A Thermal Conductivity Approach for Measuring Hydrogen in Engine Exhaust

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ABSTRACT

Thermal conductivity detection has long been used in gas chromatography to detect hydrogen and other diatomic gases in a gas sample. Thermal conductivity instruments that are not coupled to gas chromatographs are useful for detecting hydrogen in binary gas mixtures, but suffer from significant cross-interference from other gas species that are separated when the detector is used with a gas chromatograph. This study reports a method for using a commercially-available thermal conductivity instrument to detect and quantify hydrogen in a diesel exhaust stream. The instrument time response of approximately 40 seconds is sufficient for steady-state applications. Cross-interference from relevant gas species are quantified and discussed. Measurement uncertainty associated with the corrections for the various species is estimated and practical implications for use of the instrument and method are discussed.

INTRODUCTION

Hydrogen is a reactive species that can be produced both during the combustion process and catalytic emissions control processes. The presence of hydrogen in the exhaust stream can impact the performance of emissions control devices, oxygen sensors, and the combustion process. Furthermore, hydrogen can participate in the production of other chemical species of interest. Hydrogen has also come into focus recently because of interest in modeling emissions control technologies such as the lean NO_X trap. It is widely believed that hydrogen may play a key role in the catalytic processes involved with this technology. All of these cases point to the need to quantify hydrogen in the exhaust gases. It is possible in some cases to estimate the exhaust hydrogen numerically, rather than by measuring it. However, doing so requires estimating the equilibrium constant for the water-gas shift reaction, which may not always be practical (1, 2). Hence, there is a need for exhaust hydrogen measurements, both as an alternative to and as a benchmark for numerical estimations.

Detection of hydrogen is most commonly accomplished through the use of either a magnetic sector mass spectrometer or a thermal conductivity detector (TCD). Magnetic sector mass spectrometers have been used to quantify exhaust hydrogen (2, 3, 4). This method has been shown to be fast and accurate, but can be expensive, both in terms of the instrumentation and the effort involved in using the instrumentation. The thermal conductivity detector is widely used in conjunction with gas chromatographs (GCs). Use of a GC allows separation of the gas species so that cross-interference of the various gases in the TCD can be eliminated. Use of a TCD without a GC necessitates characterizing the cross-interferent species so that the TCD signal can be corrected for them. The advantage to the TCD is that instruments exist that can be readily incorporated into a standard gas analysis bench and treated just as other standard instrumentation. This can allow hydrogen measurement in a less obtrusive way for applications such as bag analysis, steady-state engine exhaust characterization, and synthetic exhaust blends on bench-flow reactors.

THERMAL CONDUCTIVITY DETECTION

A thermal conductivity detector operates by measuring the heat lost from a resistive element to the walls of the detector housing. The housing is thermostatically maintained at one temperature, while the resistive element is maintained at a higher temperature. The temperature of the element (and thus its resistance) depends upon heat lost to the lower temperature housing. For otherwise identical conditions, the heat loss is a function of the bulk thermal conductivity of the sample gas. The electrical resistance of the heated elements is measured by using a Wheatstone bridge (5, 6). Since there is sample gas flowing continuously through the detector convective heat loss is present. The cell design can help to minimize convective effects, but doing so generally results in slower dynamic response. Regardless of cell design, maintaining a constant sample flow rate is effective at minimizing biasing due to convective changes between calibration standards and samples.

Since the heat lost from the resistive element is dependent upon the bulk thermal conductivity of the sample gas mixture, TCDs are sensitive to a number of gas species. In automotive exhaust gas characterizations, instruments are typically calibrated using nitrogen as a zero-concentration standard and the gas of interest blended in nitrogen as a full-scale concentration standard. If the TCD is calibrated using nitrogen and a hydrogen (H_2) blend, then gases with a thermal conductivity higher than nitrogen will exhibit a positive response, while those with a lower thermal conductivity will exhibit a negative response. The magnitude of the response will be dependent upon the change in bulk sample thermal conductivity as compared with that of the full-scale reference standard. Thermal conductivities for several species of concern are listed in Table 1 (7). Table 1 also shows the thermal conductivities normalized to that of nitrogen. Data are for gases at 101 kPa and 25 C.

