(NASA-CR-199959) FTIR INSTRUMENTATION TO MONITOR VAPORS FROM SHUTTLE TILE WATERPROOFING MATERIALS (I-NET) 12 p

N96-17346

Unclas

G3/35 0095135

NASA-CR-199959

FTIR INSTRUMENTATION TO MONITOR VAPORS FROM SHUTTLE TILE WATERPROOFING MATERIALS *

C. B. Mattson and C. J. Schwindt
I-NET Space Services, Inc.
John F. Kennedy Space Center, Florida

ABSTRACT

The Space Shuttle Thermal Protection System (TPS) tiles and blankets are waterproofed using DimethylEthoxySilane (DMES) in the Orbiter Processing Facilities (OPF). DMES has a Threshold Limit Value (TLV) for exposure of personnel to vapor concentration in air of 0.5 ppm. The OPF high bay cannot be opened for normal work after a waterproofing operation until the DMES concentration is verified by measurement to be below the TLV. On several occasions the high bay has been kept closed for up to 8 hours following waterproofing operations due to high DMES measurements. In addition, the Miran 203 and Miran 1BX infrared analyzers calibrated at different wavelengths gave different readings under the same conditions. There was reason to believe that some of the high DMES concentration readings were caused by interference from water and ethanol vapors The Toxic Vapor Detection Laboratory (TVDL) was asked to test the existing DMES instruments and identify the best qualified instrument. In addition the TVDL was requested to develop instrumentation to ensure the OPF high bay could be opened safely as soon as possible after a waterproofing operation.

A Fourier Transform Infrared (FTIR) spectrophotometer instrument developed for an earlier project was reprogrammed to measure DMES vapor along with ethanol, water and several common solvent vapors. The FTIR was then used to perform a series of laboratory and field tests to evaluate the performance of the single wavelength IR instruments in use. The results demonstrated that the single wavelength IR instruments did respond to ethanol and water vapors, more or less depending on the analytical IR wavelength selected. The FTIR was able to separate the responses to DMES, water and ethanol, and give consistent readings for the DMES vapor concentration. The FTIR was then deployed to the OPF to monitor real waterproofing operations. The FTIR was also used to measure the time for DMES to evaporate from TPS tile under a range of humidity conditions in controlled laboratory tests.

The combination of laboratory and field tests with the FTIR instrument demonstrated superior sensitivity, ability to reject interference from water and ethanol vapors, ruggedness to be transported from the lab to the OPF and set up without special procedures or degradation of performance. The multiple component vapor analysis algorithm was developed at KSC and incorporates automatic baseline correction and shape fitting of the spectra. The analysis for DMES, TetraMethylDiSiloxane (TMDS), ethanol, methanol, isopropanol and baseline parameters uses 161 points per sample at 4 cm^{-1} resolution, and processes an eight scan sample every ten seconds. The standard deviation of the measurements is 0.013 ppm and the upper linear limit is 125 ppm DMES. Based on successful demonstration of capabilities we produced three mobile instrument carts to be used in each OPF to support future waterproofing operations. The design and building of the "DMES Carts" were accomplished in Fiscal year 1995.

INTRODUCTION

The processing of the Space Shuttle between flights is performed at KSC, and one of the major processes is the re-waterproofing of the Orbiter Thermal Protection System (TPS). The TPS consists of tiles, fiber blankets and felt materials made of silica . The TPS materials are capable of absorbing several times their weight in water. Water in the TPS can cause many problems including increased weight at launch, loss of insulation capability, and damage to the TPS from freezing or evaporation. To prevent absorption of water the TPS is waterproofed with one of several silane or siloxane products at different steps in the process all of which coat the silica surface with a hydrophobic layer of methylated silicon. The hydrophobic property of this treatment is lost during Shuttle re-entry

Distribution authorized to U.S. government agencies and their contractors; administrative/operational use; December 1995. All requests for information shall be directed to John F. Kennedy Space Center, Florida 32899.

