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ASSESSMENT OF GAS FLAMMABILITY IN TRANSURANIC WASTE CONTAINER

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ABSTRACT

The *Safety Analysis Report for the TRUPACT-II Shipping Package* [Transuranic Package Transporter-II (TRUPACT-II) SARP] set limits for gas generation rates, wattage limits, and flammable volatile organic compound (VOC) concentrations in transuranic (TRU) waste containers that would be shipped to the Waste Isolation Pilot Plant (WIPP). Based on existing headspace gas data for drums stored at the Idaho National Engineering Laboratory (INEL) and the rocky Flats Environmental Technology Site (RFETS), over 30 percent of the contact-handled TRU waste drums contain flammable VOC concentrations greater than the limit. Additional requirement(s) may be imposed for emplacement of waste in the WIPP facility. The conditional no-migration determination (NMD) for the test phase of the facility required that flame tests be performed if significant levels of flammable VOCs were present in TRU waste containers. This paper describes an approach for investigating the potential flammability of TRU waste drums, which would increase the allowable concentrations of flammable VOCs. A flammability assessment methodology is presented that will allow more drums to be shipped to WIPP without treatment or repackaging and reduce the need for flame testing on drums. The approach includes experimental work to determine mixture lower explosive limits (MLEL) for the types of gas mixtures observed in TRU waste, a model for predicting the MLEL for mixtures of VOCs, hydrogen, and methane, and revised screening limits for total flammable VOCs concentrations and concentrations of hydrogen and methane using existing drum headspace gas data and the model predictions.

INTRODUCTION

The U. S. Department of Energy (DOE) intends to begin operation of the Waste Isolation Pilot Plant (WIPP) beginning in 1998. Waste characterization requirements for shipping transuranic (TRU) waste from DOE sites to the WIPP facility are set forth in the *Safety Analysis Report for the TRUPACT-II Shipping Package* [Transuranic Package Transporter-II (TRUPACT-II) SARP] (NRC 1994) . The TRUPACT-II SARP, in evaluating gas generation rates and potential flammability of the wastes, requires that gas phase concentrations of flammable volatile organic compounds (VOCs) not exceed 500 ppmv and the hydrogen and methane concentration not exceed 5 percent. Additional requirement(s) may be imposed for emplacement of waste in the WIPP facility. In the conditional no-migration determination (NMD) for the test phase of the WIPP facility, the U.S. Environmental Protection Agency (EPA) required that each waste container emplaced underground at the WIPP facility have no layer of confinement containing either flammable mixtures of gases or mixtures of gases that could become flammable when mixed with air. The conditional NMD required that flame tests be performed if significant levels of flammable VOCs ($\geq$ 500 ppmv) were present in TRU waste containers.

Based on existing drum headspace gas data for over 800 drums stored at the Idaho National Engineering Laboratory (INEL) and the Rocky Flats Environmental Technology Site (RFETS), over 30 percent of the contact handled-TRU waste drums contain greater than 500 ppmv of potentially flammable VOCs. Under current requirements, these drums cannot be shipped. Moreover, the volume of drums that are in accessible storage that can be shipped will be significantly reduced under these requirements and near-term shipment schedules will be impacted. However, based on the existing drum data and preliminary calculations, it is anticipated that only 10 percent of the drums are potentially flammable and

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90 percent are safely shippable without treatment or repackaging. Costs associated with treatment or repackaging the waste for shipment will be substantial and flame testing, if required, will also have cost impacts. Preparing the waste for shipment and flame testing will both impact the scheduling of shipments to the WIPP facility. The flammability assessment methodology given in this paper is intended to increase the allowable concentrations of potentially flammable VOCs and thereby allow more drums to be shipped without treatment or repackaging, reduce the number of drums requiring flame testing, reduce costs, and minimize delays in waste shipments.

This paper describes an approach that includes investigating the potential flammability of TRU waste drums, increasing the allowable concentrations of flammable VOCs, and performing flammability assessments on drums. Estimates based on existing drum data indicate that when the proposed methodology is implemented, the number of drums that can be shipped without treatment or repackaging will be substantially increased. Because the methodology incorporates experimental data, validated predictive modeling of mixture lower explosive limits (MLEL) for the drums, and conservative screening of flammable gas concentrations, it is technically defensible and appropriate. The methodology takes into account the presence of all flammable gases in the wastes in determining acceptable screening limits for flammable gas concentrations in drums. Specifically, hydrogen and methane are considered in addition to VOCs.

