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ABSTRACT

Measuring the real-world performance of emission control technologies is an important aspect in the development of advanced low-emission vehicles. In addition, data acquired from such measurements can be used to improve the accuracy of air quality predictive models. Honda has developed an on-board sampling/analysis system capable of measuring on-road emissions at ULEV levels and below. Ambient air can be analyzed simultaneously. This FTIR-based system can measure several species; this paper will focus on NMHC, NO_x, and CO. Techniques were developed to address the challenges associated with acquiring accurate real-time data at concentrations below 1 ppm in an on-road vehicle. Validation studies performed with reference gases and vehicle exhaust indicate a very good correlation between the on-road analyzer system and classic bench methods for all target compounds. Dynamic studies performed by the University of California, Riverside, also show good correlation. The latter research is documented in a separate paper⁽¹⁾.

INTRODUCTION

BACKGROUND

Tailpipe emission rates are commonly determined by operating a vehicle on a chassis dynamometer under strictly controlled, reproducible conditions. For example, the US FTP-75 emission test cycle is used in California to assign emission categories; i.e., LEV, ULEV, etc. However, to achieve a more complete assessment of a vehicle's impact upon the environment, laboratory testing must be augmented by evaluating real-world emission performance. To this end, an on-board sampling/analysis system has been developed. This system has been used in the development of advanced low-emission vehicle technology, and to confirm the robustness of such technology under varying driving

conditions on actual city roadways. The data from this on-board analysis system can also be used to develop better estimates of advanced-technology emission system inventories for use in air quality simulation studies.

OBJECTIVES

Advancements in emission control technology have led to the development of vehicles with progressively lower tailpipe emission levels. Therefore, the target emission category for this analyzer was set to ≤ULEV. Since the primary objective would be on-road testing, focus was placed on the relatively low component concentrations encountered during warmed-up conditions. (Accurate cold-start measurements can be made with conventional dynamometer bench analyzers.) In addition, to assess the effect of engine intake air upon emission system performance, it would be necessary to monitor the ambient roadway air quality in real time as well. The following requirements were placed on the development of this system:

- Target components = NMHC, NO_x, and CO
- Limit of detection (LOD) near 0.1 ppm, with acceptable accuracy and precision
- Minimal weight burden on vehicle
- Robust and verifiable
- Real-time data acquisition and display, (to facilitate emission system development work)

CHOICE OF ANALYTIC TECHNIQUE

Given the requirements above, it was decided to use Fourier Transform Infrared Spectroscopy (FTIR) as the basis for this on-road analyzer. Acquiring data with a single system would facilitate synchronization with engine parameter data (simultaneously recorded on a

separate computer). Fieldwork logistics would be simplified because an FTIR requires no daily calibration per se. As an added benefit for future research, FTIR data can be re-processed to reveal concentration data of other components. (This is possible because the spectrum recorded by the FTIR contains concentration information for all infrared-sensitive components.) However, the use of this technique presented some special challenges:

- Spectral interference (primarily from H₂O and CO₂)
- Signal-to-noise ratio affected by external vibration and instrument orientation
- Demanding accuracy and LOD requirements
- Response time

Other single-systems approaches that were considered for this project included non-dispersive IR, high-resolution mass spectrometry, and gas chromatography - mass spectrometry. These were rejected due to sensitivity, size, and response time considerations, respectively. It should be noted that promising studies have been performed using FTIR as the basis for emission laboratory instrumentation; the work of Baronick, et al, is a recent example⁽²⁾.

EXPERIMENTAL

SYSTEM OVERVIEW

The initial test platform chosen for this project was a prototype Honda ZLEV (Zero Level Emission Vehicle). The exhaust emissions from this gasoline-powered vehicle are less than 1/10 ULEV levels⁽³⁾. An overview of the sampling and measurement systems is shown in Figure 1. Intake air was sampled from the front of the vehicle, and an exhaust sample was taken via a heated line inserted into the tailpipe. The samples were drawn

through a water-removal system by a dual-head pump, and then directly into the gas cells of twin FTIR spectrometers. System power was supplied through a DC-AC inverter from three nickel-metal hydride battery cells (which were developed for use in the Honda EV-Plus electric vehicle). Results were processed by two networked 400 MHz computers, and combined onto a single touch-screen flat panel display.

ANALYTIC INSTRUMENTATION

FTIR Principles

In infrared gas analysis, IR light is passed through a sample in a gas cell. Some of the infrared light is absorbed by the sample and some is passed through. The measurement of these absorbed and transmitted wavelengths of infrared light constitute an infrared spectrum. Since no two chemical species have the same infrared spectrum, the spectrum serves as a fingerprint for identifying different gas components in the sample. The intensity of the infrared absorption indicates the quantity of the component in the sample.