* This work was performed under contract NAS10- 11943 at John F. Kennedy Space Center, Florida

to the atmosphere as the methyl groups are pyrolized at the high temperatures which occur. The chemistry of these processes will not be elaborated here. The result is that every Orbiter must be re-waterproofed after every flight, and the material used is DMES. This paper discusses the development of a system to monitor DMES vapor concentration in air for control of personnel exposure following re-waterproofing of the Orbiter in the OPF.

PROBLEMS WITH DMES IN THE OPF

Because of complaints from workers, the allowed concentration of DMES vapor in the OPF has been reduced from 5.0 to 0.5 ppm. The TPS waterproofing work is done on third shift and weekends to allow time for vapors to disperse prior to the start of first shift. The DMES concentration must be verified by measurement before unprotected workers are allowed into the area. On several occasions measurements of DMES vapor above 0.5 ppm were observed well past the normal start of work. This did not cause delays in Shuttle processing schedule but added to processing cost due to unproductive time of 30 to 50 workers. On one occasion workers were kept out of the OPF for most of the first shift. The proposed Threshold Limit Value (TLV) for DMES is based on complaints of workers on the shift following re-waterproofing.

The problem was complicated by the fact that DMES concentrations were being measured with non-dispersive IR (NDIR) instruments at four different analytical wavelengths. As a consequence, "DMES" measurements in the same area, using different instruments calibrated for neat DMES, gave different readings in the field. The field instruments were originally specified to measure the previous allowed concentration of 5.0 ppm and were recalibrated by the manufacturer for 0.5 ppm measurements. The problem was probably aggravated by this extension of the original capability by an order of magnitude.

We were asked to determine the nature of the instrumentation discrepancies and to come up with a reliable, operational way to measure DMES vapor in the OPF. This paper summarizes the results of both of those efforts and describes the operational instrument system that resulted.

PRELIMINARY TESTS

Previous development work on FTIR analytical software[1] and fieldable hardware made FTIR the method of choice to approach this problem. An existing FTIR instrument was calibrated for DMES and its known by-products and was used in a series of laboratory and field tests. Preliminary tests were performed in the TVDL to evaluate the causes of discrepancies encountered in the OPF measurements and to determine the feasibility of using FTIR instruments to support waterproofing operations. Subsequent field tests gave quantitative data on the capability of the FTIR instruments in the field.

PROPERTIES OF DMES AND ITS REACTION PRODUCTS

The chemistry of DMES and other silicon compounds used for TPS waterproofing have been studied in some detail in work funded by Johnson Space Center.[2] The reaction with silica surface and produces ethanol, and water and (surface catalyzed*) reaction with water produces TMDS. DMES has a boiling point of 51 C, a flash point of -5 C, a specific gravity of 0.757 and a proposed TLV of 0.5 ppm.[3] TMDS has a boiling point of 70 to 71 C, a flash point of -9 C, a specific gravity of 0.760 and no established TLV.[4] Ethanol has a boiling point of 173 F, a flash point of 57 F, a specific gravity of 0.734 and a threshold limit value of 1000 ppm. All three of these compounds absorb light in the infrared. Figure 1 shows the IR spectrum of DMES and the analytical wavelengths used in the NDIR instruments in the OPF.

TEST APPARATUS

In the absence of a readily available chemical method for DMES vapor analysis in air, a gravimetric method was used to determine the DMES concentration produced by the vapor standard generator. Standard vapor concentrations for DMES, TMDS and ethanol were generated with a Kin Tek model 361 Precision Vapor Standard generator, modified at the TVDL for gravimetric validation of standard concentrations. Modifications involve removing the vapor generator cover and rotating the ovens 90 degrees so that the vapor source can be installed and removed from the top. Special glassware was ordered to fit the oven cavity, with glass tapered tops and tube ports

---

* We have seen TMDS produced from DMES only after injection of DMES into a silica thermal protection system tile. We have not observed TMDS produced from DMES vapor in moist air, even at 90% relative humidity.

for sweep gas entry and exit. The liquid source can be removed from the oven periodically and weighed on an analytical balance to determine the vapor generation rate. The vapor generator is otherwise operated normally. Figure 2 shows a picture of the modified Kin Tek 361 and glassware. Auxiliary dilution and humidity control were provided by a Miller Nelson research model HCS-401, mixed with the DMES and/or ethanol vapors generated by the Kin Tek.

