**POSITION FOR DETERMINING GAS PHASE
VOLATILE ORGANIC COMPOUND CONCENTRATIONS
IN TRANSURANIC WASTE CONTAINERS**

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ABSTRACT

In the conditional no-migration determination (NMD) for the test phase of the Waste Isolation Pilot Plant (WIPP), the U.S. Environmental Protection Agency (EPA) imposed certain conditions on the U.S. Department of Energy (DOE) regarding gas phase volatile organic compound (VOC) concentrations in the void space of transuranic (TRU) waste containers. Specifically, the EPA required the DOE to ensure that each waste container has no layer of confinement that contains flammable mixtures of gases or mixtures of gases that could become flammable when mixed with air. The EPA also required that sampling of the headspace of waste containers outside inner layers of confinement be representative of the entire void space of the container. The EPA stated that all layers of confinement in a container would have to be sampled until DOE can demonstrate to the EPA that sampling of all layers is either unnecessary or can be safely reduced.

A test program was conducted at the Idaho National Engineering Laboratory (INEL) to demonstrate that the gas phase VOC concentration in the void space of each layer of confinement in vented drums can be estimated from measured drum headspace using a theoretical transport model and that sampling of each layer of confinement is unnecessary. This report summarizes the studies performed in the INEL test program and extends them for the purpose of developing a methodology for determining gas phase VOC concentrations in both vented and unvented TRU waste containers. The methodology specifies conditions under which waste drum headspace gases can be said to be representative of drum gases as a whole and describes a method for predicting drum concentrations in situations where the headspace concentration is not representative. The methodology addresses the approach for determining the drum VOC gas content for two purposes: operational period drum handling and operational period no-migration calculations.

INTRODUCTION

Characterization of transuranic (TRU) wastes destined for the Waste Isolation Pilot Plant (WIPP) will include sampling of gases in the headspaces of waste drums for volatile organic compounds (VOC). The headspace gas VOC concentrations will be used to determine potential flammability of gases and VOC concentrations in drums for transportation and Resource Conservation and Recovery Act (RCRA) compliance purposes (DOE 1995). In the conditional no-migration determination (NMD) for the test phase of the WIPP facility (55 FR 47700), the Environmental Protection Agency (EPA) required that the U.S. Department of Energy (DOE) must ensure that each waste container emplaced underground at the WIPP has no layer of confinement that contains flammable mixtures of gases or mixtures of gases that could become flammable when mixed with air. For purposes of a no-migration demonstration, DOE must also characterize the nonflammable volatile hazardous constituents in TRU waste containers. The EPA stated that all layers of confinement in a container would have to be sampled until DOE can demonstrate to the EPA, based on the data collected, that sampling of all layers is either unnecessary or can be safely reduced. This position paper summarizes a methodology that has been proposed in Connolly et al. (1995) that addresses these conditions and alleviates the requirement of sampling all layers of confinement.

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A test program was conducted at the Idaho National Engineering Laboratory (INEL) to demonstrate that the VOC concentration in the void space of each layer of confinement in vented drums can be estimated using measured drum headspace and a model incorporating theoretical diffusion and permeation transport principles and that sampling of each layer of confinement is unnecessary. The model and model validation results provide information that are used to address the headspace VOC concentration representativeness issue raised by the EPA for vented containers.

This report presents the methodology for determining VOC concentrations in both vented and unvented drums for existing waste packaging configurations. The methodology specifies conditions under which drum headspace gases can be said to be representative of drum gases as a whole and describes a method for predicting drum concentrations in situations where the headspace concentration is not representative. For the purpose of predictions of gas phase VOC concentrations, innermost layers of confinement are the polymer bag layers closest to the waste; rigid inner layers of confinement, such as polymer bottles, are not included. The methodology presented in this paper addresses the approach for determining the drum VOC gas content for two purposes: operational period drum handling and operational period no-migration calculations.

VOC TRANSPORT STUDIES

The INEL test program was developed to predict innermost bag gas phase VOC concentrations from the headspace gas VOC concentrations using VOC transport models and data obtained from waste drum sampling. This program consisted of three stages.

In the first stage of the test program, a transient VOC transport model was developed to estimate the VOC concentration within laboratory-scale waste drums as a function of time (Liekhus et al. 1994a). The testing demonstrated that transient gas phase VOC concentrations can be predicted based on theoretical transport mechanisms. Model equations accounted for three primary mechanisms for VOC transport from a void volume. These mechanisms were VOC permeation across a polymer confinement layer, VOC diffusion across an opening in a layer of confinement, and VOC solubility in a polymer confinement layer.