Unlike dispersive IR spectrometers, an FTIR instrument can acquire an entire spectrum in less than one second; i.e., it can record all frequencies simultaneously in this time. FTIR uses an interferometer with a moving mirror to modulate the light by phase, producing an interferogram. This interferogram is then Fourier transformed, thereby producing the sample infrared spectrum in frequency or wavenumbers (cm⁻¹). An example of interferograms (sample and nitrogen background) and the resultant infrared spectrum can be seen in Figure 2.

The infrared spectra were analyzed using a "classical" least squares (CLS) pattern recognition algorithm⁽⁴⁾. This data reduction technique compares spectra of reference gases to sample spectra, determining a

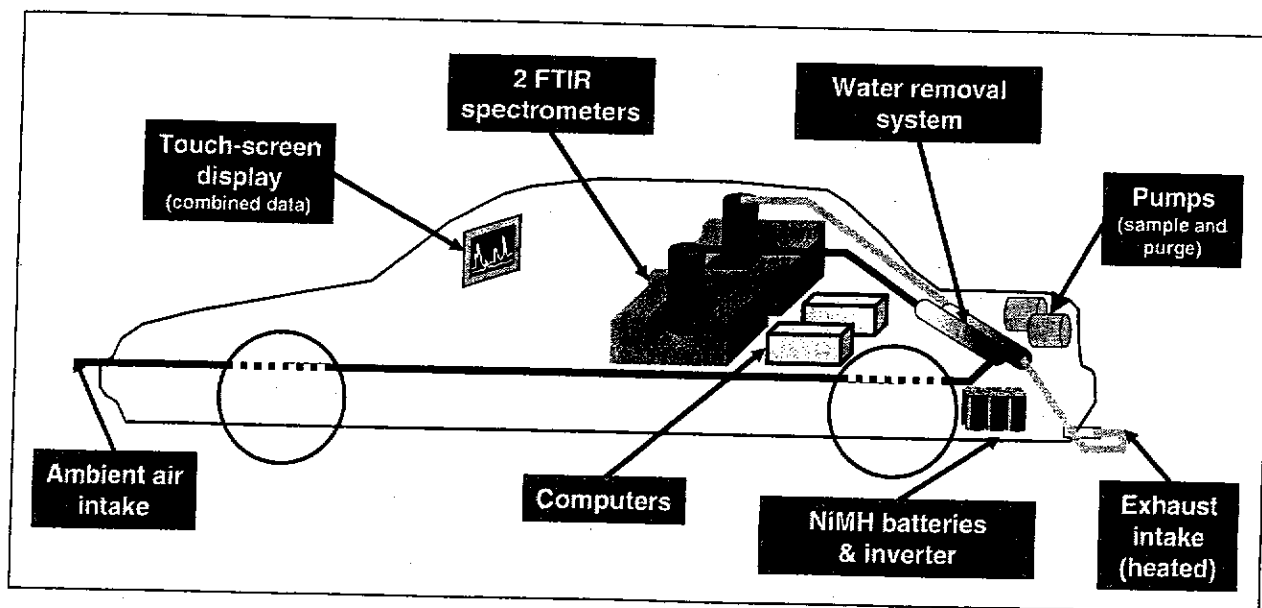


Figure 1. Overview of on-board sampling/analysis system

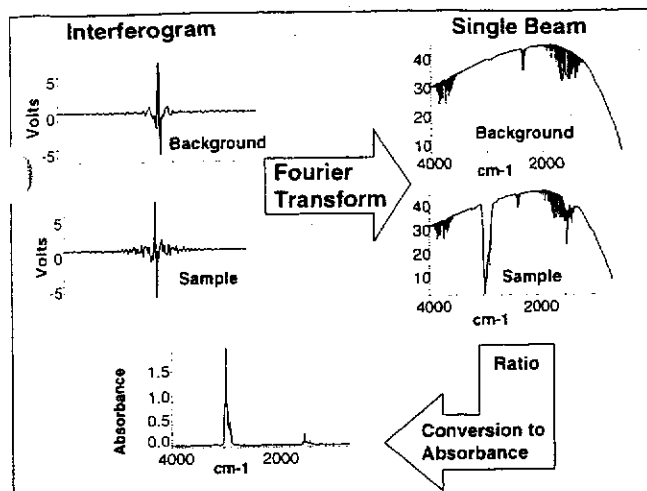


Figure 2. Production of an absorbance spectrum via FTIR

degree of fit of the reference gas spectra to the sample spectrum. The degree of fit is then reported as a concentration.