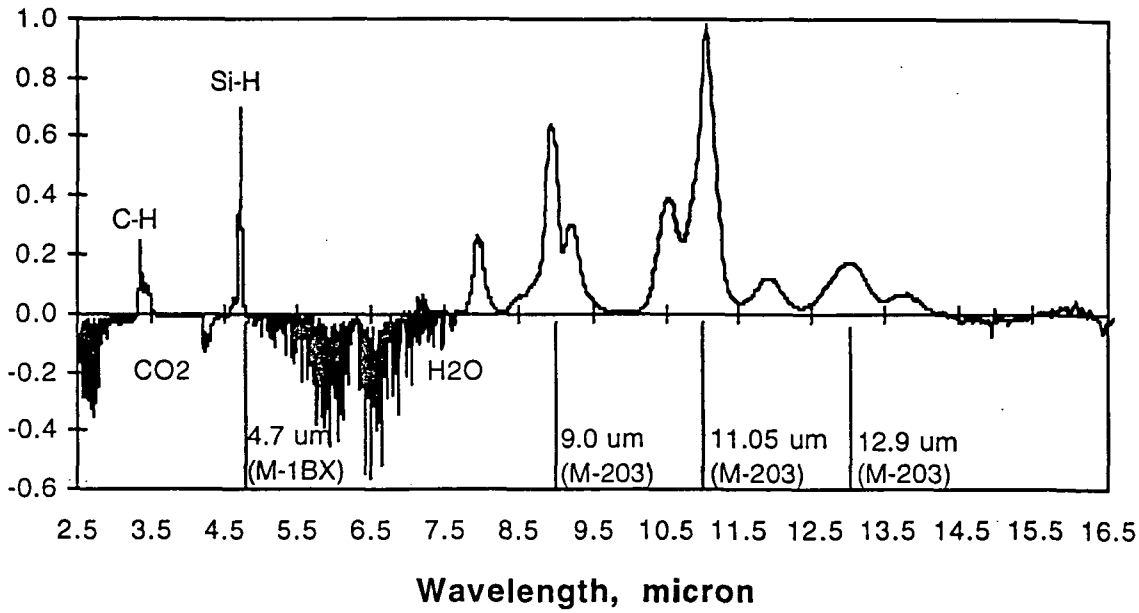
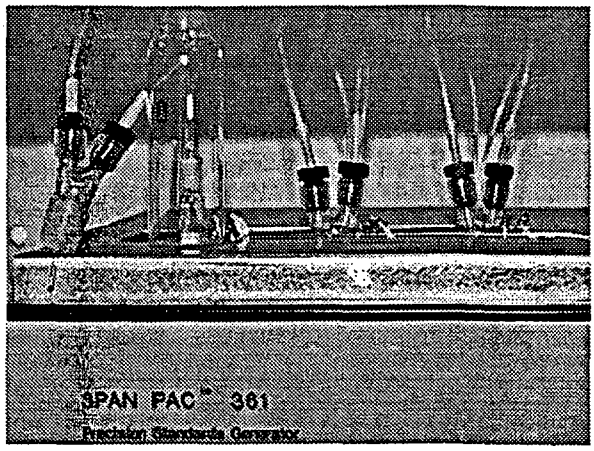


Figure 1. Spectrum of DimethylEthoxySilane. The vertical lines at the bottom of the chart show the positions of analytical wavelengths used by the various NDIR instruments for DMES monitoring at the start of this project.

Figure 2. Modified Span Pac 361 Precision Standard Generator. The top left front of the standard unit is visible showing two glass vessels installed in the ovens. The ovens have been rotated in the cabinet to be top loading. The third glass flask is resting on top of the unit with the cap removed. Inside the open flask is a pyncnometer vial filled with DMES. DMES diffuses from the pyncnometer through the tube on top into the flask. Nitrogen gas enters one port in the cap and sweeps the vapor out through the other port. . The sweep gas rate is 100 cc/min and the internal dilution flow is 1 liter per minute.