In the second stage of the INEL program, a steady-state transport model was developed to predict concentrations in laboratory-scale vented waste drums containing simulated waste sludge based on knowledge of drum headspace VOC concentration and waste drum configuration (Liekhus et al. 1994b). Experiments were performed to measure the VOC concentration in laboratory-scale vented waste drums containing two types of simulated waste sludge with differing compositions (Liekhus et al. 1994b). Experimental results were expressed as a ratio between drum headspace VOC concentration and the VOC concentration inside the innermost polyethylene bag. Model equations were used to determine the effect of model parameters on the estimated concentration difference across a transport boundary, such as the rigid drum liner or polymer bag, using permeation as the transport mechanism.

In the third stage of the INEL experimental program, the model developed in the second stage was used to estimate VOC concentrations in 64 actual waste drums from INEL and the Rocky Flats Environmental Technology Site (Rocky Flats). The effectiveness of the model in estimating VOC concentration was examined for vented waste drums containing different waste types and packaging configurations. The model results demonstrated that maximum VOC concentrations within actual waste drums can be estimated from drum headspace gas sampling data. Details of the gas sampling and analysis, equipment used, procedures employed and quality control procedures are provided in Liekhus (1995).

The VOC transport model was said to be unbiased if the 95-percent confidence limits on the mean logarithm of the ratio of the VOC concentration in the innermost layer of confinement to the maximum VOC concentration in the headspace is zero. Otherwise the model is said to have a positive or negative bias. Transport model predictions were unbiased or positively biased (i.e., over estimated) for the maximum measured concentrations of 11 VOCs within vented waste drums. These VOCs are carbon tetrachloride, chloroform, 1,1-dichloroethane, 1,1-dichloroethylene, methanol, methylene chloride, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, 1,1,2-trichloro-1,2,2-trifluoroethane, and toluene. The model exhibited a negative bias for 2 VOCs (p-xylene and acetone). The model was

unbiased in estimating the total VOC concentration within the innermost layer of confinement for waste drums containing a maximum of four layers of polymer bags that were all sampled within one day and exhibiting detectable concentrations in inner bags. The model exhibited a positive bias in estimating the total VOC concentration within the innermost layer of confinement of waste drums containing a maximum of two or five layers of polymer bags.

Model precision was characterized for 13 VOCs and three drum configurations by the lower 90/90 tolerance limit (LTL) for the logarithm of the ratio described earlier. Based on the tolerance limits, the VOC transport model predicts an innermost bag VOC concentration that, with 90-percent confidence, will not be less than 50 percent of the maximum measured VOC concentration in at least 90 percent of the waste drums for 8 VOCs and two of the waste drum configurations. These VOCs are acetone, 1,1-dichloroethane, 1,1-dichloroethylene, methylene chloride, toluene, 1,1,1-trichloroethane, trichloroethylene, and 1,1,2-trichloro-1,2,2-trifluoroethane. The VOC transport model predicts that the VOC concentration will not be less than 33 percent of the maximum measured VOC concentration in at least 90 percent of the waste drums for 3 VOCs and waste drums with a maximum of four layers of polymer bags. The three VOCs are chloroform, tetrachloroethylene, and p-xylene. For carbon tetrachloride and methanol, model estimates will not be less than 20 percent of the maximum measured VOC concentration in at least 90 percent of the waste drums.

DRUM AGE CRITERION FOR HEADSPACE GAS SAMPLING

There is a certain age criterion that must be met by a drum of TRU waste in order for headspace gas samples to be either representative of gases in the drum or appropriate to use in predicting innermost bag VOC gas phase concentration. The drum age criterion (DAC) defines the age of a drum necessary to reach 90-percent of steady-state concentration within all of the bags and the rigid drum liner. The DAC establishes the time after waste packaging necessary to wait prior to drum headspace sampling to help ensure that the headspace sample analyses are suitable for their intended use.

DACs for two packaging configurations have been determined using transient VOC transport models and indicator VOCs selected on the basis of health risks and magnitude of concentration. The DACs are given in Table I. For drums of Waste Types I and IV, the DAC is 225 days. For drums of Waste Types II and III, the DAC is 142 days.