Gas Cell

Given the size and weight challenges of an on-board installation, a 2-meter path length gas cell was initially evaluated. It quickly became clear that the 2-meter cell would not achieve the target LOD. Acceptable results were obtained upon switching to a 10-meter cell, and the improvement in sensitivity was greater than expected; Figure 3. (Both cells use the *White* optical design with multiple internal reflections; the actual length of the 10m cell is less than 50cm.) The strong infrared absorption bands from (exhaust) water became a problem with the increase in path length, as discussed later in this paper. The longer sample mixing time resulting from the 10m cell's larger internal volume was also of some concern, but the final system provided adequate temporal resolution for vehicle development work. Data acquired with 10m cells specially modified for horizontal mounting proved comparable to that from vertical cells, after alignment problems were addressed. However, the cells were mounted vertically in the final system configuration.

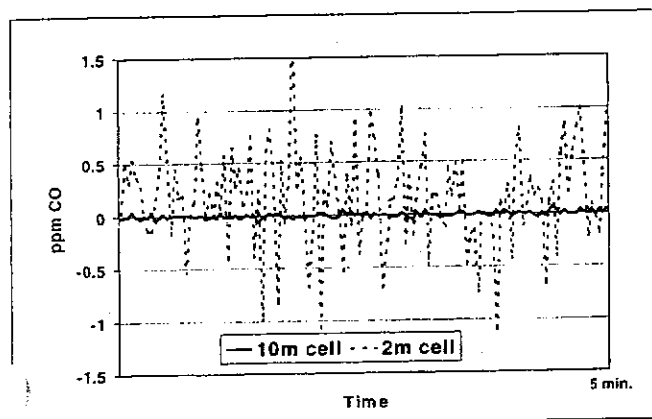


Figure 3. Concentration measurement precision; 2-meter vs. 10-meter path length gas cell filled with nitrogen

CALIBRATION

Calibration of an FTIR gas analyzer is performed similarly to that for a non-dispersive infrared or a chemiluminescent analyzer. In this case, spectra of single-component reference gases (in a nitrogen matrix) were acquired, and the resulting patterns used in a CLS spectral data analysis. The absorbance response of a reference gas coupled with its concentration determined the calibration. A sequence of concentration steps was added in order to calculate a non-linear correction, but the FTIR analyzer gave a nearly linear response over the analysis range used for this study; i.e., <100ppm for the target components.

A different approach was required for the calibration of the non-methane hydrocarbon component. Instead of using reference spectra for the individual hydrocarbon species, it was desirable to use a spectrum of a representative mixture of hydrocarbons as the reference gas in the CLS data analysis. The mixture used to calibrate the FTIR analyzer was a bag sample of engine exhaust from a prototype ULEV sampled during the first 30 seconds after a cold start. A concentration for the non-methane hydrocarbon component in the bag sample was assigned using careful bench FID and gas chromatography analyses.

The NMHC reference spectrum of the bag sample required some manipulation before it could be used in the CLS data analysis. Since the spectral analysis region for NMHC also had methane and water as interferences, these spectral components had to be removed from the NMHC reference spectrum. The lack of any sharp spectral features in this region allowed for some smoothing of the NMHC spectrum.

Validation of the NMHC calibration showed that this approach worked very well. The difference in concentration of the cold-start bag sample and the exhaust sample did not exceed the linear response range for this component. Validation of the calibration also included testing for cross-interference of water and carbon dioxide on other components. It was determined that H₂O and CO₂ had no detectable effect on the analysis of other components. As detailed below, sample treatment procedures played an important role in achieving this performance.

SAMPLE TREATMENT

Exhaust gas from gasoline-powered internal combustion engines contains roughly 14% CO₂ and 14% H₂O. Both pose interference challenges for the FTIR analysis. Dilution was never considered; the resulting sensitivity loss would have been unacceptable for this project. The CO₂ problem was mitigated by the careful choice of analytic regions in the spectra, aided by the 0.5 cm⁻¹ spectral resolution. However, the H₂O spectral features proved too pervasive; a similar countermeasure was precluded. This problem could have theoretically been partially addressed through the use of spectral

corrections for H₂O cross-interference. However, this approach necessitated a tedious calibration procedure, and the accuracy of the resulting correction proved inadequate for the low concentration ranges encountered in this study. Consequently, various techniques were tried to remove the water from both the ambient and tailpipe samples. A technique using an ice-chilled aluminum heat exchanger, water trap, and desiccants efficiently removed the water. As expected, NO₂ was unfortunately removed with equal efficiency. Studies with NO, CO, and C₃H₈ (propane) indicated no loss in this water-removal system. Since actual exhaust gas contains virtually no propane, a 15-component hydrocarbon mixture was also tested. Analysis by gas chromatography⁽⁵⁾ revealed that substantial hydrocarbon losses were occurring as early as C₆, necessitating the search for a different drying technology. (Data are shown later in this paper.)

