

Diode Laser Based Formaldehyde Measurements in a Catalytic Trace Contaminant Control System

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ABSTRACT

The development of a portable diode laser based gas sensor and its application to sensitive, selective, on-line monitoring of formaldehyde concentrations present in a catalytic Trace Contaminant Control System (TCCS) in a 5-day period in August 1999 is reported. The TCCS was originally developed for the Lunar-Mars Life Support Test program in 1996-1997 at NASA-JSC. The motivation for monitoring H₂CO levels in a sealed human rated environment is that its presence can cause headaches, throat and ear irritation at low concentrations (>100 ppb), and more serious adverse effects at higher concentration levels. Consequently, NASA has established a spacecraft maximum allowable H₂CO concentration of 40 ppb for crew exposure for a 7 to 180 days period [1].

INTRODUCTION

The spectroscopic detection and quantification of numerous trace gas species has become an important aspect in many NASA, industrial, urban, and environmental applications. There is a need to selectively detect several different molecular gas species simultaneously, by means of a single, tunable and portable sensing device capable of high sensitivity (at ppb levels), room temperature and rapid response time. To meet this need, a narrow-linewidth mid-IR spectroscopic source based on difference-frequency generation (DFG) of two near-IR diode lasers in a nonlinear optical material such as periodically poled lithium niobate (PPLN) has been developed by the Rice group [2-4]. Specifically, the sensor was applied to real-time H₂CO concentration measurements in the presence of hydrocarbons and water on a catalytic trace control contaminant system located at TDA Research, Inc., the builders of the TCCS system. The diode laser based

gas sensor was transported to TDA in Wheat Ridge, Colorado, and operated for a five-day period at TDA Research, Inc., August 16-10, 1999. The sensor was used along with a gas chromatograph and an on-line CO/CO₂ analyzer to evaluate samples of Englehard VoCat catalyst, which had been used in a 90-day human rated Lunar-Mars life support chamber test in 1997 at NASA-JSC [5]. Activity and selectivity measurements were made on samples of catalyst that had been used in the environmental test and compared to results obtained with a previously unused catalyst. Measurements also were made on samples of used catalyst that had been regenerated by heating in air at temperatures of 450°C and 260°C. In all tests, a feed consisting of 11 ppm methanol in air was flowed over the catalyst at a gas hourly space velocity of 8000 h⁻¹ and at temperatures up to 260°C. These conditions are representative of those employed during the 1997 human rated NASA-JSC chamber tests.

GAS SENSOR CONFIGURATION

The gas sensor developed for field operation, as depicted in Fig. 1, utilizes as pump sources both a fiber pigtailed widely tunable 25 mW external cavity diode laser (ECDL) operating from 814 to 870 nm and a fiber pigtailed Distributed Bragg Reflector diode laser (DBR) operating at 1083 nm wavelength. The fiber coupled output power of ~15 mW from the DBR diode laser is increased to 600 mW by a Yb-fiber amplifier using a 2W diode pump laser at 975 nm [6]. Both the ECDL and amplified DBR diode laser fiber coupled beams pass through polarization controllers before being combined using a four-port fiber beam coupler. Two percent of the combined beams are available for sensor diagnostics, such as wavelength calibration. The other 98% are directed to a ruggedized DFG-conversion stage. The collinear pump beams are imaged into the temperature

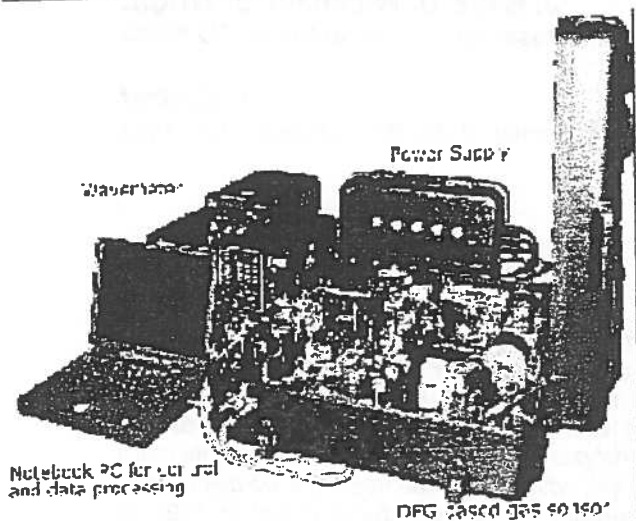
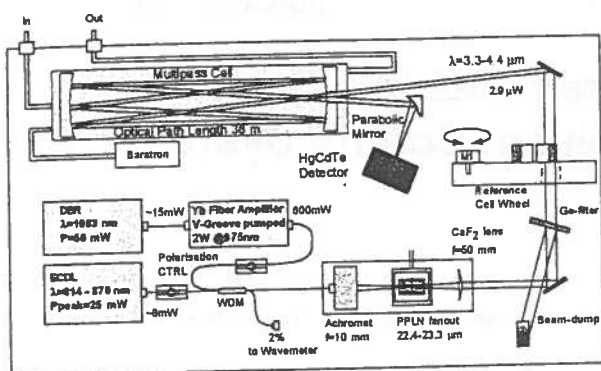