Indicator VOCs were selected by using two separate screening techniques and having the screened VOCs comprise the set of indicator VOCs. The screening techniques are consistent with the purposes for determining gas phase VOC concentrations in drums; one of the screening techniques focused on flammability issues related to operational period drum handling and the second focused on human health risk from inhalation for the operational period. To screen for operational period drum handling, the magnitude of VOC concentration in headspace gas samples from 465 INEL and Rocky Flats drums was examined.

The screening resulted in 11 distinct indicator VOCs. For drum handling, n-butanol, methyl ethyl ketone, methyl isobutyl ketone, and methanol were screened for inclusion in the indicator set. For operational period human health risk, 1,1-dichloroethylene, carbon tetrachloride, chlorobenzene, chloroform, methylene chloride, methyl ethyl ketone, 1,1,2,2-tetrachloroethane, trichloroethylene, and toluene were screened and included as indicator VOCs.

A computer program was used to calculate the required drum age or vent time for each indicator VOC for three drum categories and two drum packaging configurations. The three drum categories are:

- **Drum Category 1, Existing Vented Drums:** The existing vented drums are those that were stored as unvented drums and subsequently vented, the rigid drum liners punctured, and stored again for a period of time. Drums in this category must have been unvented for a sufficient time such that equilibrium concentrations existed within all confinement layers at the time of venting.

- Drum Category 2, Newly Packaged Vented Drums: The newly packaged vented drums consist of drums and associated rigid drum liners that were vented at the time of packaging. In this category, steady-state concentrations do not exist within all confinement layers at the time of packaging.
- Drum Category 3, Existing Unvented Drums: The existing unvented drums are those drums that have been stored as unvented drums for a period of time. The drums are to be vented (i.e., the drum liners punctured and carbon composite filters installed in the drum lids) and headspace gas samples taken from inside the rigid drum liners at the time of venting.

Two packaging drum configurations were considered in determining the DACs from the calculated drum ages and vent times. For drums containing sludges (Waste Types I and IV), there are two large bags within the rigid drum liner providing two inner layers of confinement. For solid waste (Waste Types II and III), it is conservatively assumed that five layers are within the rigid drum liner. The drum filter type is assumed to be NFT-020 for both packaging configurations; this assumption is considered conservative since NFT-020 filters are the most restrictive regarding the release of compounds of filter types being used in the DOE complex (Liekhuis 1995). The longer of the following, for each configuration and over all indicator VOCs, are taken as the DACs:

- Calculated vent time for newly packaged vented drums and
- The sum of calculated vent time for existing vented drums and calculated drum age for existing unvented drums

The DACs that result are given in Table I. Potential future packaging configurations (e.g., those using filtered bags) were not considered and will require additional analyses to determine the appropriate DAC.

DISCUSSION OF TRANSPORT MODELING

The INEL test program and its associated transport modeling demonstrates that VOC transport can be modeled based on mathematical simulation of diffusion and permeation processes. This demonstration took place in three stages: transient VOC transport from vented laboratory-scale drums, steady-state VOC transport in laboratory-scale vented waste drums containing simulated waste sludge and the application of the steady-state model to actual waste drums. Based on comparing model results to actual waste drum concentrations, the steady-state VOC transport model demonstrated that innermost bag gas phase VOC concentrations can be predicted from headspace gas concentration data. Because these predictions can be made, sampling and analysis of inner layers of confinement will not be necessary.

The predictions can be made using prediction factors that conservatively approximate the steady-state model predictions. The prediction factors are derived by solving the steady-state model in terms of the ratio between the innermost layer gas phase VOC concentration and the headspace gas VOC concentration. The prediction factors have been computed for 29 VOCs for the two packaging configurations used for the DACs. Use of the prediction factors will be conservative for cases where the actual package has fewer layers than that assumed for the prediction factor. The prediction factors are also based on conservative assumptions of filter diffusivities. The prediction factors are given in Table II and range from 1.1 to 9.5 for Waste Types I and IV and from 1.7 to 39 for Waste Types II and III. To predict the innermost bag gas phase VOC concentration, the headspace gas VOC concentration and associated prediction factor should be multiplied.

The steady-state VOC transport model and the prediction factors are valid when the DAC has been met. The DAC establishes the time after waste packaging necessary to wait prior to drum headspace gas sampling to be able to accurately predict the innermost layer gas phase VOC concentration within a drum. The innermost layer gas phase VOC concentration prediction will be the maximum predicted value. The DAC also establishes the waiting time that will ensure that the transport rates between

layers of confinement are equal and headspace concentrations can be used in calculations for emissions through the drum filter.