A drying system based on the polymer Nafion[®] was assembled for evaluation. Nafion has a Teflon[®] backbone, with periodic side chains of perfluorinated ether terminating in a sulfonic acid group. These acid groups form "ionic channels" that extend through the walls of the Nafion tubing. Each sulfonic acid group can absorb up to 13 molecules of water. Assuming the partial pressure of water in the sample exceeds that external to the Nafion tube, water molecules will travel along the ionic channels and be released outside the tubing. This mechanism is selective for water; the only (potential) exhaust species that could experience some loss are alcohols, ketones, and ammonia.

For this application, multi-tube Nafion dryers manufactured by Perma Pure Incorporated were selected for use, after comparison to a single-tube configuration. This dryer consisted of a bundle of 0.76mm (OD) Nafion tubes contained within an aluminum shell. Fittings near each end of the shell permitted a purge gas to flow countercurrent to the sample; Figure 4. Two dryers in series were used for both of the sampling systems.

The exhaust sample was heated (70°C) from the tailpipe through half of the first dryer. There were two reasons for this: (1) the interaction of liquid water with Nafion is endothermic, and leads to a cascade failure reaction. Therefore the exhaust gas must be kept above the dew

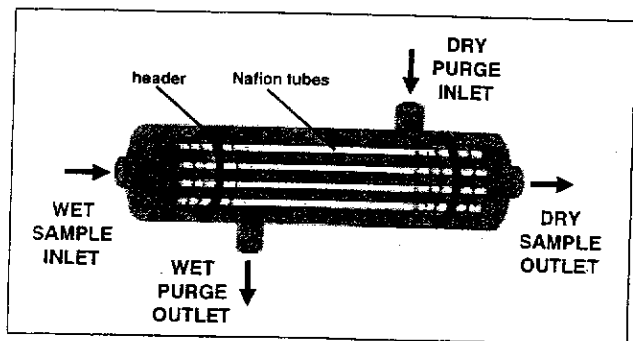


Figure 4. A Nafion drying system designed to facilitate purging with a dry gas. (This design by Perma Pure, Inc.)

point temperature until most of the water has been removed. (2) The initial water absorption and transport by Nafion proceed as a First Order Kinetic reaction, in which absorption becomes more rapid with increasing temperature⁽⁶⁾.

The second dryer for each sample stream was blanketed with ice water. The purpose here was to coax more of the retained water from the sulfonic acid groups, since this residual water becomes the limiting factor after the initial First Order reaction. Leckrone, et al, have recently quantified this effect⁽⁷⁾.

The ultimate performance of the Nafion dryers is dependent upon the partial pressure of water in the purge gas. Dry nitrogen was considered for this application, but the weight and safety ramifications of carrying a compressed gas on board a passenger vehicle precluded this choice. Ambient air would normally have an insufficient dew point for this application. However, good results were obtained by pulling ambient air through a specially constructed dehydrating system with a vacuum pump. The resulting negative pressure in the dryer shell lowered the partial pressure of the water in the treated ambient purge gas to an acceptable level. (It should be noted that Nafion is non-porous; in the absence of a water vapor pressure gradient across the tubing wall, drying will not occur, regardless of the overall pressure gradient.)

The residual hydrocarbon content of new Nafion dryers translated to a >20ppm increase in the system background. The source of this contamination was most likely the epoxy headers near the ends of the dryer. A curing process was developed to eliminate this contamination.

A comparison of the Nafion-based dryer performance with that of previous dryer versions can be seen in Figure 5. The 15-component hydrocarbon mixture was passed through a given drying system at 7 L/min, and collected into Tedlar[®] bags. These bags were subsequently analyzed on a gas chromatograph, and the resulting concentrations compared to the label values. The Nafion system produced acceptable results for all

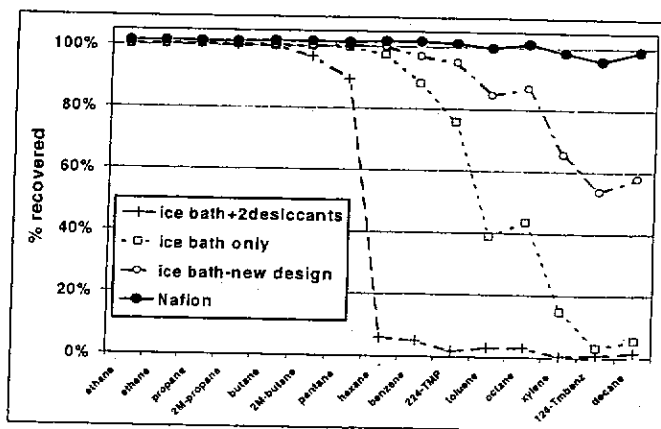


Figure 5. Comparison of drying system performance, in terms of hydrocarbon recovery.

components, with only a slight (4%) loss for a C₉ aromatic.