Fig. 1: Schematic and photograph of the DFG-based gas sensor

controlled antireflection coated periodically poled LiNbO_3 [PPLN] crystal using a $f=10$ mm achromatic lens. Both single mode fiber launched pump and signal beams possess gaussian beam profiles and when mixed in a 19 mm long PPLN crystal, produce a diffraction limited mid-IR DFG-beam of $\sim 2.9 \mu\text{W}$ power with a ~ 40 MHz linewidth at a wavelength of $\sim 3.5 \mu\text{m}$ [2]. The DFG beam is then collimated using a $f=50$ mm CaF_2 lens, passing through a Ge-filter to block the unconverted pump beams and directed to a multi pass cell (physical length ~ 30 cm, actual path length: 18 m or 36 m) for direct absorption spectroscopy at a reduced pressure (~ 80 Torr). The sensor was calibrated against a Scott Specialty H_2CO certified standard of 772 ppb, which was verified by permeation tube calibration procedures available at the National Center for Atmospheric Research (NCAR), Boulder, within the given accuracy of $\pm 5\%$ of the Scott standard mixture. Furthermore, the fast measurement response time of typically 5-10 seconds, including averaging and automated data processing, allows real time monitoring. The sensor is operated and controlled using LabVIEW software code running on a laptop PC. A 16 bit PCMCIA data acquisition card is used to acquire the absorption signal synchronized to a trigger signal, the gas sampling pressure and temperature. The card also controls a shutter via a digital TTL line for background light subtraction necessary for absolute spectroscopic absorption measurements. The entire sensor including both optical

and electronic elements is packaged into a suitcase with outside dimensions of $61 \times 53 \times 20$ cm. and weighing 25 kg. An additional small suitcase ($30 \times 25 \times 14$ cm) contains a diaphragm pump and mass-flow controller which are used for extractive gas sampling at reduced pressure for optimum spectral selectivity and sensitivity.

EVALUATION OF TRACE CONTAMINANT CONTROL SYSTEM (TCCS)

The laser based DFG multi-component gas sensor optimized for real-time formaldehyde concentration measurements at the ppb level near $3.5 \mu\text{m}$ (2831.6 cm^{-1}) was installed on the TCCS test rig at TDA Research, Inc. (Wheat Ridge, Colorado) as shown in Fig. 2 and operated for a period of five days (August 16-20, 1999). The purpose of this investigation was to determine if the VoCat catalysts used during the 1997 NASA-JSC 90 day Lunar Mars comprehensive life support test in a 20 foot chamber [2] had been affected by their use in these tests. To accomplish this, samples of catalyst used at JSC were tested and compared to samples of previously unused catalyst along with used catalyst that had been regenerated by treatment in air at either 260°C or 400°C . All catalyst samples were tested using a feed consisting of 10-12 ppm methanol in air at a flow rate of 6.25 SLPM corresponding to a gas hourly space velocity of 8000 h^{-1} . Water was added to the feed to saturate the feed to 50% relative humidity. The experimental arrangement in Fig. 2 shows the DFG based gas sensor connected to the outlet of the catalytic converter installed on the TDA-TCCS test rig.

