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Project Summary

Evaluation of Ignitability Methods (Liquids)

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The purpose of this research was to evaluate the ignitability Methods 1010 (Pensky-Martens) and 1020 (Setaflash) as described by Office of Solid Waste (OSW) Manual SW846. This effort was designed to provide information on accuracy and precision of the two methods. During Phase I of this task, six standards and simple mixtures were tested. In addition during Phase II, twelve actual wastes were tested.

The results of Phase I determined that both methods are applicable to characterize the ignitability of liquid wastes. During Phase I, no significant interferences were identified. During Phase II experiments, however, water-containing wastes could not be tested using Method 1020. No direct comparison of Phase I results and data published in literature reports was made due to the uncertainty associated with the previously published data. A search of the Chemical Abstract Data Base provided more reliable information than previously published data for *p*-xylene flash point.

Based on standards and simple mixtures results, no significant difference existed between the accuracy and precision of the two methods. The results of actual waste experiments, however, showed significant differences between the methods. The Setaflash method, when applicable, was determined to be more accurate and more precise than the Pensky-Martens. The Pensky-Martens method is not applicable for wastes which have flash points below 13°C (55°F). The Setaflash method is not applicable to complex mixtures with substantial amounts of water and high surface tension.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, 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

Disposal of solid wastes at landfill sites presents several potential hazards apart from intrinsic toxicity of the disposed materials. The ignitability of waste substances is of concern because of the imminent danger of uncontrolled burning, and the probable toxicity of the combustion products.

A waste has been defined in the Resource Conservation and Recovery Act (RCRA) (40 CFR 261.21) as hazardous if it exhibits any of the following ignitability characteristics:

1. "It is a liquid, other than an aqueous solution containing less than 24% alcohol by volume, and has a flash point less than 60°C (140°F), as determined by a Pensky-Martens Closed-Cup Tester, using the test method specified in American Society of Testing Materials (ASTM) Standard D-93-79 or D-93-80, or a Setaflash Closed-Cup Tester, using the test method specified in ASTM Standard D-3278-78, or as determined by an equivalent test method approved by the Administrator under the procedures set forth in RCRA section 260.20 and 260.21.
2. It is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture, or sponta-

neous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard.

3. It is an ignitable compressed gas as defined in 49 CFR 173.300 and as determined by the test methods described in that regulation or equivalent test methods approved by the Administrator under RCRA section 260.20 and 260.21.
4. It is an oxidizer as defined in 49 CFR 173.151."

Specific ignitability tests have been developed and refined under several previous work assignments to this contract, "Development and Evaluation of Test Procedures for Ignitability Criteria for Hazardous Waste."

The directions for using the Pensky-Martens Closed-Cup tester and the Setaflash Closed-Cup tester to determine ignitability are set down in Method 1010 and Method 1020 respectively in the OSW publication SW846.

In order to identify wastes which are subject to this hazard, this work assignment, "Evaluation of Ignitability Methods (Liquids)," was undertaken. The purpose of this task was to evaluate Ignitability Methods 1010 and 1020 as described in OSW Manual SW846 using standards during Phase I and waste samples during Phase II and to provide precision and accuracy data for these methods.

Some refinements of the procedures were necessary to perform the evaluation. However, since the goal of this project was to evaluate existing methods rather than improve them, only small modifications, if any, were made.

Since the equipment is designed for such measurements, all of the experiments measured temperatures in degrees Fahrenheit (°F). When data were reported in degrees Centigrade (°C), the data were calculated and approximated to the nearest decimal unit.

Experimental Procedures

Setaflash Experiments

The standards and simple mixtures were tested in triplicate using the Setaflash equipment, following the procedure specified by Method 1020. Using a 2 mL syringe, the sample (2 mL) was introduced through a tight port into the closed test chamber, which had been previously heated to within 3°C below the expected flash point. No stirring is provided. After allowing approximately one minute for temperature equilibration, a small flame (4 mm in diameter) was directed into the cup through a small window. Careful observation was made as to whether the sample flashed or not. If there was no flash, the temperature was sequentially increased by 0.5°C until a flash was observed. A repeat determination was then performed using a fresh sample.

Pensky-Martens Experiments

Standard samples were analyzed in triplicate for flash point by the Pensky-Martens closed-cup tester in accordance with the procedure given in ASTM D-93. In this procedure, the sample cup was cleaned, dried, and filled to the mark with sample. Approximately 50 mL of sample are required. The cup was then placed in the heater, and the cup lid was lowered and locked into place. The thermometer was inserted. The test flame was lit and adjusted to 4 mm in diameter. The heater was turned on and set so that the temperature of the solution rose 5-6°C (9 to 11°F) per minute. The stirrer was turned on. Every 1°C (~2°F), the shutter was opened, and the test flame was lowered into the vapor space of the cup. The sample was not stirred while the flame was lowered into the cup. The flash point was the temperature at which the test flame application caused a distinct flash in the interior of the cup.