The magnitude of the cross-interference introduced by a given species is a function both of its thermal conductivity and concentration. Fortunately, hydrogen has the highest thermal conductivity of the gases that are likely to be present in engine exhaust. This results in interferent gases having a fractional response as hydrogen. Since nitrogen is used as a zero concentration standard, its interference is excluded through calibration. Other gases that may be present at large concentrations in engine exhaust include H_2O, CO_2, O_2, CO, and hydrocarbons. Of these, H_2O, CO_2, and O_2 are present at concentrations high enough that small changes to the instrument sensitivity may result from complex boundary layer issues. Although many other species could potentially cause interference, they are not generally present at sufficient quantity in diesel exhaust to warrant investigation.

DETERMINATION OF INTERFERENCES

EXPERIMENTAL SETUP – A commercially available thermal conductivity instrument was procured. The selected instrument was a Rosemount Analytical MLT1 instrument equipped with a thermal conductivity detector for hydrogen measurement, plus a non-dispersive infrared (NDIR) detector for measuring carbon dioxide (CO_2). The CO_2 instrument was included to allow internal correction for CO_2 cross interference with the H_2 measurement. This instrument was selected because it was compatible with an existing Rosemount NGA2000 gas analysis system already in place and because of the availability of internal correction for CO_2 cross interference. The TCD itself is of a design which is field-configurable for either a fast response time with high sensitivity to flow rate or a slow response time with low sensitivity to flow rate (5). For the purposes of this study, the TCD was left in the fast-response configuration that was set by the factory. The instrument was installed into the existing instrumentation system. The instrument was supplied with a non-condensing sample stream at constant flow rate. The sample conditioning system (pump, chiller, and flow controls)

were already present in the analysis system to supply non-condensing sample to other instruments, so very little accommodation was required for the TCD. The TCD range was 0 – 2% H_2. The instrument was calibrated with a 1% H_2 in N_2 calibration standard. A 10-point gas divider was used to aid in calibration and cross-interference determinations. Once a target sample flow rate was identified, care was taken to maintain this flow rate at all conditions.

Table 1. Thermal conductivity data for several gases of interest.

Species	Thermal Conductivity W / (m * K)	Normalized to Nitrogen
Nitrogen	0.0259	1
Hydrogen	0.181699	7.015
Oxygen	.02662	1.028
Carbon Dioxide	0.0166	0.641
Carbon Monoxide	0.0232	0.896
Nitric Oxide	0.02536	0.979
Nitrogen Dioxide	0.1151	4.444
Nitrous Oxide	.01674	0.646
Methane	0.034238	1.322
Ethane	0.02012	0.777
Ethyne	0.02006	0.775
Ethene	0.01778	0.686
Propane	0.01674	0.646
Propene	0.01778	0.686
Butane	0.014644	0.565
1-Butene	0.01444	0.557

FLOW RATE EFFECTS – A calibration gas was introduced to the TCD instrument using the gas divider. The sample flow was initially set at 700 ml/minute and the response noted. The flow was varied and the resultant responses were again noted. The detector response was found to be linear with flow rate. An increase or decrease in the flow rate of 50% from the base condition was found to result in a 100% increase (for increased flow) or decrease (for decreased flow) compared with the base condition. All subsequent experiments were carried out with a flow rate of 700 ml/minute. At this flow rate, the time response of the TCD was noted to be approximately 40 seconds from initial response to final value.