Both empirical and theoretical models for predicting MLELs are considered. A model will be selected for use in flammability assessments that performs well relative to experimental data, adequately accounts for gas mixture compositions in drums, and demonstrates an acceptable level of conservatism. Screening limits are based on population statistics for flammable gas concentrations in the innermost layers of confinement in the drums, including the model-based maximum permissible hydrogen and methane concentration (MPHMC). The methodology for evaluating drums involves comparisons with screening limits, comparisons with less conservative drum-specific limits as necessary, and flame testing for drums that exceed these limits.

The MPHMC will be used to establish maximum allowable generation rates for hydrogen and methane gas. These rates, which will be calculated using the TRUPACT-II SARP methodology, must be determined because total concentrations of flammable VOCs may exceed the limit of 500 ppmv previously used in determining gas generation rates. The results will lead to preparing an application to the Nuclear Regulatory Commission (NRC) that will modify the current restrictive limits. This will ultimately allow more waste to be shipped to the WIPP facility without repackaging or treatment.

This paper provides the technical basis for and description of the flammability assessment methodology as developed to date. First, a description of the testing to determine MLELs of TRU waste container gas mixtures is provided. Models that have been identified for assessing mixture flammability are described next. Following this, a description of the approach for determining the screening levels based on statistical analyses is presented. Finally, the steps of the flammability assessment methodology are given.

FLAMMABILITY TESTING PROGRAM

Considerable experimental data exist on the flammability of gas mixtures found in industrial and mining applications, such as mixtures comprised of hydrogen, methane, carbon monoxide, carbon dioxide, nitrogen, and oxygen. However, no experimental data are available for the types of gas mixtures observed in TRU waste containers. The objective of the flammability testing is to experimentally determine the lower explosive limit (LEL) for various TRU waste container gas mixtures. The Fire and Explosions Group of the U.S. Bureau of Mines Pittsburgh Research Center (Bureau) will conduct the flammability testing to determine the LEL of gas mixtures that are representative of those observed in TRU waste containers. The Bureau was chosen based on their expertise, decades of experience, and access to a wide range of combustion and explosion test facilities to conduct state-of-the-art flammability research.

The gas mixtures to be evaluated are composed of flammable and nonflammable VOCs listed in the *Transuranic Waste Characterization Quality Assurance Program Plan* (DOE 1995a) and hydrogen. To facilitate the experimental design, the flammable VOCs have been organized into functional and LEL groups. Functional groups for flammable VOCs are groups of VOCs with similar chemical structural characteristics. LEL groups for flammable VOCs are groups of VOCs with LELs that fall within a prescribed range of LEL values. The functional groups and associated functional group numbers (FGN) to be considered are aromatics (FGN = 1), ketones (FGN = 2), alcohols (FGN = 3), and alkanes/alkenes (FGN = 4). The LEL ranges and associated LEL group numbers (LGN) to be considered are 0.9%–1.3% (LGN = 1), 1.4%–2.6% (LGN = 2), and 5.6%–6.7% (LGN = 3). There is a general correlation between functional groups and groups based on LEL. That is, VOCs of a functional group tend to have LELs in a particular range. Table I summarizes flammable VOCs by functional and LEL groups.

The flammability testing will be done in two phases and will be based on a factorial experimental design that utilizes the LEL groupings. The factors are the presence or absence of each of three flammable VOC LEL groups in the mixture, the presence or absence of hydrogen in the mixture, and the presence or absence of nonflammable VOCs in the mixture.

The objective of the first phase is to provide the necessary data to develop an empirical equation that expresses the flammable gas MLEL as a function of the concentration of each of the factors (i.e., concentrations of each of the three flammable VOC LEL groups, the concentration of hydrogen, and the concentration of nonflammable VOCs). The first phase will involve the testing of approximately 40 mixtures at ambient room temperatures (i.e., approximately 70°F). These mixtures will be composed of varying ratios of 1,1-dichloroethane, methyl ethyl ketone, toluene, hydrogen, and carbon tetrachloride.