Results and Discussion

The six standards and simple samples selected for use during Phase I of this task were analyzed in triplicate and the results were corrected for barometric pressure.

Preliminary Experiments

Preliminary experiments with waste samples acquired during Phase I were performed. During these tests, it was determined that all of the wastes had a flash point below room temperature as measured with the Setaflash method. A modification of Methods 1010 (Pensky-Martens) and 1020 (Setaflash) was implemented to allow for flash point measurements below 21°C (70°F). The modification consists of cooling the testing cup with dry ice, introducing the sample once the testing cup is cold, then allowing the temperature of the testing cup to raise slowly as the experiment begins. This modification has proven successful for a very wide range of temperatures using the Setaflash method. For the Pensky-Martens method, however, it was determined that this procedure is practical only down to about 10 to 13°C (50° to 55°F due to the fact that Pensky-Marten equipment has a very massive cu which cools and reheats very slowl making the operation impractical.

The decision was made that wast samples with measured flash points be low 55°F would be spiked with a wast oil and/or carbon tetrachloride (CCl_4) i order to raise the temperature of mea surement above the minimum permit ted by the Pensky-Martens method This decision was based upon the fac that the purpose of this task was to de termine accuracy (measured for stand ard samples) and precision of the meth ods under consideration and not to tes the wastes. The fact that some of the collected wastes had low flash point was purely circumstantial and spikin them with a waste oil would not alte the goal of this task.

Waste Mixtures

A 5-gallon waste motor oil sample was collected from a local service station. Varying amounts of this waste oi were added to those waste samples which had low flash points. Mixtures o the wastes and carbon tetrachloride were also prepared.

The mixtures were than tested using the Setaflash method which required only a 2 mL sample per determination. In order to raise the flash point above room temperature, a considerable amount of spiking material was required, in most cases more than 70% o either used motor oil or CCl_4. These results demonstrated that the spiking o the waste samples was impractical and this strategy was abandoned.

All the data have been corrected for atmospheric variations. The data obtained by the Setaflash method for waste 2258-14-08-3 were corrected by adding 1°F in order to compensate for the difference obtained for the *p*-xylene control which was 1°F below that value allowed by the Method 1020 (Setaflash) description.

Several wastes tested by the Setaflash method showed no measurable flash point below 110°C (230°F). This phenomenon was observed primarily on those wastes that contained substantial amounts of an aqueous phase and had a large surface tension as determined by empirical observation; the high surface tension prevented the waste from dispersing evenly throughout the cup and since only 2 mL of sample was required, part of the cup remained empty. If agitation was

provided, then a flash occurred (note that the Pensky-Martens method includes stirring). If a larger flame than the one specified by the method was applied, a flash was observed, however, this flash was usually at a higher temperature than expected. This observation may constitute a severe interference to the Setaflash method because it may determine that some ignitable wastes do not flash.

The Setaflash method did not determine a flash point for two of the three replicates performed on waste 2258-14-08-1. This was attributed to the evaporation of some volatile component before the measurement was performed and the residue did not flash. This phenomenon may be enhanced by the small amount of sample required (2 mL).

Conclusions

Comparison and evaluation of Methods 1010 and 1020 during Phase I and Phase II gave the following conclusions:

a. Based on the testing of standards and simple mixtures, both Methods 1010 and 1020 were found to be applicable to characterize the ignitability of liquids.
b. No significant interferences were found in the measurement of ignitability of standards and simple liquid mixtures.
c. A comparison of open-cup and closed-cup experiments shows that open-cup values are approximately 7°C (20°F) higher than those obtained in closed-cup experiments.
d. No statistically significant difference was found between the results obtained during Phase I using standards and simple mixtures for the two methods under consideration.
e. From the results of experiments with actual waste samples, it was also determined that the Pensky-Martens method is not practical to use with wastes of low flash points (13°C or 55°F) and the Setaflash method is not applicable to complex aqueous mixtures which have high surface tension.
f. Experiments with actual waste samples also established that flash point measurements made with the Setaflash method were more precise than the Pensky-Martens method. Also, the Setaflash was found to be more accurate based on tests with *p*-xylene. Finally, it was concluded that the Setaflash system is easier to use and requires much less sample than the Pensky-Martens system.

Recommendations

From the results presented in this report, the authors recommend:

a. The use of Method 1010 (Pensky-Martens) to test the flash point of ignitable wastes, despite the fact that the method does not easily allow measurement of flash points below room temperature. The Pensky-Martens system can identify those samples that flash at or below room temperature and this is enough to label them hazardous. Although the Setaflash method is more accurate and more precise, the Pensky-Martens method has a wider range of applicability to the needs of EPA.
b. The use of Method 1020 (Setaflash) when a determination of low temperature flash points is required.
c. Further research, using synthetic, well characterized, complex mixtures to confirm the conclusions obtained during this study.

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***John D. Pfaff** is the EPA Project Officer (see below).*
The complete report, entitled "Evaluation of Ignitability Methods (Liquids)," (Order No. PB 85-241 255/AS; Cost: $11.50, subject to change) will be available only from:
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