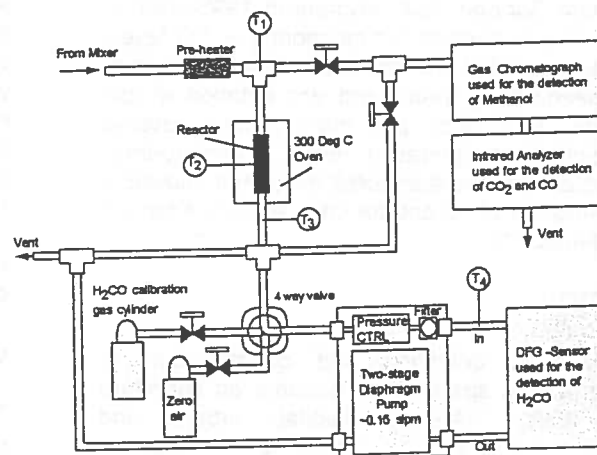


Fig. 2: Schematic of the TCCS and DFG based gas sensor system (colored) experimental set-up

In order to ensure accurate operation of the DFG based gas sensor for the selective detection of formaldehyde, two gas cylinders containing a calibration mixture (Scott Specialty gases, $\text{H}_2\text{CO}=772$ ppb balanced with 66.1 ppm CH_4) and a zero air gas mixture (Scott Specialty gases, TechniPure) were installed, respectively. Either gas cylinder was periodically switched into the sample line of the DFG based gas sensor using a 4-way valve switch to ensure calibration and selectivity to potentially interfering gases. The continuous sample gas flow through the

DFG-sensor was provided by a compact flow control system (built inside a small suitcase) that consists of a two-stage diaphragm pump, a flow controller and micro-particle filter. For the detection of methanol and CO/CO₂ a gas chromatograph (SRI instruments, FID detector, Detection limit: 1 ppm @S/N=5) and an infrared analyzer (ZRH, California Analytical, range: 0-200 ppm ± 2 ppm) were alternately connected to the catalytic reactor input and output. Furthermore, thermocouples were placed at various TCCS/DFG based gas sensor control and sampling positions as indicated in Fig.2 by T1 to T4. The catalytic conversion efficiency of MeOH to CO₂ was used as an indicator, representing a range of VOC's to be oxidized by the catalyst under investigation.

Table1

#	Variable / Sensor	Location / Description
1	Temperature / Thermocouple	T1 / Inlet, Pre-heater
2	Temperature / Thermocouple	T2 / Reactor
3	Gas Temperature / Thermocouple	T3 / Outlet
4	MeOH / GC	Inlet & outlet of reactor, Gas Chromatograph, ZRH, California Analytical, range: 0-200 ppm
5	CO ₂	Inlet & outlet of reactor, SRI instruments, FID
6	Flow-rate / Flow-meter	Inlet of reactor
7	Flow-rate / Flow-meter	Outlet of GC / IR Analyzer
8	H ₂ CO / DFG-sensor	Outlet of reactor
9	Gas Temperature / Thermocouple	T4 / Inlet DFG-sensor
10	Pressure / Baratron	DFG based gas sensor / sampling gas pressure
11	Temperature / Thermistor	Adjacent to DFG based gas sensor / Ambient room temperature
12	Absorption line position / DFG-sensor	DFG based gas sensor / Software detected absorption peak position, stability indicator
13	Detector bias voltage / DFG-sensor	DFG based gas sensor / Bias signal off-set, stability indicator
14	DFG-probe signal / DFG-sensor	DFG based gas sensor / Optical probe power, stability indicator

For an evaluation of the performance of different used and new VoCat's (Volatile organic Catalyst) in the TCCS system the following parameters were acquired by the TCCS and DFG based gas sensor system as listed in Table 1.

The parameters #1 to #7 are indicators used for the control of the TCCS, whereas #8 to #14 are required input parameters to compute the absolute formaldehyde concentration and are stability indicators of the DFG

based gas sensor. It should be noted that an unrelated experimental rig with two 500 °C heaters, situated 4 m away from the TCCS rig, caused changes of room temperature, competing with the laboratory air conditioning system. In order to correlate any direct temperature perturbation to the operation of the DFG-sensor an additional calibrated thermistor was placed adjacent to the DFG-sensor.

EXPERIMENTAL RESULTS

During the five day testing period of the TCCS under different conditions and use of different VoCat samples, the DFG based gas sensor operated daily 8 to 11 hours. Only one power glitch caused by a thunderstorm shut down the external cavity diode laser (ECDL). However, operation was restored instantly without any adjustment or noticeable effects of wavelength or power drifts.

