❖EPA

Project Summary

Benzene Continuous Emission Monitoring Systems for Gasoline Bulk Storage

Jon N. Bolstad

The full report summarizes a study of continuous emission monitors for measuring benzene emissions from gasoline bulk storage terminals. The work was performed for the Quality Assurance Division, Source Branch, of the U.S. Environmental Protection Agency (EPA) by Pacific Environmental Services under Contract No. 68-02-3997, Task 33. The EPA is considering regulating the emissions of benzene from bulk storage of gasoline products and is likely to require data regarding benzene emissions. The evaluation of continuous emission monitors for benzene is a necessary part of the overall effort.

This study was performed in three phases: a literature review, a laboratory evaluation, and a field evaluation. The study objectives were to determine the commercial availability of continuous monitors for benzene and the reported performance of these units, evaluate their suitability for measuring benzene in gasoline vapors, and determine their applicability to the source category.

There are no benzene-specific continuous emission analyzers commercially available. If a benzene-specific system is required, and semicontinuous (i.e., gas chromatographic analysis) is not acceptable for regulatory purposes, nondispersive ultraviolet analysis holds promise for accomplishing this task. The nondispersive ultraviolet technique can be used to measure benzene in a matrix of other hydrocarbons, and nondispersive ultraviolet continuous systems do exist, so combining the laboratory experience with the continuous monitor experience into a proto-type benzene continuous monitor appears to be a promising (and cost-effective) means to obtain such an instrument.

This Project Summary was developed by EPA's Environmental Monitoring Systems 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

The U.S. Environmental Protection Agency (EPA) is considering regulating benzene emissions from the gasoline bulk storage industry. A means of measuring benzene emissions may be required if the regulation contains specific emission limits rather than specific equipment or operating practices. This study was undertaken to evaluate the current availability and performance of continuous emission monitors (CEMs) for benzene in the event that continuous benzene monitoring was deemed necessary in the regulation. This investigation focused on the availability and performance of existing commercial instruments, but the findings are intended to serve as the basis for developing a test method suitable for *Federal Register* promulgation.

The study was performed in three phases: a literature review, a laboratory evaluation, and a field evaluation. The objectives were to determine the commercial availability of continuous monitors for benzene and the reported performance of these units, evaluate their suitability for measuring benzene

in gasoline vapors, and determine their applicability to the source catgeory.

Experimental Procedure

Literature Review

The technical literature was reviewed to determine potential analytical procedures for measuring benzene and to establish the expected range of total hydrocarbon emissions and the benzene fraction of the total emissions from the gasoline bulk storage industry. Manufacturers of chemical analysis instrumentation were surveyed both by direct contact and through the literature to ascertain the types of analyzers being produced; their suitability for use in an explosion-prone environment; their range and sensitivity; their utility requirements; and other considerations germane to the use of each instrument as a bulk storage terminal continuous emission monitor. Other instruments were also tested as potential process monitoring devices or to measure a benzene surrogate.

Laboratory Testing

A test plan was designed, and selected instruments were subjected to quality assurance (QA) testing in the controlled environment of the laboratory. Certified calibration gases of benzene/air mixtures were used to define the repeatability of the test instruments, as well as detection limits, response times, and drift characteristics. In addition to benzene/air mixtures, a cylinder gas mixture simulating gasoline vapor was used to test the ability of these instruments to detect benzene without interference from the other compounds expected in the terminal samples. The measurement techniques considered during this study included: gas chromatograph (GC) with flame ionization detector (FID), GC with photoionization detector (PID), GC with argon ionization detector (AID), and a nondispersive infrared (NDIR) analyzer. A nondispersive ultraviolet (NDUV) analyzer was also desired, but no commercial unit was found.

Field Tests

Five lower explosive limit (LEL) analyzers were field tested, by using a heated-oven GC with a PID as the reference analyzer. Two instruments employed NDIR detectors, and the other three used catalytic oxidation to generate a measurement signal. The field tests were conducted at a terminal in Baltimore. This terminal uses a refrig-

ertion condenser to recover vapors from a five-bay loading rack. Samples were extracted from the exhaust stack through a stainless steel sampling line to a manifold in a remote sampling trailer. The GC was equipped with a gas sampling loop, whereas the LEL analyzers were used in a flow-through or flow-over configuration.