The objective of the second phase is to investigate the effects of VOC substitution within a group and to evaluate the effects of concentration on the predicted LEL. The second phase will involve the testing an additional 30 mixtures, half of which would be tested at an elevated temperature of 146°F. The second phase will also involve additional chemicals, possibly acetone, benzene, cyclohexane, 1,1-dichloroethene, cis-1,2-dichloroethene, methanol, or methane, depending on the results of the first phase.

The results of the flammability testing will provide the empirical data needed to develop an empirical model for predicting flammable limits for mixtures of flammable gases in TRU waste containers. The results will also be used to evaluate the performance and adequacy of other predictive models.

MODELS FOR ASSESSING MIXTURE FLAMMABILITY

Four models for assessing mixture flammability have been identified through literature searches and discussions with flammability experts. The literature search identified documents that pertain to flammability limits and predictive methods. The search identified three theoretical models that are applicable to the problem. An empirical approach to modeling MLELs that would directly utilize experimental results was also identified. The four models being considered are an empirical model, the Le Chatelier rule, the group contribution method, and the adiabatic flame temperature method.

Empirical Model

The data obtained from the flammability testing will be used to develop an empirical model for predicting lower flammable limits for mixtures of VOCs and flammable inorganic gases in TRU waste containers. The empirical model is an equation that expresses the flammable gas MLEL as a function of the concentrations of each compound tested. The coefficients in the equation are obtained through standard least-squares statistical techniques and can be tested for their significant contribution towards predicting the MLEL. Experimental errors can be used to determine confidence limits for the predictions.

Le Chatelier's Rule

The Le Chatelier rule is an empirical equation developed by Le Chatelier in the late 19th century that enables the flammability limits of a mixture to be calculated if the flammability limits of individual components of a mixture are known. The effects of a few inert or nonflammable compounds (i.e., carbon dioxide and nitrogen) on the MLEL can be evaluated using a graphical method. The Le Chatelier rule has been tested for many mixtures that are important in transportation, industrial applications, and mining.

Group Contribution Method

The group contribution method provides an estimate of the flammability limits of a mixture based on knowledge of the chemical structure of each flammable compound in the mixture. The method does not account for the presence of inert (i.e., nonflammable) compounds that may be present in the mixture. Several group contribution methods have been proposed by various researchers (Shebeko et al. 1983; Season 1991; ASTM 1994; AIChE 1994) for estimating the LEL of individual compounds. However, no group contribution method has been proposed for mixtures of flammable gases. Based on an extension of the method for estimating the LEL of pure compounds (Procedure B) of the American Institute of Chemical Engineers (AIChE) Data Prediction Manual (AIChE 1994), the LEL was estimated for each of the gas mixtures and compared with the corresponding LEL estimated using the Le Chatelier rule. The absolute average error between the two methods was approximately 2 percent, with the group contribution method predicting a higher LEL in almost all cases.

Adiabatic Flame Temperature Method

The adiabatic flame temperature method is based on calculating and comparing the adiabatic flame temperature of a potentially flammable gas mixture with the critical or limiting adiabatic flame temperature. In the event of an explosion, energy is released by the combustion of the flammable compounds. Initially, the energy is absorbed by (1) unreacted reactants, (2) the combustion products, and (3) inert or nonflammable gases. Eventually, however, the energy will be dissipated from the system by various heat transfer processes. If a flammable gas mixture explodes in an adiabatic system (one in which there is no transfer of heat to or from the system), then it is possible to calculate an adiabatic flame temperature that corresponds to the temperature of the system after the explosion. The minimum temperature at which a flame can be sustained is referred to as the critical or limiting adiabatic flame temperature.

A number of computer codes are available to perform the complex thermodynamic chemical equilibrium calculations, including the American Society of Testing and Materials (ASTM) CHEETAH code (ASTM 1994), the National Aeronautic and Space Administration (NASA) Lewis Research Center CET93/CETPC code (McBride et al. 1994), the Lawrence Livermore National Laboratory (LLNL) CHEETAH code (Fried 1995), the University of Arizona CHEMEQ code (Wendt 1993), and the NASA CET93/CETPC code (NFPA 1988). If the adiabatic flame temperature of a potentially flammable gas mixture calculated by the code is above the critical or limiting flame temperature, then the mixture is flammable.