CARBON DIOXIDE – As mentioned previously, this instrument was procured with an internal CO_2 measurement for correcting the TCD cross-interference caused by that gas. Nevertheless, the instrument was checked for interference from CO_2. The instrument was first calibrated then the gas divider was used to provide a varying concentration of CO_2 to the instrument, using N_2 as a diluent. The internal CO_2 measurement was found to be within tolerances. The TCD itself exhibited a positive nonlinear response, which is shown in Figure 1. The response even with the internal cross-interference compensation enabled is still significant, but remains at a level that is less than 5% of the full-scale value. The internal cross-interference compensation modifies the raw signal by first subtracting the reading attributable to the CO_2 that is present, then correcting the resulting value for a sensitivity decrease due to the CO_2. Both the CO_2 response and the sensitivity decrease are a function of the CO_2 concentration in the sample and were calibrated with an extensive set of experiments by the supplier. The reported change in sensitivity at a low (5%) CO_2 level were less than 2%, suggesting that similar effects by other gases likely to be present at concentrations of 1% or less will be negligible.
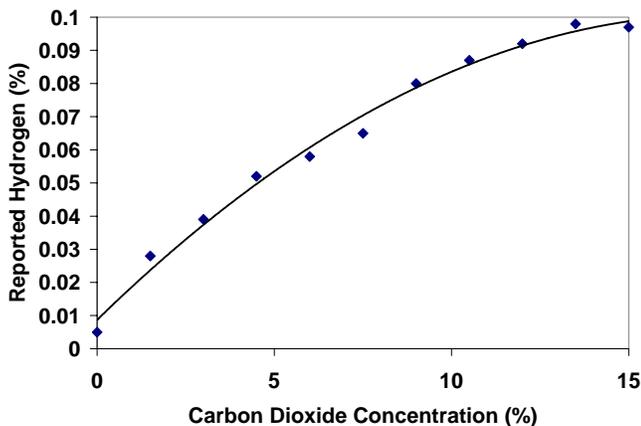
Figure 2 shows the TCD response to CO_2 with the internal cross-interference compensation disabled. The response was found to be negative, as expected, and slightly nonlinear. A second-order curve was found to fit well ($R^2 = 1$) with a very small second-order term. This curve represents the response of the TCD to CO_2, but does not take into account the degradation of the H_2 sensitivity, as does the internal cross-compensation correction.
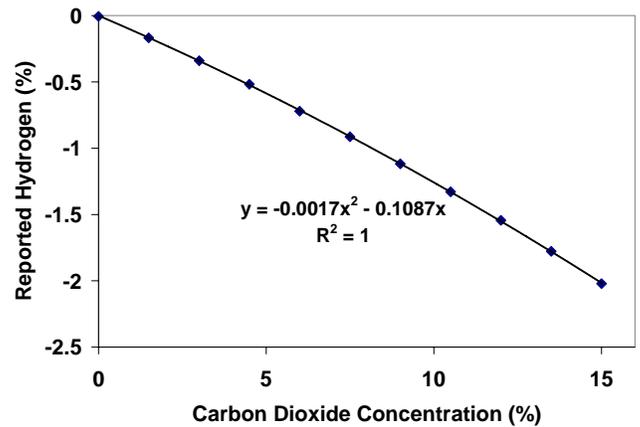

Figure 2. TCD response (as hydrogen) to varying CO_2 concentration with internal cross-interference compensation disabled.

The gas divider was next used to verify the veracity of the internal cross-interference compensation with both H_2 and CO_2 present in the sample. This was accomplished by once again using the gas divider, but replacing the N_2 diluent with CO_2 calibration standards. The gas divider was an imperfect tool for this purpose since it did not allow independent variation of the H_2 and CO_2 concentrations, but did nevertheless provide a means of accurately introducing mixtures of the two gases. Three CO_2 standards were used: 15% CO_2, 5% CO_2, and 1% CO_2 in balance of N_2. The errors are shown on Figure 3. Errors have been expressed as percent of full scale to allow inclusion of points where the H_2 concentration was zero. As with the CO_2 in N_2 data, the errors produced by CO_2 in the sample were always less than 5% of full-scale, including conditions where the CO_2 concentration was very high and the H_2 concentration was very low. Errors were lowest at points where the concentrations of both gases were moderate.
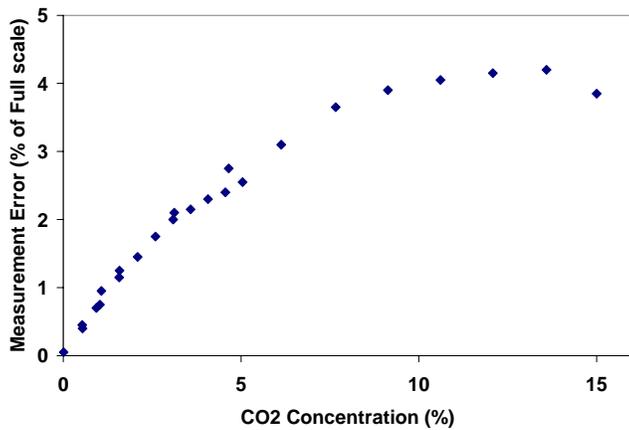

Figure 1. TCD response (as hydrogen) to varying CO_2 concentration.

