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Project Summary

Development of VOST Sample Analysis Protocol for Water-Soluble Volatile POHCs and PICs

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This report gives results of a literature review and laboratory research associated with applying the volatile organic sampling train (VOST) to the sampling and analysis of water-soluble, volatile, Principal Organic Hazardous Constituents (POHCs) and Products of Incomplete Combustion (PICs). Previous studies resulted in methods development for analysis of volatile POHCs and PICs, but did not address compounds soluble in water.

The POHCs and PICs studied were acetaldehyde, acetone, acetonitrile, acrolein, acrylonitrile, 1,4-dioxane, ethyl acetate, methyl ethyl ketone, methyl formate, propionitrile, propylamine, and pyridine. The collection efficiency of each component of the VOST was established for each compound. The accuracy of current analytical methods for analysis of volatile POHCs and PICs when applied to volatile, water-soluble POHCs and PICs was determined. New analytical techniques were developed through literature search and experimentation, and were evaluated against existing methods. An accuracy goal of 60-150% pollutant recovery was set, along with an analytical goal of 25% or less relative difference.

Modifications to the existing method of analysis (purge and trap) include elevating the purge temperature from the standard (20°C) to 60°C, adding 1 g of either sodium chloride or sodium sulfate salt to the sample before purging, and a combination of both modifications. The modifications improved purge efficiency by about 100% or more for the compounds analyzed. Even with the modifications, the highest purge efficiency for 1,4-dioxane was no greater than 21%. The resulting purge efficiencies for these compounds ranged from 19.1% for 1,4-dioxane to 127% for acetaldehyde.

The alternate analytical method of direct aqueous injection into a liquid chromatograph was performed with condensate from the pyridine VOST analysis. VOST recovery of pyridine with this analytical method was at best 23%. Other compounds (acrolein, acrylonitrile, 1,4-dioxane, and methyl formate) did not meet the VOST recovery objective of 60-150% recovery. Pyridine was analyzed by direct aqueous injection on the liquid chromatograph because the purge efficiency was poor and the liquid chromatograph offered a viable alternative.

This Project Summary was developed by EPA's Air and Energy Engineering Research 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).

Background

Sampling and analysis for determination of the concentration of organic pollutants in stack gas effluents present unique problems due to the minute concentrations involved and the variety of

compounds present. Exacting analytical procedures using advanced equipment are required. One of these methods, developed after years of research, is the Volatile Organic Sampling Train (VOST).

The VOST was developed by the U.S. EPA to sample volatile organic chemical constituents in smoke stacks. One application of VOST is the sampling of gaseous effluent from hazardous waste incinerators. The primary goal of this sampling is to determine the destruction and removal efficiency (DRE) of volatile Principal Organic Hazardous Constituents (POHCs) and Products of Incomplete Combustion (PICs). DRE calculations are used to demonstrate compliance with federal regulations.

A protocol for sampling and analysis of volatile POHCs and PICs with VOST has been developed. However, it did not provide guidance for analysis of volatile POHCs and PICs that are water-soluble.

Under an EPA contract, the VOST procedures were evaluated with regard to water-soluble, volatile POHCs and PICs in order to develop an addendum to the existing VOST sampling and analysis protocol. A literature search and laboratory research were conducted into the analytical methods associated with the application of the VOST method to water-soluble, volatile POHCs and PICs. The results of that research are summarized in this document.

The sample collection media in the VOST include a Tenax trap, a condensate collector, and a Tenax/charcoal trap. The standard method of analysis for a volatile POHC or PIC involves a thermal desorption unit, purge and trap apparatus, and a GC/MS. The purge and trap procedure specified in the existing protocol may not be suitable for analysis of some water-soluble, volatile POHCs and PICs. This document summarizes results of experiments to develop modified methods of analysis for those situations in which the VOST may be used to sample water-soluble volatile POHCs and PICs.