DETERMINING SCREENING LIMITS FOR FLAMMABLE GASES

A predictive model that performs well relative to experimental data, adequately accounts for gas mixture compositions in drums, and demonstrates an acceptable level of conservatism will be selected for use in determining drum-specific MLELs. The model will be selected from the models previously discussed. The MLELs predicted using the model will account for the presence of flammable VOCs, hydrogen, and methane in the drums. Because all flammable gases are included in the MLELs, the maximum concentration of hydrogen and methane that can be tolerated without the gas phase mixture becoming potentially flammable is the difference between the MLEL and the total concentration of flammable VOCs. This difference is the MPHMC.

To date, over 500 drums stored at the INEL and the RFETS have been sampled and analyzed for a specific suite of VOCs, hydrogen, and methane under the existing Transuranic Waste Characterization Program (TWCP). The samples were obtained from headspace gases under the drum lid with the rigid drum liner punctured. Additional drum sample analyses that are currently being gathered under the TWCP will be used in finalizing the flammability assessment methodology. The analyses will be used in determining screening limits for flammable gases.

The process for determining the screening limits for flammable gases is summarized in Figure 1. First, the experimental and modeling work must be completed. The results will be used to choose a method for predicting MLELs. The chosen method will be used to obtain drum-specific MLELs using predicted innermost confinement layer headspace concentrations for existing drum data. The MLELs and the sums of flammable VOC innermost confinement layer concentrations will be used to compute drum-specific MPHMCs for existing drum data. Finally, screening values will be statistically determined for the sum of flammable VOCs and for MPHMCs.

METHODOLOGY FOR ASSESSING FLAMMABILITY OF GAS MIXTURES IN TRU WASTE

Flammability assessments for individual drums are comprised of sequential evaluations, as necessary. The methodology consists of the following steps in evaluating individual waste drums for flammability (see Figure 2):

1. Analyze drum headspace gas.

2. Predict innermost-layer headspace concentrations of flammable VOCs, hydrogen, and methane.

3. Sum innermost-layer concentrations of flammable VOCs and sum innermost-layer concentrations of hydrogen and methane.

4. Compare the flammable VOC sum with the flammable VOC screening limit and the hydrogen and methane sum to the MPHMC screening limit. If the both sums are below their associated limits, the drum may be shipped; if not, then go to step 5.

5. Compute the drum-specific MLEL, drum-specific MPHMC, and the sum of innermost concentrations of flammable VOCs, hydrogen, and methane.

6. Compare the flammable VOC, hydrogen, and methane sum with the drum-specific MLEL and compare the hydrogen and methane sum with the drum-specific MPHMC. If both sums are below the drum-specific limits, the drum may be shipped.

7. If at least one of the sums exceeds the respective limit, perform a flame test that simulates the gas mixture. If the flame test indicates that the mixture is not flammable, the drum may be shipped; otherwise, the waste must be either repackaged and reevaluated or another option must be taken, such as waste treatment.

SUMMARY

The methodology will substantially increase permissible concentrations of flammable VOCs and consequently, the number of drums that can be shipped to the WIPP facility without treatment or repackaging. This increase will alleviate schedule impacts associated with near-term shipment of drums in accessible storage. The increase will also reduce schedule and cost impacts associated with waste repackaging or treatment. Furthermore, because the methodology incorporates experimental data, validated predictive modeling of actual drum lower explosive limits, and conservative screening of flammable gas concentrations, it is technically defensible and appropriate.

This work will be integrated with several other ongoing programs. Specifically, the results of the drum headspace gas sampling analysis being performed by the INEL and the RFETS under the TWCP will be used to develop the flammability screening limits. The results of the TRUPACT-II Gas Generation Testing Program and the TRUPACT-II Matrix Depletion Program will be used to establish new wattage limits by waste type. The TRUPACT-II compliance documentation will have to be revised to reflect the revised container wattage limits. Based on the revised wattage limits and the new methodology for determining flammability, an application for an amendment to the TRUPACT-II Certificate of Compliance will be submitted to the NRC for approval.