If the drum is unvented (Drum Category 3) and the DAC has been met, modeling shows that the headspace gas within the rigid liner is representative of the drum gases within all layers of polymer confinement, because equilibrium has been reached. If the drum is vented (Drum Categories 1 and 2) and the DAC has been met, the innermost gas concentration can be predicted from the headspace gas concentration using the prediction factors in Table 2. The predicted innermost bag concentration is concluded to conservatively represent the maximum concentration within a drum. In addition, if the DAC has been met, the headspace concentration for Drum Categories 1 and 2 can be said to represent headspace concentrations that control the rate of emissions through the drum filter over time.

PROPOSED APPROACH

The proposed approach provides prescriptions for determining drum gas phase VOC concentrations for operational period drum handling and operational period no-migration calculations for each of the three drum categories. The prescriptions are based on the DAC being met prior to headspace sampling and involve methodologies outlined below. Either headspace gas measurements or predictions of innermost bag concentrations, as appropriate, will be used.

Operational Period Drum Handling

Gas phase VOC concentrations in drums will be determined for the purpose of assessing flammability. The maximum gas phase VOC concentration is the concentration of interest for this assessment. The approach is to use predicted concentrations for the maximum in cases where the headspace concentration is not representative of the maximum. The basic steps to the approach are as follows:

1. Determine the drum packaging configuration.
2. Establish and meet the DAC.
3. Sample and analyze headspace gas.
4. Determine Drum Category. Determine drum concentrations as follows:
 - a. For existing vented drums (Drum Category 1), determine the predicted value using the factors in Table II. The predicted value will be used for the drum concentration.
 - b. For newly packaged vented drums (Drum Category 2), the predicted value will be used as for existing vented drums (see a.).
 - c. For existing unvented drums (Drum Category 3), headspace concentrations within the rigid drum liner will be used, because the DAC ensures representativeness.

The selected flammable VOCs concentration values will be summed for each drum.

Operational Period No-Migration Calculations

Gas phase VOC concentrations in drums will be determined for the purpose of calculating VOC emissions through drum filters. Because steady-state conditions are required, the VOC emission rate from a vented drum is a function of the drum headspace VOC concentration and the VOC diffusion characteristic across the drum filter. VOC concentrations in inner layers of confinement are not used, and thus are not selected for the drum concentration; rather, the approach is to use headspace concentrations. The basic steps to the approach are as follows:

1. Determine the drum packaging configuration.
2. Establish and meet the DAC.
3. Sample and analyze headspace gas.
4. Determine Drum Category. Determine drum concentrations as follows:
 - a. For existing vented drums (Drum Category 1), the headspace concentration will be used.
 - b. For newly packaged vented drums (Drum Category 2), the headspace concentration will be used as for existing vented drums.
 - c. For existing unvented drums (Drum Category 3), headspace concentrations within the rigid drum liner will be used.

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TABLE I
Drum Age Criteria

Waste Types I and IV (days)	Waste Types II and III (days)
225	142

TABLE II
Factors for Prediction of Innermost Bag Gas Phase VOC Concentration
from Headspace Gas VOC Concentration

	Waste Types I and IV	Waste Types II and III
Acetone	1.9	5.1
Benzene	1.5	3.4
Bromoform	1.1	1.7
n-Butanol	1.5	3.2
Carbon tetrachloride	1.6	3.9
Chlorobenzene	1.3	2.3
Chloroform	1.5	3.5
Cyclohexane	9.5	39
1,1-Dichloroethane	1.7	4.1
1,2-Dichloroethane	1.4	2.7
1,1-Dichloroethylene	2.1	6.1
cis-1,2-Dichloroethylene	1.5	3.3
Ethylbenzene	1.4	3.2
Ethyl ether	3.8	13
Methanol	2.3	6.8
Methyl ethyl ketone	1.8	4.5
Methyl isobutyl ketone	1.8	4.8
Methylene chloride	1.6	3.7
1,1,2,2-Tetrachloroethane	1.2	1.8
Tetrachloroethylene	1.3	2.3
Toluene	1.2	2.3
1,1,1-Trichloroethane	1.8	4.8
Trichloroethylene	1.3	2.4
1,1,2-Trichloro-1,2,2-trifluoroethane	3.6	13
1,2,4-Trimethylbenzene	1.4	2.8
1,3,5-Trimethylbenzene	1.4	3.0
m-Xylene	1.4	3.1
o-Xylene	1.4	2.7
p-Xylene	1.2	2.1