Also, higher room temperature caused the development of optical fringes due to thermal expansion that were not observed at lower temperatures. This limited the sensitivity to minimum detectable concentrations of 30 - 50 ppb on the average for S/N=1. In case of unconverted methanol at the output of the reactor, the formaldehyde sensitivity is determined by the methanol concentration at the reactor output¹ (e.g. $c_{H_2CO}=4000$, $c_{eff}=50\%$, \Rightarrow 400 ppb (10% error)).

For each test, the formaldehyde concentration and catalytic reactor temperature is plotted vs time. In a separate figure the conversion efficiency of MeOH² and formaldehyde selectivity³ is plotted vs reactor temperature and time.

H₂CO CONCENTRATION MEASUREMENT OF A USED VOCAT [TEST 1]

In this measurement a VoCat sample used at NASA-JSC, was investigated. The formaldehyde concentration was monitored at different reactor temperatures ranging from 180 to 260 °C. Starting at a reactor temperature of 180 °C, the temperature was increased in steps of 10 °C to 260 °C. Fig. 3 shows that the TCCS formaldehyde generation directly tracks the applied temperature profile. When the temperature was increased from 180 to 190 °C at 11:45h, the TCCS feedback circuit followed a

1 MeOH limited sensitivity (ppb) =

$$\frac{c_{MeOH}^{inlet} (ppb)}{15} \left(1 - \frac{\eta_{eff} (\%)}{100} \right)$$

2 MeOH conversion efficiency η_{eff} (%)

$$= \frac{c_{MeOH}^{inlet} (ppb) - c_{MeOH}^{outlet} (ppb)}{c_{MeOH}^{inlet} (ppb)} \cdot 100$$

3 Formaldehyde selectivity (%) = $\frac{c_{H_2CO}^{outlet} (ppb) \cdot 100}{C_{MeOH}^{oxidized}}$

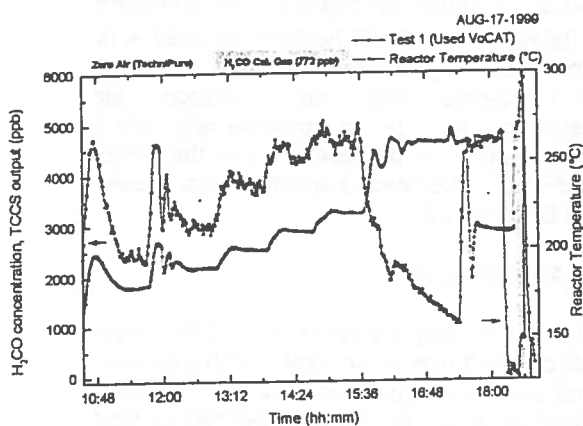


Fig. 3: Formaldehyde and catalyst temperature trend observed in Test 1

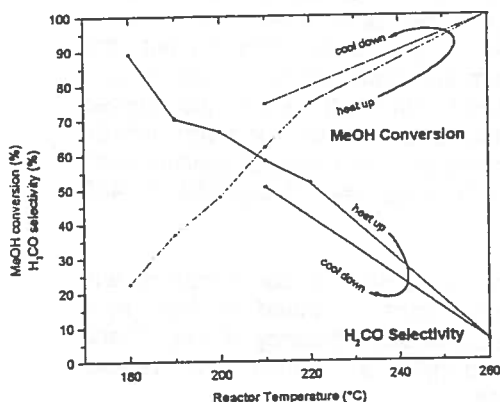


Fig. 4: TCCS activity in Test 1

harmonic oscillation relaxation function and settled at the pre-set temperature 35 minutes later. This relaxation time was reduced to ~5 minutes as the feedback circuit was optimized. Temperature changes of ~1 °C resulted in a ~150 ppb change of the formaldehyde concentration as measured by the DFG based gas sensor. When the reactor temperature was set to 260 °C, the formaldehyde concentration decreased and reached a level of 1 ppm after 95 minutes. At this point the reactor temperature was further reduced to 210 °C to determine whether the catalyst surface was regenerated at 260 °C. This was not the case, since the formaldehyde concentration quickly increased to a comparable high level of 4.5 ppm that was observed earlier in the test.

