting that the use of very well qualified data for model calibration might improve the overall quality of the predictions.

Conclusions and Recommendations

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 implications for application 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 low enough that the model predicts loss of target compounds, 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, but restrictions imposed during shipment may govern the maximum pressure allowable.
- (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 am-

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

bient 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.

The model developed in this program shows considerable promise for qualitative and semi-quantitative explanation of physical adsorption phenomena 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 hu-

midities. 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.

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The complete report, entitled "Theoretical Evaluation of Stability of Volatile Organic Chemicals and Polar Volatile Organic Chemicals in Canisters," (Order No.

PB92-166941/AS; Cost: \$17.00; subject to change) will be available only from:

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