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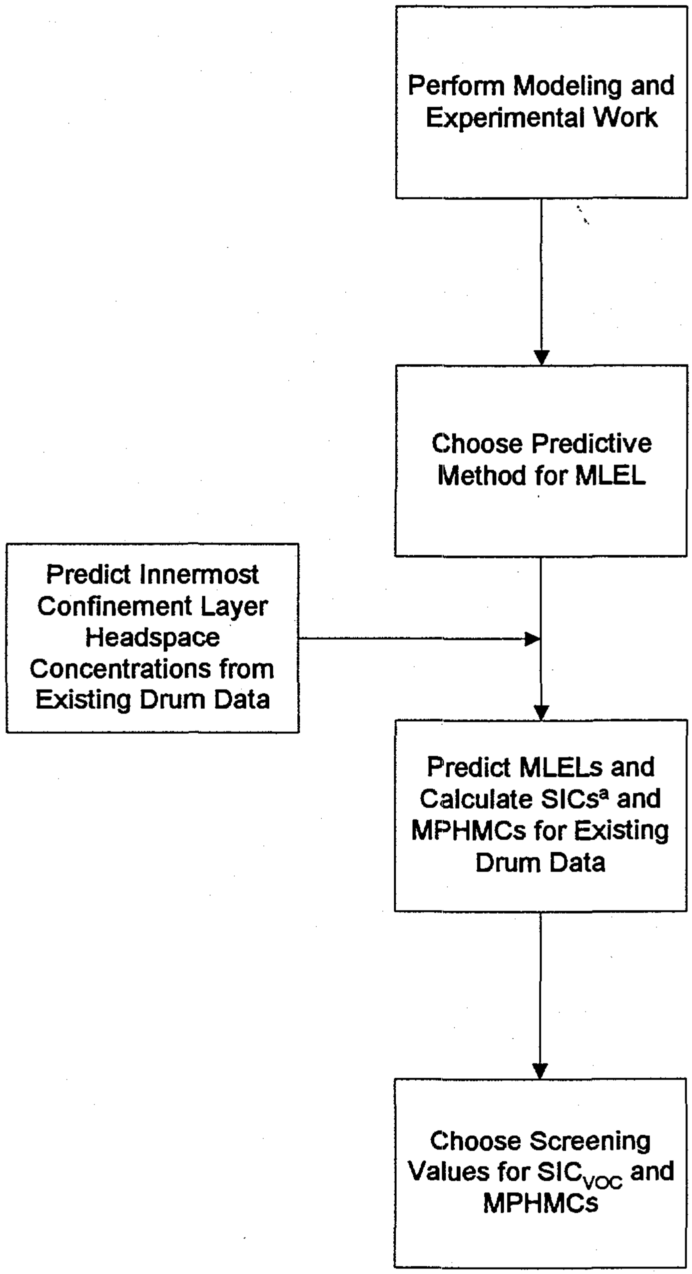
Table I. Classifications of Flammable VOCs

Flammable VOC	Structural Type	Functional Group No.[a]	LEL (%)	LEL Group No.[b]
Acetone	ketone	2	2.6	2
Benzene	aromatic	1	1.3	1
Butanol	alcohol	3	1.7	2
Chlorobenzene	aromatic	1	1.3	1
Cyclohexane	cycloalkane	-	1.3	1
1,1-Dichloroethane	alkane	4	5.6	3
1,2-Dichloroethane	alkane	4	6.2	3
1,1-Dichloroethylene	alkene	4	6.5	3
cis-1,2-Dichloroethylene	alkene	4	5.6	3
Ethyl benzene	aromatic	1	1.0	1
Ethyl ether	ether	-	1.9	2
Methanol	alcohol	3	6.7	3
Methyl ethyl ketone	ketone	2	1.9	2
Methyl isobutyl ketone	ketone	2	1.4	2
Toluene	aromatic	1	1.2	1
1,2,4-Trimethylbenzene	aromatic	1	0.9	1
1,3,5-Trimethylbenzene	aromatic	1	1.0	1
o-Xylene	aromatic	1	1.1	1
p/m-Xylene	aromatic	1	1.1	1