Figure 3. TCD errors for mixtures of CO_2 and H_2.

OXYGEN – Although O_2 has a TC very close to that of N_2, the concentration of O_2 in the exhaust is typically high and varies widely depending upon the mode of operation of the engine. O_2 cross-interference was accomplished by first calibrating the TCD with N_2 and H_2 calibration gases, then by introducing a blend of O_2 in N_2 with the gas divider. Figure 4 shows the response of the TCD to the varying O_2 concentration. Data are indicated by points, with a best-fit line (R^2 = 0.9978) also shown. The TCD was found to report O_2 as a false-positive indication of H_2. The slope of the line indicates the magnitude of the cross-interference. The TCD reports each 1% O_2 as 0.0162% H_2.
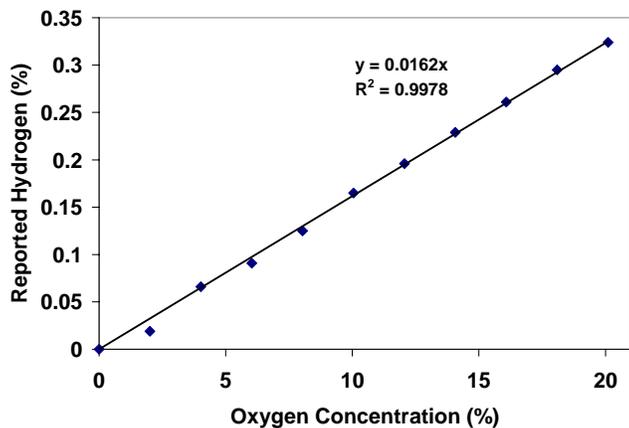

Figure 4. TCD response (as H_2) to varying O_2 concentration.

O_2 can be present in exhaust in relatively high concentrations, perhaps high enough in some cases to cause a small change in the sensitivity of the instrument

to H_2. This was the case with CO_2. O_2 and H_2 mixtures were introduced using the gas divider to check for this possibility. O_2 concentrations as low as 2000 ppm up to 20.1% were checked in the presence of H_2. The maximum error in the H_2 measurement after correction for O_2 response was 0.7% of full scale. These results were deemed to be acceptable with no further correction for O_2 required.

HYDROCARBONS - The hydrocarbon (HC) content of diesel exhaust is normally quite low; however, activities with lean-NO_X traps and new combustion regimes may result in conditions where the HCs are high enough to be of concern. Many of the HCs in diesel exhaust are species that exhibit a relatively high boiling point, and thus have a relatively low vapor pressure at reduced temperatures. Hence, many of these HCs will be condensed and removed by the chiller used for sample dehumidification. This is a beneficial effect that reduces the impact of these hydrocarbons on the TCD measurement. The chiller is maintained at a temperature of 2 C, and thus will partially condense any hydrocarbons that have a boiling point higher than 2 C. In practical terms, the C_1-C_5 hydrocarbons will be unaffected by the chiller. Hence, it is appropriate to investigate the cross-interference caused by these compounds.

The data from Table 1 show that with the exception of methane, HCs will result in a negative response in the TCD. It is a simple matter to measure both the total HCs and methane in the exhaust with a heated flame-ionization detector (FID). FIDs are typically calibrated with propane as a standard, and also with methane for methane-only modes. FID response to other compounds is not the same as the response for propane, but propane is generally accepted as a representative standard for calibration. The data from Table 1 also show that the TCs of the C_2-C_4 HCs are within 20% of that of propane, suggesting that it is also a possible surrogate for the total HC content that is experienced by the TCD. Methane will cause a positive response by the TCD, and so must be treated separately from the other HCs.