SYSTEM ENVIRONMENT

The instrumentation is basically designed for use on a vibration-free laboratory bench in a controlled environment. Relocating such instrumentation to the interior of a passenger vehicle is challenging, given the unpredictable dynamics resulting from road surface irregularities and vehicle motion. One of the initial concerns was the effect of the vehicle acceleration force vector upon the interferometer (moving mirror) component of the FTIR. Nicolet suggested that this force should be perpendicular to the motion of the mirror; (Figure 6). This configuration did in fact prove to be best, although the mirror was still subjected to coaxial forces during vehicle turning maneuvers.

The main area of concern was the unpredictable mechanical vibration and shock transmitted to the FTIR as the vehicle encountered imperfections in the road surface. An attempt was made to characterize these forces through the use of an accelerometer, but the test results only confirmed our prediction that the vibration frequencies varied widely. Several studies were performed involving dampening systems, changes in FTIR location, etc. The final conclusion was that the FTIRs were best isolated by simply placing them on the rear seat of the vehicle. (This was not completely unexpected; the seat was designed to help isolate a passenger from road-induced vibrations, and the weight of the instrumentation was comparable to that of a small person.) Also, placing the FTIRs side-by-side on the rear seat exposed them to an identical environment, and the instrument electronics could be kept within the specified temperature range.

Finally, each FTIR received some internal modifications; refer to Figure 6. For example, the laser and IR source were secured more firmly to prevent movement.

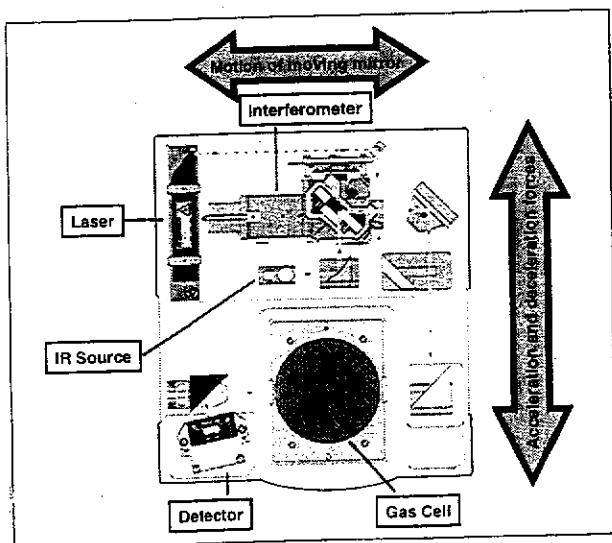


Figure 6. Overhead view of FTIR interior, showing location of main components and direction of force vectors.

USER INTERFACE

To facilitate viewing of the real-time data during a road test, the output from the FTIRs was consolidated into a single, flat panel touch-screen display. The custom program written for this purpose also allowed the data to be filtered prior to display. For example, in the rare case that a "bad" interferogram was acquired during on-road testing, the software could be set to ignore this data point. Varying degrees of data smoothing could be performed, if desired. The software could also be set to compensate for the mass of water removed from the sample prior to analysis.

RESULTS AND DISCUSSION

SYSTEM SPECIFICATIONS

The final system specifications were as follows. Information is shown for a single sampling/analysis system.

Analytic System

| | |
|-----------------------|-----------------------------|
| FTIR base unit : | Nicolet model Protégé™ 460 |
| Detector : | MCT, LN ₂ cooled |
| Spectral resolution : | 0.5 cm ⁻¹ |
| Gas cell : | 10m path |
| Sample conditions : | 70°C, 93kPa (absolute) |
| Sample flow rate : | 12 L/min (max) |
| Scans/sample : | 2 complete |

Drying system

| | |
|----------------|--|
| Nafion dryer : | 0.76mm (OD) tube bundle |
| Purge gas : | dehydrated ambient air under negative pressure |

SYSTEM VALIDATION

All system development and validation documented in this paper was performed at the Honda R&D Los Angeles laboratory.