Fig.4 summarizes the percent methanol converted and the selectivity for formaldehyde as a function of reaction temperature. The figure shows that, as the temperature is increased from 180°C to 260°C, the selectivity for formaldehyde decreases and the methanol conversion increases. At 180°C the catalyst has low activity and high selectivity for formaldehyde. It shows further that at 180°C the catalyst converts only 20% of the methanol in the feed and 90% of the methanol converted forms formaldehyde. More favorable results are obtained at

higher temperature. When the temperature is increased to 260°C the percent conversion is increased to 100% and the selectivity for formaldehyde is less than 10%.

MEASUREMENT OF REGENERATED VOCAT FOR FORMALDEHYDE SELECTIVITY [TEST 2]

At the conclusion of Test 1, the same used catalyst was heated to 450°C in a 1 SLPM flow of air for 16 hours and then retested to determine its activity for methanol conversion and its selectivity for formaldehyde. The sample was tested at 180°C and 260°C using a feed composition and flow rate identical to that used in Test 1.

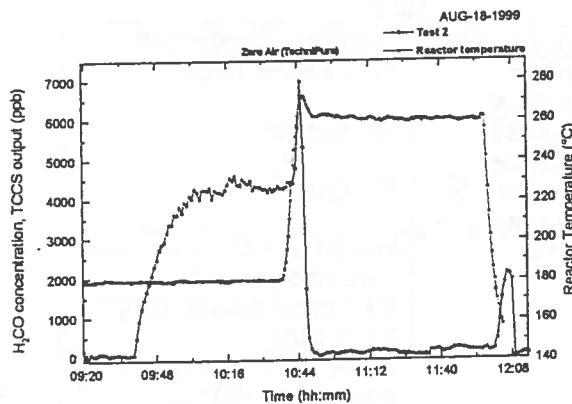


Fig. 5: Formaldehyde and catalyst temperature trends in Test 2

The results of this test are shown in Fig. 5. The figure shows that at a temperature of 180 °C, the formaldehyde concentration increased and leveled off at about 4.5 ppm. When the reactor temperature was increased to 260°C, the formaldehyde concentrations were reduced to about 100 to 200 ppb with a background noise level corresponding to 40 ppb (S/N=1) as determined by zero air sampling from 11:23h to 11:35h. Compared to the previous day, the concentration was about 5 to 10 times less at the same reactor temperature. At 12:07h the temperature was again reduced and caused an increase of the formaldehyde concentration. The test was then terminated.

Fig. 6 shows percent methanol conversion and selectivity for formaldehyde during the test. The figure shows that at 180°C, the percent conversion initially is close to 100%. However, during the time at 180°C, the percent conversion decreases, reaching a value of about 70% after about 1 hour 20 minutes at 180°C. Comparison of the activity measured during this test at 180°C to that obtained in Test 1 at the same temperature shows that regenerating the catalyst by heating it in air increased the activity from about 10% to at least 70%. At 260°C the conversion is steady at 100%. Prior to regeneration, Fig. 4 shows that 100% activity was also obtained at this temperature. Fig. 6 also shows that the selectivity for formaldehyde is lower after regeneration. The formaldehyde level increases from 30% to 50% during the one hour and 20 minute period at 180°C and was

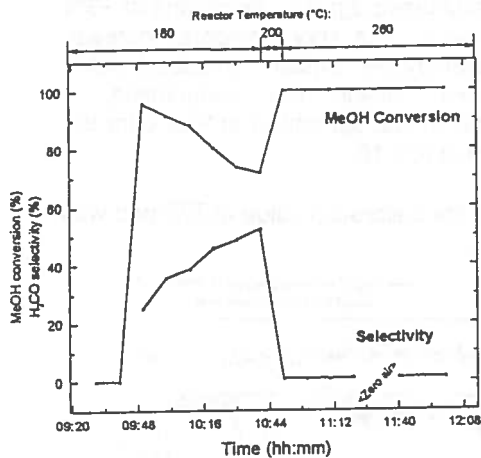


Figure 6: TCCS activity / efficiency in Test 2

less 1% at 260°C. Before the catalyst was regenerated however, the catalyst selectivity was approximately 90% at 180°C, and 10% at 260°C.