Several data points were taken to characterize the HC concentration after the chiller. This was accomplished by measuring the engine-out HCs with a heated flame ionization detector (HFID). A second HFID was configured to sample the gas stream exiting the chiller. The measurements were made a relatively low engine power setting, but at a variety of exhaust gas recirculation (EGR) levels. The results showed that the post-chiller HC level was never more than 20% of the raw exhaust HC concentration, and most measurements were 5 – 7% of the raw exhaust concentration. Methane production was also very low. Since diesel HCs are generally less than 1% even during extreme modes of operation, the post-chiller HCs should remain less than 1000 ppm under most conditions, although conditions that exhibit fuel reformation and cracking will likely produce more post-chiller HCs. These results

underscore the relatively low impact that the HCs should have on the TCD measurement.

As with O_2, the cross-interferences were investigated by first calibrating the TCD with N_2 and H_2 calibration gases, then introducing methane and propane calibration standards with the gas divider. However, since the methane and propane standards were in a balance of air, rather than nitrogen, the results had to be corrected for the O_2 content. The O_2 content of the diluted methane and propane standards was kept constant by providing a 20.1% O_2 in N_2 standard as the diluent gas for the gas divider. This resulted in nearly constant oxygen content as the methane and propane content was varied. Correction for the O_2 interference was accomplished by measuring the oxygen content with a paramagnetic oxygen instrument in parallel with the TCD. The known oxygen response (Figure 1) was applied and the methane-only and propane-only responses identified. The methane-only response is shown in Figure 5.
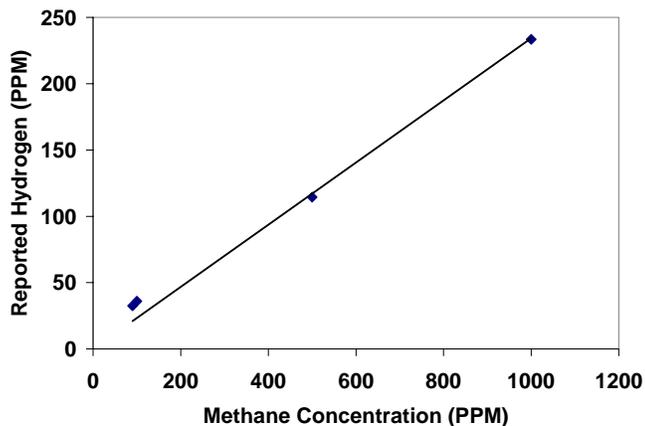
Figure 6. TCD response (as hydrogen) to varying C_3H_8 concentration.

Figure 5. TCD response (as H_2) to varying CH_4 concentration.

The data points on Figure 2 show the individual methane concentrations with a best-fit line (R^2 = 0.9888) also shown. In this case, the TCD again exhibited a positive response as hydrogen. The best-fit line indicates that each part-per-million (ppm) of CH_4 is reported as 0.2343 ppm of H_2. The propane response was obtained in the same way; that is, the propane in air standard was flowed, then the oxygen contribution to the response subtracted resulting in the propane-only response. The results are shown in Figure 6. The TCD exhibits a negative linear (R^2 = 0.9979) response to propane. Each ppm of propane is reported as -0.1004 ppm of hydrogen.
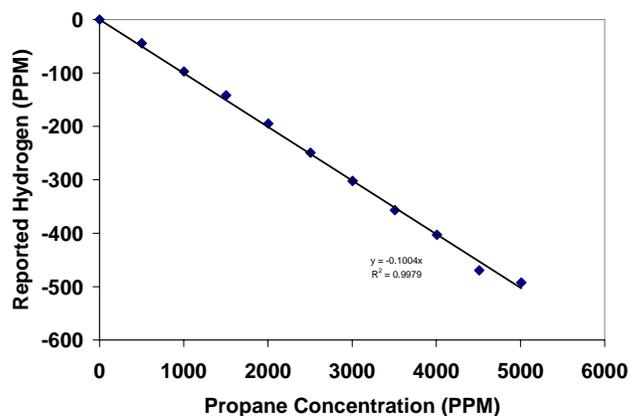
Additionally, a 2500 ppm C_3H_8 standard in balance nitrogen was supplied to the TCD through the gas divider. The gas was flowed at several concentrations and agreed well with the data obtained in balance of air. The C_3H_8 in N_2 standard was also compared with a 1016 ppm C_2H_2 and 1026 ppm C_2H_4 standard, both in balance N_2. The C_3H_8 standard was found to have a more negative response (-70 ppm) at 1000 ppm concentration than either the C_2H_2 or the C_2H_4 standard. The C_2H_4 showed essentially zero response, while the C_2H_2 standard showed a very small (70 ppm) positive response. All three values are within 1% of full scale of each other. These results suggest that for most cases C_3H_8 can be considered a suitable surrogate for the mix of HCs experienced by the TCD with regard to cross-interference correction.