Gas mixture testing

The performance of the analysis system was initially checked by using reference gases of known concentration; Figure 7. Standards A and B contained NO, CO, C₃H₈, and CO₂ (14%). Standard C was similar, but did not contain NO. Standard D was a freshly prepared gas that contained only NO in a nitrogen matrix (to ensure stability). To confirm that the FTIR system had remained stable throughout the course of this study, the runs were bracketed with analyses of high-purity nitrogen.

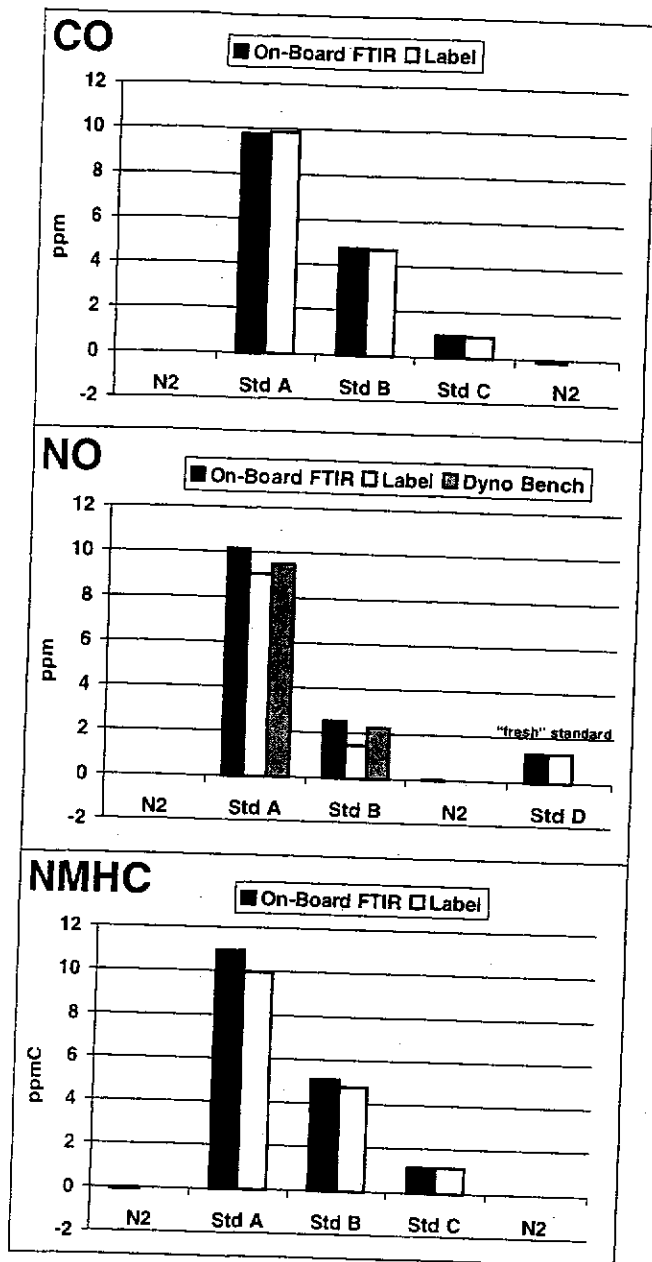


Figure 7. System validation; reference gases.

CO and NMHC results were very good, regardless of the fact that no pure hydrocarbons were used in the calibration of the FTIRs. Dynamometer bench analyzers were used to arbitrate a discrepancy between the FTIR NO results and the labeled concentrations of standards A and B. The bench analyzer corroborated the FTIR results; the NO concentration in these reference gases had changed with time. The FTIR system results for the "fresh" NO standard ("D") were virtually identical to the labeled concentration. The nitrogen analyses confirmed that the system did not drift between the first and last reference gas runs.

Comparison with traditional methods

In another set of validation experiments, bench instruments in use as ambient air analyzers were borrowed from Honda's Japan R&D laboratory:

