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Research Triangle Park NC 27711

Research and Development

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Project Summary

Develop, Evaluate and Validate Continuous Emission Monitors for Designated Hazardous Pollutants

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The objectives of this project were: (1) to assess the state of the art of commercially-available continuous emission monitors of vinyl chloride monomer (VCM) and (2) to conduct actual experiments to evaluate two monitors in the laboratory and in a (six month) field testing program.

A single process GC modified for dual-channel operation, with both a flame ionization detector and a photoionization detector, were used during this study to represent the two monitoring systems. Three one-week EPA Method 106 tests were conducted during the six-month field testing program to measure the relative accuracies of the monitors at a VCM plant.

The precision of both types of detectors was in the 1% range when evaluated in the laboratory.

The relative accuracies for both types of detectors were <10% for VCM concentration between 2 to 10 ppm.

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

This project concerned itself with: (1) commercially-available continuous emission monitors (CEM) for vinyl chloride monomer (VCM); (2) their reliability in long-term field operation; and (3) the relative accuracies of the CEMs compared to the EPA reference method.

The project focused on the six-month field testing program and the use of EPA reference Method 106 to measure the relative accuracies of the CEMs during the field test. Because of the very low concentration of VCM in the stack emissions, the sampling line was connected to a process line, and nitrogen was used to dilute the VCM concentration to the 1-10 ppm, which was the CEM measurement range.

Two types of signals, digital and analog, were collected and sent by telephone line to the data processor. The maintenance trips for changing compressed gases on the gas chromatographs were made every other week. Additional trips were made as needed, whenever there were process upsets and GC shut-downs.

Three one-week, Method 106 Tedlar bag sample/GC-FID analyses were conducted with the sampling line tie-ins to the CEMs, to measure the relative accuracies of the FID and PID.

Apparatus and Procedure

A process GC manufactured by Applied Automation (Model 102) was used for this work. A Hnu System, Inc., Model P152 photoionization detector (PID) with a 10.2 ev lamp and a BC-2 instrument control computer (Action Instruments) were selected and installed up-stream in series to the FID detector on the Applied Automation process GC.

The laboratory experiments were de-

signed to evaluate the separation of the vinyl chloride from the possible interferent species present in the process gas stream. A process gas stream sample was collected and analyzed. Significant concentrations of ethylene, ethylene dichoride, and small amounts of light chlorinated hydrocarbons and hydrogen chloride were found present in the gas stream. Analytical windows for the detectors were set, back flush time was determined, and non-stainless steel parts on the instrument were replaced due to the corrosive nature of the hydrogen chloride present in the stream. After all the parameters were optimized, a one-month reliability test was conducted in the laboratory.

The instrument was installed at a VCM plant, was connected to a reactor off-gas stream, which was diluted with nitrogen to bring the vinyl chloride concentration down to the 1 to 10 ppm range.

The process GC measured the VCM concentration every two minutes, and two readings were recorded from each detector (FID and PID) as analog and digital readings. The field record was transmitted by modem approximately once each day, which included the 51 hours of data immediately preceding the phone call. An inspection trip was made to the field site every other week to check the instrument, change gases, and verify the transmitted data. Calibration was conducted by remote control over the telephone line once a day.

Three one-week EPA reference Method 106 tests were conducted during the six-month field test program; during the first week following the installation, the thirteenth week, and the last week of the field program. Each test consisted of taking twelve one-hour integrated bag samples, and the VCM measurements were made immediately at the completion of each sample collection on a separate gas chromatograph.

Results and Discussion

The selection of the Applied Automation Model 102 process GC was primarily due to limitation of funds and the ready-availability of the GC in this laboratory. The selection of the PID with a digital integrator to be installed in series with the FID on the process GC was partially due to funds limitation and partially because the separation of the vinyl chloride from other interferences was the same for FID or PID, and a second set of column and oven were not necessary.

Because remote-linkage of the data systems was necessary, the compatibilities and the electron noise insulation were very important in the selection of the digital integrator and the data system. An Epson HX-20 briefcase computer and a Wirteck MCS analog interface were chosen and connected to the BC-2 digital integrator system to eliminate the noise problems.

A month-long laboratory test resulted in a net of 97% of usable data recovery, less than 3% span drift (with 10 ppm VCM), and the precisions of the four method combinations were all within 1%.

The field testing program started during November 1983. Overall data recovery efficiency was approximately 80%. Severe weather conditions during January and February of 1984 caused significant problems in the continuing operation of the field monitors because the monitors were installed outdoors in a trailer, without heating during the winter. (The test site was in the state of Louisiana, and the severe winter conditions were unusual and, therefore, not expected.)

The relative accuracy measurements by use of the Method 106 for three one-week bag samples gave a bias within 8% by average. In general, when the concentration level dropped to below 1 ppm i the sampling line, the relative accuracies become far worse (approximately 30%). This was due to the calibration problems of the monitor in this low concentration range. While the VCM concentrations stayed in the 2 to 10 ppm range, the relative accuracies stayed within 2 to 3%.

Conclusions and Recommendations

Both detectors (FID and PID) successfully completed 6 months of operation under the field conditions. Because of its better sensitivity, and the fact that only one compressed gas (carrier gas) is needed for its operation, the PID is a better choice than the FID for long-term remote field operation.

During the field evaluation program, non-linearity of the monitor calibration was developed. This may be caused by the increasing contamination of the column by the heavier fraction in the sample gas or by the degradation of the column packing material. Additional studies should be directed toward understanding this problem.

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The complete report, entitled "Develop, Evaluate and Validate Continuous Emission Monitors for Designated Hazardous Pollutants," (Order No. PB 85-201 176/AS; Cost: $10.00, subject to change) will be available only from:
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