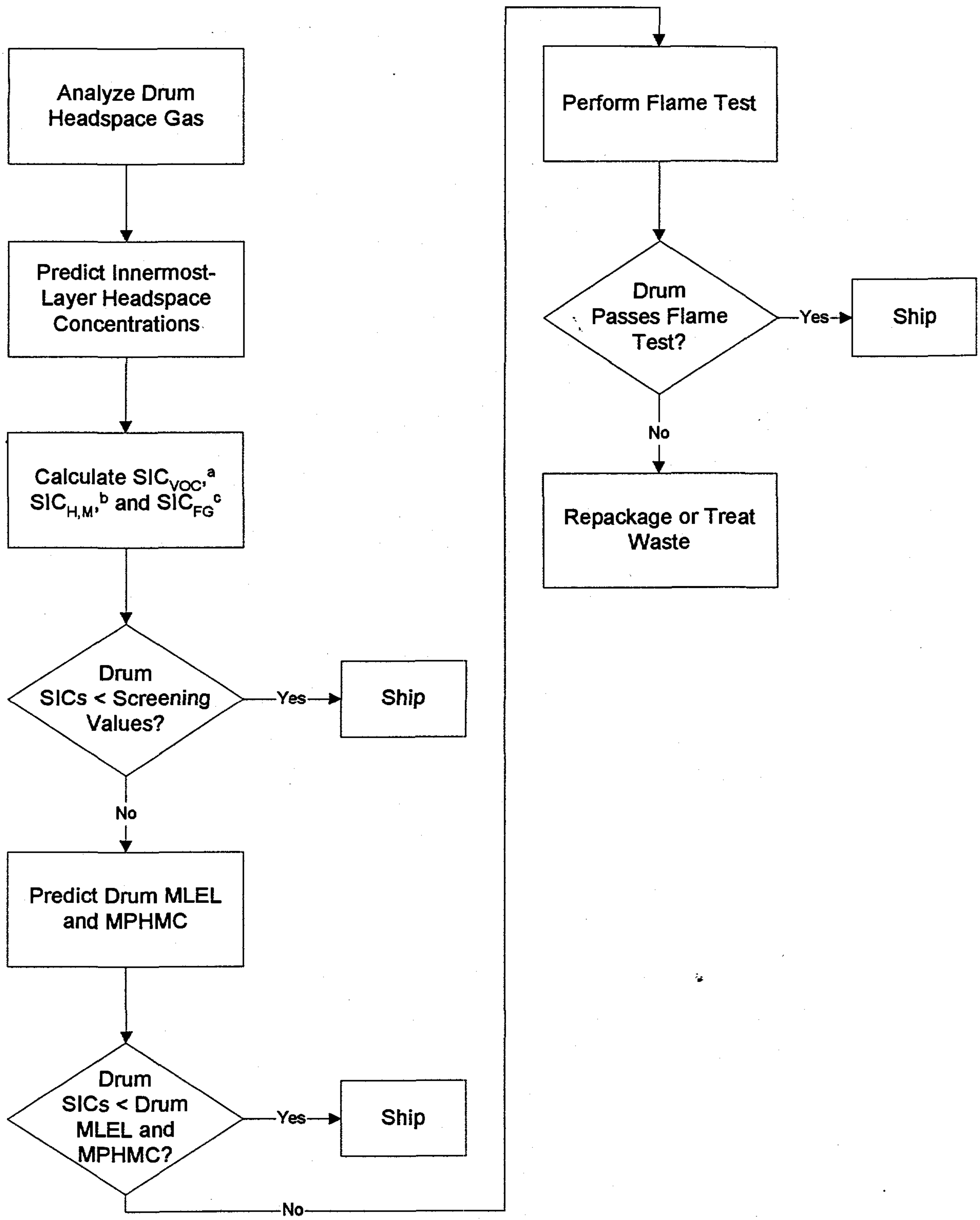
[a]Functional group numbers are assigned as follows: (1) aromatics, (2) ketones, (3) alcohols, and (4) alkanes/alkenes.

[b]LEL group numbers are assigned as follows: (1) 0.9%-1.3%, (2) 1.4%-2.6%, and (3) 5.6%-6.7%.



[a]Sum of innermost confinement layer concentrations

Figure 1. Steps in Evaluating Individual Waste Drums for Flammability



[a]Sum of innermost confinement layer flammable VOC concentrations
[b]Sum of innermost confinement layer hydrogen and methane concentrations
[c]Sum of innermost confinement layer flammable gas concentrations

Figure 2. Process for Determining the Screening Limits for Flammable Gases