Objectives

The primary objective of this project was to provide technical information for the development of a protocol for VOST sampling of volatile, water-soluble POHCs and PICs. In order to accomplish the primary objective, four secondary objectives were identified:

1) Identification of suitable representative water-soluble compounds for use in methods analysis and development.
2) Determination of the accuracy of current analytical methods for analysis of water-soluble, volatile POHCs and PICs.
3) Development of new analytical techniques through literature search and experimentation, and evaluation of these techniques by comparison to existing methods.
4) Determination of the collection efficiency of each component of the VOST for each compound.

Scope of Work

Compounds were identified for study based on criteria developed in the planning phase. Ten compounds were then evaluated with regard to purge efficiency. Then, modifications and alternatives to the purge and trap method were developed, evaluated, and compared to establish a preferred analytical technique. Finally, VOST experiments were run for selected compounds, and recovery efficiencies for each component of the VOST (i.e., Tenax trap 1, condensate, Tenax trap 2, and charcoal trap) were determined using the preferred analytical technique. Although the overall objective of the project included development of modifications to the analytical protocol, it was beyond the scope of the project to develop modifications to the sampling protocol (e.g., substitution for Tenax).

Summary and Conclusions

Analytical Method Modification Summary

The standard purge and trap procedure for analyzing volatile POHCs and PICs in VOST impinger condensate was considered potentially inadequate when used to analyze water-soluble volatile POHCs and PICs. Improved analytical techniques were developed and evaluated. Modifications to the standard purge and trap method included elevating the purge temperature to 60°C and adding 1 g of sodium chloride or sodium sulfate salt to the condensate before purging. An alternative analytical method using direct aqueous injection in a high pressure liquid chromatograph (HPLC) was also investigated.

The basis of comparison between alternate methods was purge efficiency, defined as the ratio of the GC/FID curve area response generated by a given quantity of pollutant after purge and trap of the pollutant, to the direct aqueous injection into the GC/FID.

The mean purge efficiency for the 12 compounds studied, at room temperature purge without salt addition, was 20.7%, and ranged from 0.0% for pyridine to 44.6% for acrolein. The mean purge efficiency using alternate optimal methods was more than 3.7 times greater.

Analytical Results Summary

The highest recovery efficiencies achieved for each POHC or PIC evaluated using the VOST are given in Table 2-1 of the full report. These recovery efficiencies are the cumulative pollutant recoveries achieved through the combined collection in all components of the VOST system (Tenax trap 1, condensate impinger, Tenax trap 2, and charcoal trap), divided by the standard weight used in the VOST run. The recovery values reported were the highest cumulative recoveries demonstrated through a series of three runs for each compound, using standard (unmodified) VOST analytical protocol.

Conclusions

1) The VOST protocol for sampling and analysis of volatile POHCs and PICs can be adapted to include the analytical protocol for some volatile, water-soluble POHCs and PICs.
2) The distribution of the trapped compounds in the various components of the VOST train (Tenax trap 1, condensate trap, Tenax trap 2, and charcoal trap) is highly variable and appears to be compound-specific.
3) Purge efficiency of VOST condensate can be greatly enhanced by elevating the purge temperature and by salting the sample with 1 g of NaCl or Na_2SO_4 before purging. However, even with these modifications, purge efficiency for some compounds, though improved, will still be low.
4) Na_2SO_4 appears to improve purge efficiency to a greater extent than NaCl when used in similar circumstances (i.e., in conjunction with a 60°C purge temperature).
5) VOST recoveries of 60-150% were demonstrated using the methods mentioned above for five water-soluble, volatile POHCs and PICs: acetaldehyde, acrylonitrile, ethyl acetate, methyl ethyl ketone, and propionitrile.
6) VOST recoveries of 60-150% were not demonstrated, even with the methods mentioned above, for five water-soluble, volatile POHCs and PICs: acetonitrile, acrolein, 1,4-dioxane, methyl formate, and pyridine.

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The complete report, entitled "Development of VOST Sample Analysis Protocol for Water-Soluble Volatile POHCs and PICs," (Order No. PB 87-165 239/AS; Cost: $18.95, subject to change) will be available only from:
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