The data presented in Fig.5 and Fig.6 clearly show that the regeneration step, which consisted of heating the catalyst to 450°C in air for 16 hours had two beneficial effects. First, it increased the catalyst activity at 180°C. Second the regeneration step produced significant reductions in formaldehyde selectivity at both 180°C and 260°C.

MEASUREMENT OF USED VOCAT. THE CATALYST IS INSTALLED AND HEATED TO 260 °C AND MAINTAINED FOR 22 HOURS [TEST 3]

In Test 3, a second sample of used VoCat catalyst was regenerated, by heating it in air for an extended period of time. However, in this case, the catalyst was heated only to 260°C, which is the maximum temperature possible in the NASA TCCS system. Thus, this test provides a more realistic simulation of a catalyst regeneration procedure that could be carried out during a mission. As was the case in Test 2, the catalyst is exposed to a feed of 11 ppm methanol in air at a gas hourly space velocity of 8000 h⁻¹, however activity and selectivity

measurements were made only at 260°C.

The results of this test are shown in Fig.7 and Fig.8. Fig. 7 shows the concentration of formaldehyde increases rapidly as the catalyst temperature is heated to 260°C, reaching values of up to 8 ppm. However, after about 15 minutes at temperature, Figure 7 shows that the formaldehyde concentration decreases rapidly reaching a value of 1 ppm at steady state.

Fig.8 shows the percent methanol conversion and formaldehyde selectivity during Test 3. The figure shows that the selectivity follows the formaldehyde concentrations shown in Fig.7. The selectivity reaches a maximum of about 80% as the catalyst is heated to 260°C, and then decreases rapidly reaching a steady state value of about 10%. The percent methanol conversion is 100% during the entire test (Fig.8).

Comparison of selectivity data presented in Fig.6 and Fig.8 allows us to compare the effect of regenerating the catalyst at 450°C and 260°C. Fig. 6 shows that following regeneration at 450°C, the catalysts selectivity for

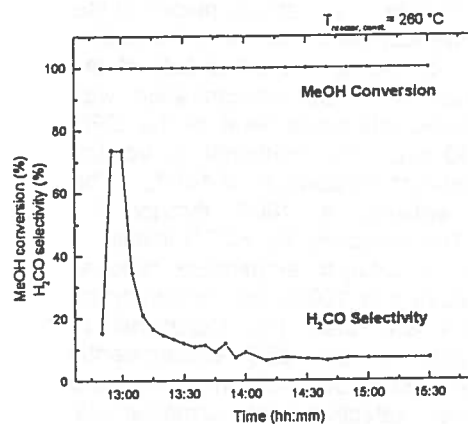


Figure 8: TCCS activity / efficiency in Test 3

formaldehyde at 260°C is less than 1%. On the other hand, Fig. 8 shows that regeneration at 260°C is not as effective, resulting in a selectivity of 10% at 260°C. Moreover, the results of Tests 1, 2 and 3 show that regenerating the catalyst samples used in the JSC closed environmental test reduced the selectivity for formaldehyde and produced higher catalyst activity compared to results obtained with a used catalyst sample that had not been regenerated. In addition, the results indicate that 450°C is a more effective regeneration temperature than 260°C.

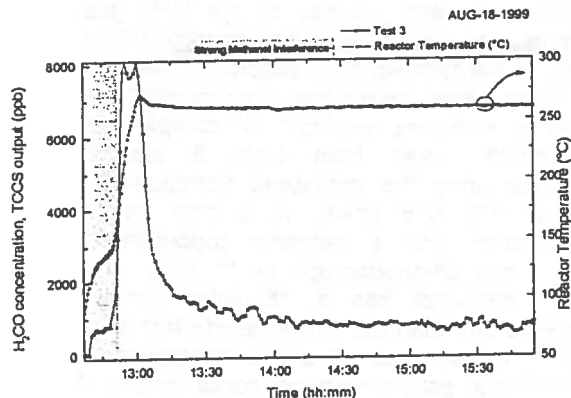


Figure 7: Formaldehyde concentration and catalyst temperature trend for Test 3

At 4:00 am on 8/19/99, 15 hours into the test, the air flow stopped. The air flow was re-established at 10:30 am and the test continued as "Test 3b". The results of this test are shown in Fig.9. This figure shows that formaldehyde levels ranging between 0.4 ppm and 0.8 ppm were measured after the air flow was reestablished. The levels are not significantly different from those

obtained in Test 3, and show that the catalyst was not affected by the lack of air flow.