CARBON MONOXIDE – As with HCs, the CO concentration in diesel exhaust is normally quite low; however, non-traditional operating modes for these engines may at times result in CO emissions that are significant to the TCD measurement. The cross-interference caused by carbon monoxide was investigated in the same way as for other gases. In this case, data were collected using both N_2 and 20.1% O_2 in N_2 as diluent gases for the gas divider. The results of both conditions are shown in Figure 7. The TCD exhibits a slightly non-linear response to CO. The data collected with CO diluted with N_2 exhibit a slightly stronger response than when O_2 was present in the mix. Examination of the data showed that the difference between the curves was within the error that could result from a 1% of full-scale error in the oxygen measurement. The response (as H_2) from CO can be calculated as Ax^2+Bx, where A = -4.77×10^{-8} and B = -9.28×10^{-3}. As a quick estimate, the response as H_2 is generally about 1% of the CO concentration.
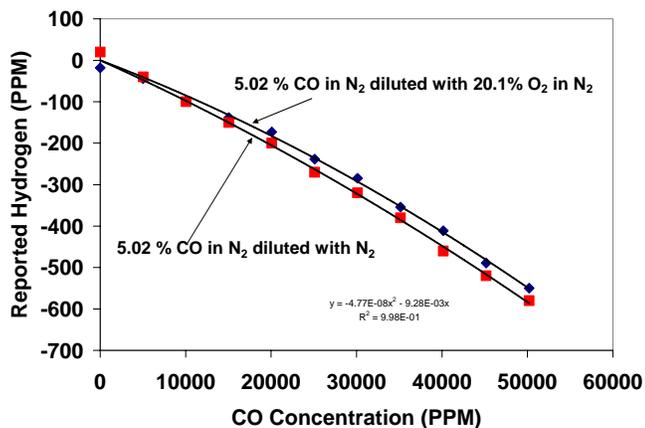
Figure 7. TCD response (as hydrogen) to varying CO concentration.

The chart is labeled with:
- "5.02 % CO in N_2 diluted with 20.1% O_2 in N_2"
- "5.02 % CO in N_2 diluted with N_2"
- $y = -4.77E\text{-}08x^2 - 9.28E\text{-}03x$
- $R^2 = 9.98E\text{-}01$

Axes: Reported Hydrogen (PPM) vs CO Concentration (PPM)

OXIDES OF NITROGEN – NO_X is a problematic pollutant in diesel exhaust that is often present in the hundreds of ppm. The TC of NO suggests it should have little response, but the TC of NO_2 is higher. N_2O is often present as well, but generally at very low concentrations. Cross-interference by these compounds was also investigated, using nitrogen as a diluent in the gas divider. NO caused no significant interference at concentrations as high as 991 ppm. NO_2 interference was also insignificant at concentrations as high as 85 ppm. N_2O was only checked to a concentration of 20 ppm, but also showed insignificant response. Interferences from these compounds could be significant at higher concentrations, particularly with NO_2. The concentrations that were checked for this study were deemed acceptable for the application in which the TCD is being considered.

WATER – Water vapor is a large constituent of engine exhaust and is known to have a large effect on most TCDs. As the TCD being used for this study required a non-condensing sample, the water was mostly removed from the sample by the chiller. An experiment was conducted to investigate the interference caused by water and to verify that any water left after the chiller was not problematic. The gas divider was again used, this time with a humidified nitrogen gas diluted with a dry nitrogen gas. A few points that remained overall non-condensing were investigated. The data showed that the water in the sample caused a positive interference in the TCD. Next, the sample system was fed a humidified nitrogen stream, and the conditioned sample fed to the TCD. The TCD reading remained constant both when the sample stream was humidified and when it wasn't. This result confirmed that although water has a positive response to the TCD, the sample system removes enough water to prevent a problematic cross-interference.