Results and Discussion

Laboratory Testing

Five separate instrument configurations were evaluated during the laboratory testing phase of this project. The NDIR analyzer was the only unit with the capability to operate in a continuous analysis mode. The other instruments were a mid-sized laboratory-type GC equipped with a temperature-programmable oven and FID and PID detectors, a portable heated-oven GC with an AID, and a portable ambient-temperature GC with a PID.

GC/FID/Heated Oven—The response was linear over the entire range of sample concentrations of interest (1 to 100 ppm), though the calibration curves show some day-to-day variation and some deviation from linearity. Least-squares linear regressions calculated for the daily analytical results yielded correlation coefficients ranging from 0.9441 to 0.998, averaging 0.98. With a 100-μL sample size, the intercept of the linear calibration lines averaged –0.53 ppm, ranging from –0.33 to +1.04 ppm. The standard error of estimate (predicted value) from the linear regression calculations ranged from 0.24 ppm to 6.00 ppm, averaging 2.29 ppm. The relative standard deviation (RSD) and the absolute standard deviation of replicate analyses were used as measures of precision (repeatability). Ninety-five percent of the values were less than 50 percent of the RSD and the arithmetic average RSD was 13.77 percent. FID analysis of a paraffinic-aromatic-naphthenic hydrocarbon mixture normally yields individual component results very nearly proportional to the weight fraction of the components in the mixture, as the FID acts as a "carbon counter" for compounds consisting only of carbon and hydrogen. The benzene concentration in the gasoline vapor standard was 3.28 percent by weight. Thus, as expected, the average benzene fraction of the chromatographed sample (16 analyses) was 3.23 percent, with a standard deviation of 0.90 percent.

GC/PID/Heated Oven—The precisio and accuracy of the PID performance we very similar to that of the FID. The linea regression performed for the multipoi calibrations shows strong linearity, wit correlation coefficients ranging fro 0.946 to 0.999, averaging 0.984. Th standard error of estimate for th predicted values ranged from 0.828 t 7.38 and averaged 2.83 ppm. N unexpected differences in performanc were observed between PID lamps c different ionization energies; th expected lower relative response factc for the lower-energy lamp (9.5 electror volts (eV) vs. 10.2 eV) was observed. A with the FID, the lower limit of reliabl detection was about 2 ppm; use of th 9.2-eV lamp would increase th detection limit to 4 ppm. Some portio of the gasoline vapor is not detected b the 10.2-eV PID (compounds witl ionization potentials greater than 10.: eV), which thus yields a lower tota response and higher calculated benzen fraction of the total compared to FIC analysis. The average benzene fraction of the total response was 4.96 percent with a standard deviation of 4.14 percent Although the average value is consisten with expectations, the deviation is considerably higher than that obtained with the FID.

GC/AID/Heated Oven—The portable heated-oven GC with AID obtained foi testing was built for ambient (ppb-level) measurements, and the unit was available for only a short period of time. As a result, the relatively high concentrations being tested prevented obtaining any reliable quantification data.

GC/PID/Ambient Oven—The test unit, a portable GC with PID and ambient temperature oven, with appropriate column packing and programming of the flow control valves permitted an adequate separation of benzene from gasoline vapors, in contrast to expectations. The unit was evaluated both with syringe injections of benzene standards and with samples pumped from a Tedlar® bag. Plotted peak heights at particular detector gain settings were measured for comparison to the data machine-reported in parts per million or volt-seconds. Apparently, because the internal volume of the analytical system was large compared to the sample volume, a measurable amount of the previous sample remained in the system. Succeeding analyses of identical samples gave results closer to the true value. The unit was not available long

enough to perform rigorous tests on its ability to quantify benzene in gasoline vapor, although a few tests were conducted to ensure that it could be done. Two replicate analyses gave results of 206.8 and 212.5 ppm benzene, which agree well with the GC/PID/heated-oven results.

NDIR—The NDIR analyzer was able to quantify the benzene-in-air standards reasonably well, but, as expected, could not disinguish benzene from the rest of the components in the gasoline vapor mixture.

Field Testing

LEL Analyzers—When compared to each other, the LEL analyzers had a fairly consistent response to gasoline vapors. The response characteristics of the LEL analyzers to specific hydrocarbon compounds are not known. The instruments' responses all followed the same general trend, that is, an increase in one meant an increase in the others. When least-squares linear regressions were calculated between the GC (the independent variable) and each of the LEL analyzers, the correlations were not particularly good, with r^2 values in the 0.4-to-0.8 range. Comparing the individual LEL analyzers with the average value of all four yielded much better correlations, as shown in Table 1. Analyzer D was not operating properly, so the low value is not surprising. The high correlations for the catalytic oxidation units (Analyzers A,B,C) are not unexpected considering the detection method.