TEST OF NEW VOCAT CATALYST SAMPLE [TEST 4]

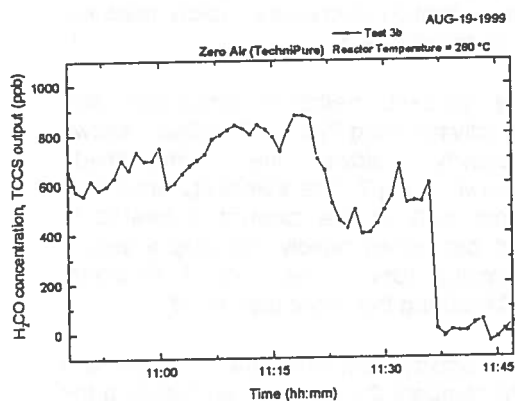


Figure 9: Continued formaldehyde concentration for Test 3b. Steady state parameters: 100% MeOH conversion, 6.5 % H₂CO selectivity.

A previously unused sample of VoCat was placed in the reactor and tested under conditions similar to those that were used in Tests 1-3. During the entire test of the unused sample VoCat the H₂CO concentration was below the minimal detectable noise level of the DFG based gas sensor (30 ppb). The methanol conversion reached 100% at a catalyst temperature of 100°C. The percent conversion remained at 100% through the duration of the test. The selectivity for H₂CO initially is about 5%, but once the catalyst temperature reaches 100°C, and the conversion is 100%, the selectivity for formaldehyde remains less than 1%. Compared to catalysts samples used in the JSC environmental chamber tests, the unused VoCat is much more active and has much lower selectivity for formaldehyde. However Fig.4 and Fig.6 show that regenerated and non regenerated catalysts required much higher temperatures to obtain 100% activity. Fig. 4 shows that the non regenerated catalyst required a temperature of 260°C for 100% activity and Fig.6 shows that at 180°C, the regenerated catalyst converted only 75% of the methanol at 180°C. In addition, at temperatures of 100°C and greater, the selectivity of the unused catalyst for formaldehyde was less than 1%. However the selectivities of the used catalysts were much greater. The non regenerated catalyst was 90% selective for formaldehyde at 180°C (Fig.4), while the catalysts regenerated at 450°C showed a selectivity that increased from 30 to 60% in a one hour 20 minute period at 180°C.

FINAL CALIBRATION

A formaldehyde gas calibration was carried out using a 772 ppb H₂CO calibration mixture. The concentration measured by the DFG based gas sensor reached the calibration value after 40 minutes. For the subsequent 8 minutes, the readings exceeded the calibration value up

to 14 % and then decreased again to deviations of ~3% of the calibration value. This short temporal increase may have been caused by the formation an optical etalon in the DFG based sensor. For comparison, a formaldehyde calibration test performed at Rice prior the test at TDA is shown in Fig. 10.

The 4.5 % off-set to the calibration value of 772 ppb was

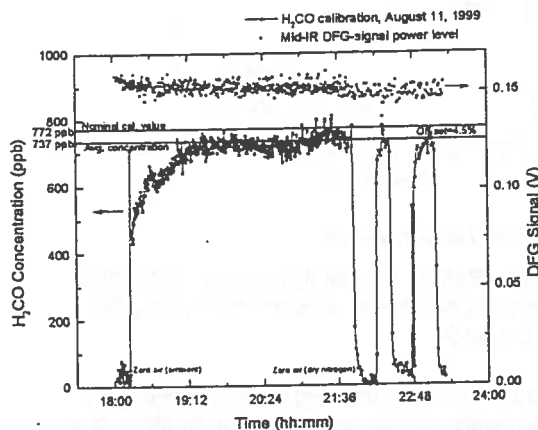


Figure 10: Calibration of the DFG based gas sensor for formaldehyde

adjusted for the test at TDA and was due to an inaccurate absorption linestrength given in the Hitran 1996 spectroscopic database. In addition the formaldehyde calibration gas cylinder was tested using a different laser based sensor at NCAR, Boulder, CO. A calibration value of 762 ppb ± 5% was determined, which agrees with the value provided by the manufacturer of the calibration gas cylinder (Scott Specialty Gases, Inc.) and the concentration measured by the DFG based gas sensor.

