United States Environmental Protection Agency
Research and Development

Atmospheric Sciences Research Laboratory
Research Triangle Park NC 27711

EPA/600/S3-87/035 Feb. 1988

EPA

Project Summary

Evaluation of a Method Using an FID for Methanol Measurement in Auto Exhaust

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This report evaluates a simplified technique for estimating methanol emission rates in auto exhaust. The technique, referred to as the FID Bubbled Method or FBM, is based in principle on the notion that while hydrocarbons are not readily absorbed in water, methanol is. Hence, by using a Flame Ionization Detector to measure the organic mass in samples before and after bubbling them in water, the quantity of methanol originally present can be estimated by taking the difference between the measurements. Evaluation of the method was done by comparing methanol measurements using the FBM with measurements made using an established reference method. Results showed poor to fair agreement between the two methods. The FID Bubbled Method appeared better at estimating methanol emission rates from evaporative tests than exhaust tests and also exhibited better accuracy for sample containing higher levels of methanol. When test data obtained with the FBM are used to calculate total organic mass emission rates, the results are within 3 percent of results obtained using the relatively complex method in the proposed standard for methanol cars.

This Project Summary was developed by EPA's Atmospheric Sciences 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).

Introduction

In August 1986, the EPA published a notice of proposed rulemaking for standards for emissions from methanol-fueled motor vehicle engines. Since that time, comments regarding the proposed standard have been solicitated from a number of automobile manufacturers. Of the comments received, many have addressed the "overly complex" instrumentation requirement set forth in the standard for measurement of organic compounds. In accordance with the proposed standard, gas and liquid chromatographs (GCs and LCs) would be required for methanol and formaldehyde analyses in addition to the flame ionization detectors (FIDs) required for regulated hydrocarbon analyses.

The consensus of recommendations received from commentators proposes that the separate measurements of methanol and formaldehyde not be required, thus eliminating the need for GC and LC analyses. Manufacturers contend that reasonably accurate measurement of total organics can be had through the sole application of an FID, in one form or another. Some further suggest or recommend the use of correction factors to account for differences in FID response and photochemical reactivity between the organic components.

With regard to these comments, the concerns of instrument complexity are valid and sole use of the FID to measure total organics would greatly simplify the procedure. The use of a correction factor to compensate for the FIDs low response to methanol would be appropriate if the fraction of methanol to total organic emissions remained constant, however, the fraction varies significantly with fuel and vehicle. Correction factors appropriate to a given situation might be estimated based on experience or perhaps through use of simplified approximation methods.

One simplified method, referred to here as the FID Bubbled Method (FBM), measures total organics with an FID, bubbles the sample through water to remove the methanol fraction, then remeasures the remaining hydrocarbon (HC) fraction. The difference between the total organics and the remaining HC fraction represents an estimate of the methanol fraction.

The principal objective of this study was to evaluate methanol measurements made using the FBM on emissions for a methanol-fueled automobile. Basically it consisted of comparing methanol measurement made using a technique known as the FID Bubbled Method or FBM with measurements made using an established reference method. The reference method utilized a gas chromatograph to analyze methanol which had been trapped in a water solution.

The test vehicle, a 1983 Methanol Escort, was driven through a series of FTP driving cycles on a chassis dynamometer. For each test run, three sets of data were obtained corresponding to the cold transient (CT), hot stabilized (HS), and warm transient (WT) test phases of the FTP. Two fuels were used during the study: M-85 fuel (a blend containing 85 percent methanol/15 percent unleaded wintergrade gasoline) and M-100 fuel (pure methanol). Use of both fuels enabled evaluation of the FBM over a wider range of possible methanol emission rates.

Conclusions and Recommendations

The following conclusions have been made based on the experimental study carried out using both the FBM and GC method (reference method) for measuring methanol levels in auto exhaust:

1. Comparison between the FBM and GC method for methanol measurement are fair to poor with differences between methods ranging from 11 to 112 percent.
2. Comparison between the methods is better with methanol evaporative emissions than with methanol exhaust emissions. Comparison is worst for emissions from the Hot Stabilized Test Phases where methanol concentrations are the lowest (<4ppm).
3. Absorbtion of some non-methanol organics (<10 percent) in the bubbled water solution contributes to method error. However, the main source of method error is probably associated with the hot FID's response sensitivity to water vapor in the bubbled sample.

When data obtained from the FBM are used to calculate the total organic exhaust emissions (OMHCE) from the Escort, the results are close to those calculated using data obtained from separate FID, GC (methanol), and LC (formaldehyde) analyses. With the Methanol Escort operating on M-85 fuel, the FBM produces a result for total organic matter emissions about 2.6 percent lower than the reference method. With the M-100 fuel, the difference between methods is less than 1 percent.

Based on the results obtained in this study, the main source of error with the FBM is likely associated with the response sensitivity of the detector to high water vapor concentrations in the bubbled sample. Further studies should be undertaken to better understand this phenomena and its effect on analyzer accuracy. Use of sample dryers before analysis should also be investigated as a means of removing water vapor from samples which have been bubbled in water.

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The complete report, entitled "Preliminary Evaluation of a Method Using an FID for Measurement of Methanol in Auto Emissions," (Order No. PB 88-104 344/AS; Cost: $9.95, subject to change) will be available only from:
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