Benzene/Total Hydrocarbons—Virtually no benzene (<1 ppm) was found in the exhaust gas samples, but significant amounts were present in the inlet to the condenser. Several tests of the inlet gas to the refrigeration system showed from 0.64 to 5.86 percent of the total chromatographable (PID detection) organic compounds was benzene. To analyze the inlet gas with the LEL units, the inlet stream was diluted with ambient air until the LEL readings were on scale. No attempt was made to quantify the actual dilution rate; it was estimated to be about 20:1 at the lowest ratio and 100:1 at the highest ratio. The sampled gas concentration of benzene for the inlet samples (diluted) ranged from 0.2 ppm to 13.1 ppm, and the undiluted concentration in the inlet gas was estimated to be from 12 to 590 ppm. No relationship between benzene and total hydrocarbons as measured by the LEL analyzers was observed. However, the same general GC-LEL relationship discussed above held with the inlet samples as with the outlet samples.

Conclusions

Currently, no commercial analyzer is available that can provide a continuous measurement of the benzene concentration in the exhaust gas from a bulk gasoline storage terminal. Process GCs designed for field use are available and could be modified to serve as semicontinuous analyzers with acceptable precision and accuracy, but they are usually expensive. If continuous analysis is required, inexpensive "total" hydrocarbon analyzers could be modified to measure the expected range of hydrocarbon concentrations. The results would not quantitatively relate to benzene emissions unless there were data to correlate total hydrocarbons with benzene. As alternatives to process GCs, several different configurations of laboratory GCs could accomplish the requisite benzene separation and quantification. Either FIDs or PIDs could be used, and isothermal operation of packed columns would be acceptable. A heated column is not necessary to achieve the benzene separation from the other components of gasoline vapor, but might be necessary to achieve analytical cycle times short enough to make the GC useful as a semicontinuous instrument.

Only one methodology seems to hold much promise for near-term development as a continuous benzene monitor—NDUV. Commercial NDUV instruments are used for other analytes, so many of the operating problems and issues have been resolved. The unknown is whether a unit could be built at a reasonable cost combining the needed sensitivity and interference-rejection capabilities to measure ppm-level benzene in a gas stream containing percent-level hydrocarbons, including other aromatic compounds. Although procedures still in their infancy, such as tunable atomic line molecular spectroscopy, hold promise, sufficient data do not exist to assess the probable performance of such instruments.

Recommendations

The NDUV technique for benzene monitoring holds sufficient promise to warrant further investigation. Some manufacturers have expressed an interest in pursuing this development. This could permit relatively inexpensive (to EPA) research. A prototype instrument could be built and subjected to laboratory and short-term field tests similar to those described in the full report to establish the performance specification data for the applicable regulations. A surrogate monitor does not seem practical, because a great deal of data would be required to develop the correlations between the surrogate (total hydrocarbons) and benzene emissions necessary for regulatory purposes. Both the benzene and total hydrocarbon emission rates are affected by product composition and by the terminal and control device operating conditions. The limited field tests indicate that developing the required correlations would be difficult, at best.

The use of a dedicated GC also warrants investigation if one analysis ever 3 to 5 min is considered adequate. A specially configured instrument would need to be tested to establish performance characteristics, because data extrapolated from this study would not reflect long-term unattended operation.

Table 1.   *LEL Analyzer Regression Summaries*

Analyzer	Slope (Standard error)	Intercept	Correlation Coefficient
A	1.323 (0.0298)	−1.545	0.976
B	1.321 (0.0257)	−4.354	0.982
C	0.980 (0.0390)	4.625	0.929
D	0.377 (0.0411)	1.273	0.636

Jon Bolstad is with Pacific Environmental Services, Reston, VA 22090; the
*EPA authors **Robert G. Fuerst** and **Thomas J. Logan** (also the EPA Project*
Officer, see below) are with the Environmental Monitoring Systems
Labaoratory, Research Triangle Park, NC 27711.
The complete report, entitled "Benzene Continuous Emission Monitoring
Systems for Gasoline Bulk Storage," (Order No. PB 88-125 679/AS; Cost:
$14.95; subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use $300

EPA/600/S4-87/034