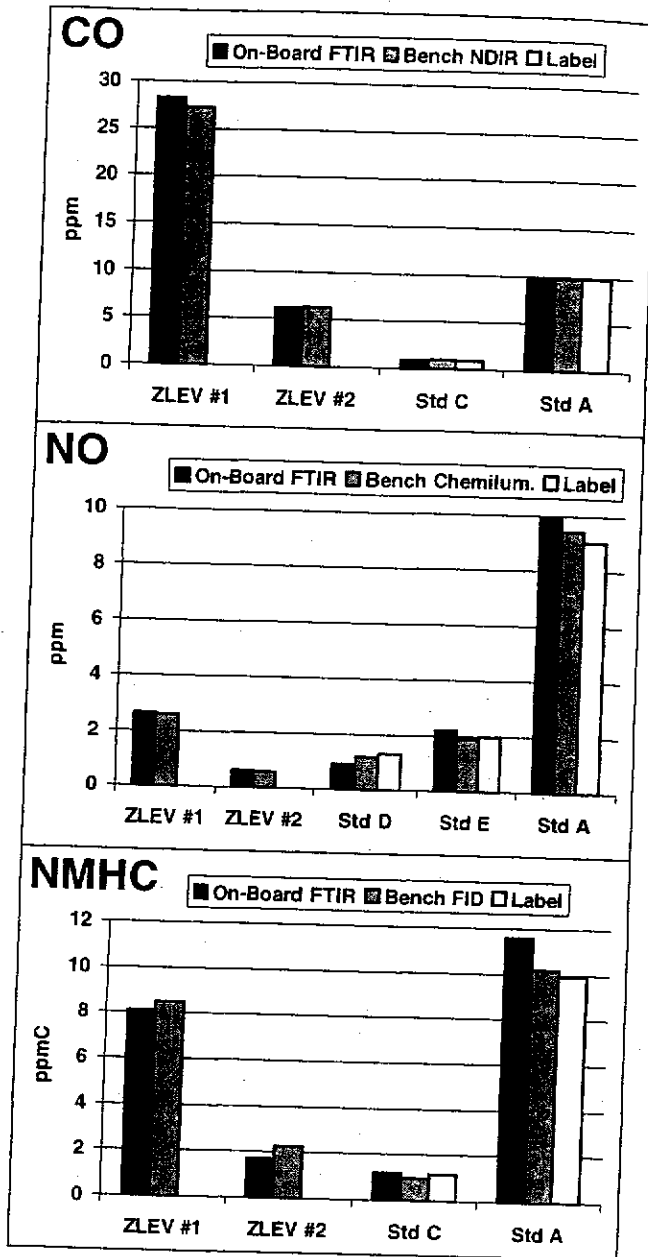


Figure 8. System validation; exhaust samples and reference gases. Comparison of on-board analyzer and bench instrumentation results.

- CO analyzer : Non-dispersive infrared (Horiba model APMA 360)
- NO/NO₂ analyzer : Chemiluminescence (Horiba model APNA 350E)
- HC analyzer : FID with NMHC catalytic "cutter" (Horiba model FIA-222)

Actual exhaust gas samples were analyzed in addition to reference gases. (Some of the same reference gases from Figure 7 were used, but new analyses were performed.) To prepare the exhaust samples, a ZLEV-class vehicle was started under cold conditions, while a slipstream of undiluted exhaust gas was pumped into a large Tedlar bag. The "ZLEV#2" sample was made by diluting the first sample with nitrogen. As can be seen in Figure 8, the FTIR system compared very favorably with

the bench analyzer for the exhaust samples and gas mixtures.

Validation of Drying System

A 5-component mixture was analyzed with the on-board analyzer, with and without the drying system attached. As previously shown in Figure 5, this reference gas consisted of C₂ to C₁₀ hydrocarbons, each at a nominal concentration of 1 ppmC. Alkane, alkene, and aromatic species were represented. This mixture covered the approximate range of NMHC typically found in tailpipe exhaust, but not the concentration distribution. Regardless, the NMHC concentration determined by the FTIR system was within 1 ppmC of the totaled label concentration, as shown in Figure 9. The post-dryer results corroborate the previous gas chromatograph data; the hydrocarbons survive their journey through the drying system virtually unaffected. An NO₂ reference gas was analyzed in the same manner. Again, the post-dryer result was within 1 ppm of the labeled concentration.

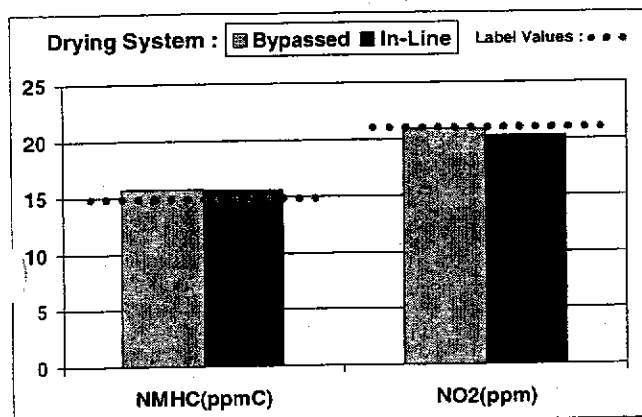


Figure 9. Survival of NMHCs and NO₂ in the drying system.

On-road results

At the conclusion of the initial on-road validation studies performed by UC Riverside in the Los Angeles area⁽¹⁾, minor enhancements were made to the on-board analyzer system. The system was then shipped to Japan for a few weeks, to evaluate its performance in the Tokyo area.