METHANOL INTERFERENCE

During the individual VoCat sample test series the methanol conversion efficiency is shown to be a function of the catalyst temperature. During warm-up or cool down cycles, methanol levels of up to 10 ppm were present at the TCCS output. These high levels of methanol vapor were also detected by the DFG gas sensor in form of three distinct methanol absorption lines in close vicinity to the formaldehyde absorption line. For comparison, Fig.11 shows an overlay of a formaldehyde spectrum with a methanol spectrum of comparative absorption strength taken from tests 5 and 3 respectively. Comparing the measured formaldehyde concentration of 730 ppb (taken at a time before reaching equilibrium) and a methanol concentration measured by a gas chromatograph of 11 ppm, it is estimated that methanol has a 15 times weaker absorption linestrength than the formaldehyde transition at 2831.6 cm⁻¹. In the case of a low formaldehyde concentration of ~100 ppb, a methanol concentration of 1.5 ppm would cause an uncertainty of 100%. However, at higher formaldehyde levels such as at the ppm level as observed in Test 1, a methanol interference of 1.5

ppm would only introduce a systematic error of less than 10 %.

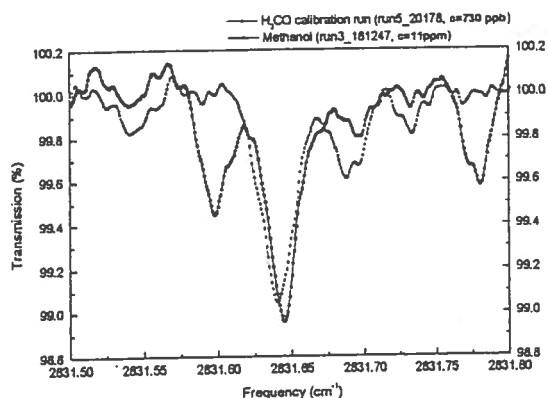


Figure 11: Overlay of methanol and formaldehyde absorption spectra of comparable absorption strengths

SUMMARY AND CONCLUSION

This work describes state of the art gas sensor technology based on direct laser absorption spectroscopy and its role in optimizing a TCCS prototype for the International Space Station (ISS) program. Formaldehyde concentration measurements conducted during the 90-day Phase III Life Support test program at NASA-JSC in 1997 showed levels of 20 to 30 ppb and between 50 and 70 ppb for the last 30 days of the test. After 83 days into the test, the output of the TCCS in the human rated test chamber was also monitored and showed unexpectedly high H_2CO levels [2]. Details are given for a second generation diode laser based gas sensor architecture that is compact and robust, utilizing the latest commercially available optical fiber beam delivery and fiber amplifier technology from the telecommunications industry. This sensor was used to investigate possible H_2CO formation over used and regenerated monolith catalyst, taken from the 90 day chamber test TCCS, as well as fresh catalyst from the same lot. Tests were carried out at TDA Research over a five-day period in August 1999. Measurements were made at a gas hourly space velocity of $8,000\text{ h}^{-1}$ and at temperatures up to 260°C , conditions representative of those employed in the chamber tests.

The test results showed that catalysts samples, which had been used in the 1997 TCCS test at NASA-JSC were much less active for methanol conversion at all temperatures and also showed much higher selectivity for formaldehyde compared to the sample of previously

unused VoCat catalyst. For example, at 180°C the catalyst used in the TCCS test converted only 20% of the methanol in the feed and had 90% selectivity for formaldehyde. By contrast, the previously unused catalyst converted 100% of the methanol and had a selectivity of less than 1% for formaldehyde at the same test temperature. (Greater than 99% of the methanol was converted to CO_2 .) Regenerating used catalyst samples by heating the catalyst in air appeared to increase activity and reduce selectivity for formaldehyde. A VoCat sample regenerated at 460°C had 70% activity and 50% selectivity at the end of a 1-hour, 20-minute period at 180°C . In addition, a sample regenerated at 260°C was more active and less selective for formaldehyde at a test temperature of 260°C compared to a non-regenerated sample used in the TCCS tests.

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