UNCERTAINTY ESTIMATION

The need to correct instrument response for several possible interferences presents the opportunity for error stack-up to be significant. An understanding of the magnitude of the potential uncertainty is important to establishing a lower bound on the measurement that can be relied upon. Taking the square root of the sum of the squares of the errors introduced by each species measurement is widely accepted as an estimate of uncertainty. Performing this calculation and assuming errors of 1% of full scale for O_2, HC, CO, and H_2, plus 4% of full scale (as H_2) for the CO_2 interference yields an uncertainty estimate for this method of 0.083% (830 ppm) H_2, or 4.15% of full scale of the H_2 measurement. This estimate is highly dependent upon the full scale values of these measurements. For the purposes of this calculation (and the application being developed) the full scale values were 25% for O_2, 5% for CO, 1% for HC, and of course 2% for H_2. Including a term to account for CO_2 measurement error in addition to the error estimated from the data in Figure 2 does not impact the uncertainty significantly. In fact, the total uncertainty is dominated by the approximately 4% of full scale error introduced by CO_2. Reductions in the uncertainties of the other species will not significantly reduce the overall uncertainty. Reducing the CO_2 level in the sample stream would have a dramatic effect on the uncertainty, but engine conditions that produce significant amounts of H_2 are almost certain to contain high CO_2 concentrations as well. CO_2 traps for instrumentation are commercially available and may be useful for reducing CO_2 interference with the TCD if lower uncertainty is needed. It may also be possible to reduce the CO_2 cross-interference through inclusion of a fixed amount of CO_2 in both the zero and span calibration gases. This approach could be useful if H_2 producing conditions are found to also produce a sufficiently narrow range of CO_2 concentrations.

DISCUSSION

APPLICATION OF CORRECTIONS – The cross-interference of several gases of concern have been identified for this TCD instrument. The corrections can be applied in data-collection systems, producing a corrected H_2 measurement in-situ, or the corrections can be post-processed to correct the H_2 measurement during subsequent data analysis. In either case, applying corrections to the TCD reading is a straightforward process that is similar to linearization algorithms for non-dispersive infrared (NDIR) instruments. In practice, the O_2 and CO_2 corrections have the most significance, since those species are present in large and variable concentrations relative to other exhaust species.

Although several species have been identified potentially induce a cross-interference for the TCD, most cases result in a conservative measure of the H_2 that is present. O_2, NO_2, and CH_4 are the only species that are likely to be present in exhaust that result in a significant

positive cross-interference for H_2 in the TCD. NO_2 and CH_4 are generally not present at high enough concentrations to cause a significant error. CO_2 also results in a small positive cross-interference because its interference is slightly overcompensated, but produces a negative response in the TCD prior to correction. The other gases of concern (other HCs, CO, NO_X) exhibit very small responses and are also generally present at much lower concentrations. Several of these species taken together are somewhat self-correcting, as some have small positive responses and others small negative responses. Many HCs will be removed by the chiller, further reducing their impact. In fact, it may be appropriate in many cases to simply neglect the small effects from HCs.

PRACTICAL CONSIDERATIONS – The commercial TCD instrument selected for this study is capable of measuring H_2 at levels as low as 200 ppm. However, species present in complex exhaust mixtures result in the uncertainty of the measurement rising to 830 ppm. If H_2 is present at percent levels, this uncertainty level is not problematic. Percent levels of H_2 are likely to be present only during fuel-rich operation of the engine, which is a condition of interest. The relatively high uncertainty is likely to be problematic for conditions where H_2 production might only be a few hundred ppm, such as conditions where high CO concentrations might lead to H_2 production through steam reformation or water-gas shift reaction. Since correction of the cross-interference from O_2 can be corrected with somewhat less uncertainty than that of CO_2, measurements using bag samples diluted with air are likely to be successful provided that the dilution ratio is not too large. Diluting sample bags with N_2 would increase the likelihood of success. A CO_2 trap would almost certainly represent a reliable solution with bag sampling as the CO_2 content of the sample is already reduced compared with undiluted sampling.