Data collected in the Tokyo area are shown in Figure 10. Roadway (ambient) pollutant concentrations were found to be roughly similar to those measured in the Los Angeles area. However, roadway concentrations approaching an order of magnitude greater were measured within long tunnels; (data not shown). Traffic conditions were typically stop-and-go, alternating with cruise periods.

The data shown here are not smoothed, other than two-scan averaging performed by the FTIRs. This produced an approximate two-second sampling rate for this data

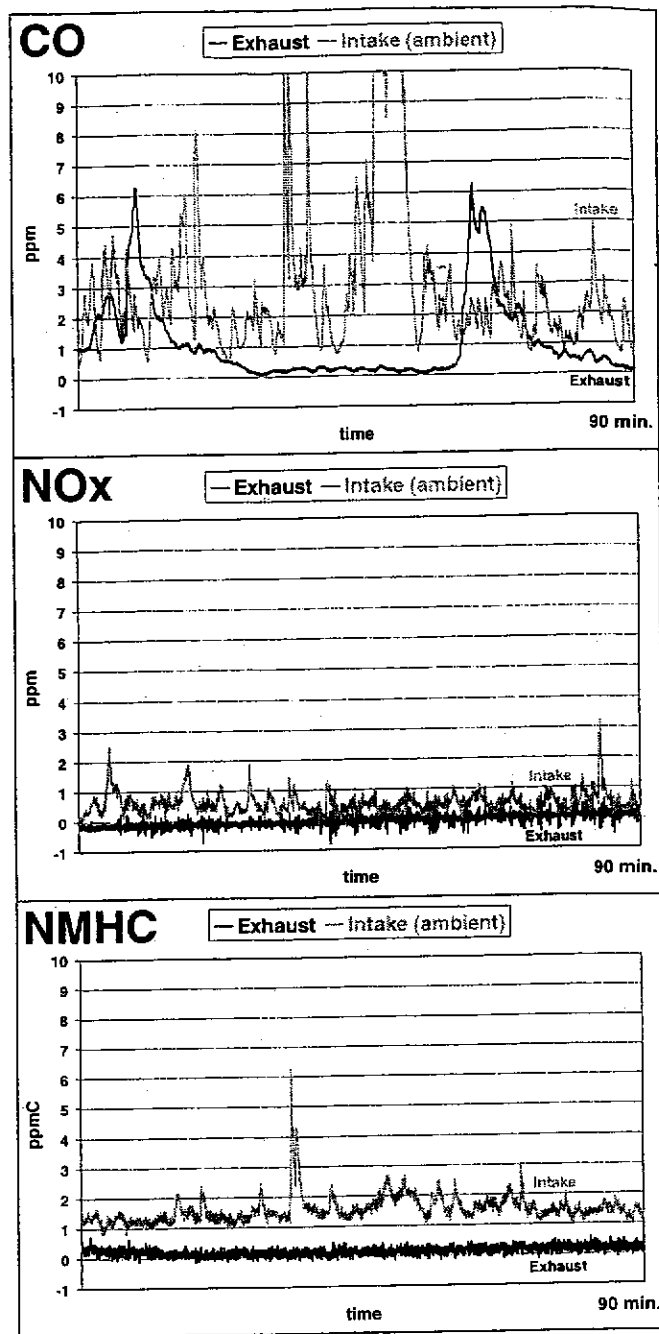


Figure 10. On-road results; Honda ZLEV with on-board analyzer.

set. The detection limit for all target compounds was approximately 0.1 ppm for such on-road testing. For this road test, NO₂ remained below the detection limit for both sample streams; the observed NO_x concentrations resulted from NO alone. In the rare cases where NO_x concentrations over 5 ppm were measured in the ambient sample during road tests, NO₂ was found to contribute approximately 20% to the total NO_x value. This ratio is similar to that expected in diesel vehicle exhaust⁽⁸⁾.

FUTURE WORK

Preliminary work indicates that accurate mass emission data can be calculated from a combination of the

concentration data acquired on-road and information from the vehicle's engine management computer⁽¹⁾. Improvements in temporal resolution are possible through increases in gas cell throughput; scan time can be correspondingly decreased by a factor of four, if needed. Work is also in progress to simplify the installation of this system into other platforms.

CONCLUSIONS

An on-board emission analysis system has been developed for use on advanced low-emission vehicles. The performance of this system has been validated through comparison with traditional bench analyzers, and demonstrated through the acquisition of on-road data from a 1/10 ULEV level vehicle. Novel calibration and sample-handling techniques were used together with unique hardware and software in the development of this system. This on-board analyzer is now in use within Honda R&D as a development tool for advanced emission-control systems.

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