Given the measurement uncertainty introduced by the correction of cross-interferences, applications requiring H_2 measurements at low-ppm levels would not be well served by this technique. In these cases, mass spectrometry techniques would be a better selection because they do not suffer from the cross-interferences that give rise to the higher uncertainty for the TCD-based method. However, for steady-state applications where the H_2 concentration is in the thousands of ppm, the TCD method is a reliable, cost-effective technique.

EXHAUST MEASUREMENTS – This approach for H_2 measurement is being used in a project investigating non-traditional combustion regimes for diesel engines. These regimes typically utilize high levels of EGR which can produce high CO levels in the exhaust, especially when used in fuel-rich engine operation. To date, this TCD approach has been utilized for measurements of exhaust H_2 in fuel-lean environments and near-stoichiometric conditions with varying levels of exhaust gas recirculation (EGR), up to 55%. Some of these high-EGR conditions produce large amounts of CO and

may produce H_2 in small amounts. Conditions near (or rich of) stoichiometry may produce more H_2. As discussed previously, the amount of measurement uncertainty generally precludes accurate quantification of the H_2 at levels lower than about 800 ppm. More accurate quantification is possible above that level.

In low-EGR conditions, the TCD method returns H_2 values that were slightly negative, but within 1% of full scale error of zero concentration. A negligible amount of H_2 would be expected at these fuel-lean, low-CO (<800 ppm) conditions. This response is encouraging, especially given that the CO_2 levels at these conditions were generally about 6.5%.

As the EGR was increased, both CO and CO_2 increased. The TCD instrument also showed an increased H_2 measurement. The H_2 measurement was 600 ppm after correction for O_2, CO, CO_2, and HCs. Comparing this measurement with another point of similar CO_2 concentration but lower H_2 (185 ppm) showed that the increase in H_2 between the two points was higher than the expected increase in error due to the CO_2 increase between the two points. This suggests that ppm-level concentrations of H_2 are likely present, but absolute quantification at these levels wasn't possible. A comparison between this approach and a mass-spectrometer approach cited earlier (4) would validate the TCD method for lower levels of H_2, and is being planned for future studies. H_2 was found to increase as the air/fuel ratio was decreased. Concentrations in excess of 4,000 ppm were produced as the engine approached stoichiometric conditions. This concentration is about 5 times higher than the maximum measurement uncertainty, showing that the instrument can detect and quantify H_2 in engine exhaust that results from combustion. However, there was no means of independently assessing the accuracy of the measurement. Several air/fuel ratio conditions were examined with the gas sample taken behind an oxidation catalyst to assure that variations in air/fuel ratio (lean of stoichiometry) were themselves not causing false H_2 measurements. Insignificant H_2 was expected at these conditions, and the instrument reported slightly negative values within 1% of full scale error of zero concentration.

A short experiment was conducted in an attempt to validate H_2 measurements in engine exhaust in a controlled manner. The instrument was used to measure exhaust gas at a fixed engine condition that was unlikely to produce significant amounts of H_2. H_2 calibration gas was introduced at varying levels into the sample stream with the engine exhaust. The methodology reported here was used to correct the instrument reading for cross-interferences caused by the presence of O_2 (~14%) and CO_2 (~6%). The O_2 and CO_2 concentrations varied slightly as the amount of H_2 calibration gas was varied. The resulting concentrations were within 200 ppm of the correct values for all conditions examined (up to 2500 ppm). Further efforts to reduce the error and uncertainty in the H_2

measurement are ongoing, including the use of a molecular sieve CO_2 trap.

CONCLUSIONS

- Several gases present in engine exhaust produce cross-interferences for TCD-based H_2 measurements, but these interferences were corrected with measurements from instrumentation typically in place in engine research facilities.

- The TCD response time is sufficient for using the instrument for steady-state sampling applications.

- Uncertainty estimation shows that the TCD can produce reliable H_2 measurements at H_2 concentrations in the thousands of ppm, but measurement uncertainty may be too high at concentrations in the hundreds of ppm.

- It may be possible to further reduce uncertainty and error introduced by the presence of high levels of CO_2.

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