In order to compare the four NDIR instruments and the FTIR side by side, the DMES vapor was delivered into a plastic bag with a flow of about 50 liters per minute. Only two NDIR instruments could sample from the

bag at one time to ensure that excess flow was available entering the bag. The FTIR sampled air from the bag at 5 liters per minute along with the NDIR instruments. The test instruments were then exposed to the standard DMES, ethanol and humidity conditions produced by the Kin Tek and Miller Nelson vapor generators.

COMPARISON OF INSTRUMENT RESPONSE

The response of the current field instruments to DMES, Ethanol and water are summarized in Table 1. The responses in **bold** represent false positive readings in response to ethanol and water vapors. Clearly the NDIR instruments tested are not capable of discriminating DMES from water and ethanol vapors at this sensitivity.

Table 1. Summary of Results: Response of FTIR and NDIR instruments to DMES, Ethanol and Water Vapors. All readings +/- 0.1 ppm. The NDIR instruments use a carbon filter to provide clean air to set the instrument zero. The readings with the filter ON represent zero readings, and the readings with the filter OFF are the normal instrument response.

Instrument	Zero	DMES 0.4 ppm	Water, 80% RH	Ethanol, 0.8 ppm Filter ON	Ethanol, 0.8 ppm Filter OFF
FTIR	0.0	0.0	0.0	0.0	0.0
M-1BX, 4.7 um	0.0	0.5	**2.9**	0.1 +	**0.5**
M-203, 9.0 um	0.0	1.5	**5.8**	0.0	**0.5**
M0203, 11.05 um	0.0	0.4 +	**0.1**	0.0	**0.1**
M0203, 12.9 um	0.0	0.35 +	**0.3**	0.0	**0.2**

Note in particular the response to water vapor even though water has no significant absorption at these infrared wavelengths. This is due to the very strong absorption of water outside the analytical band combined with the non-zero (typically 10^{-5}) transmission of interference type filters in the "stop" bands. Changes in water vapor in the percent range, over a very wide band, cause out of band signal comparable to the desired signal from DMES at 0.5 ppm.

CONCLUSIONS FROM THE LABORATORY TESTS

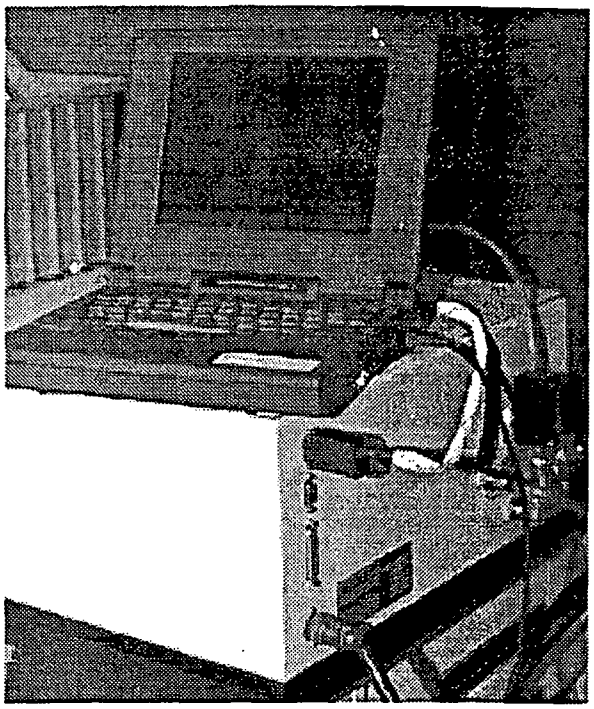
Table 1 clearly shows that the NDIR instruments respond to realistic concentrations of water and ethanol vapors, and can produce false positive readings in excess of 0.5 ppm under the conditions of use in the OPF. The results in Table 1 show that the analytical wavelength of 11.05 um gives the best rejection of interference from water and ethanol vapors. Based on these results, the Miran 203 instruments used in the field were recalibrated at the factory to analyze for DMES at 11.05 um. This minimized the immediate problem and ensured that different instruments would give similar results.

In addition the results show that an FTIR instrument calibrated for all of these vapors simultaneously can reject the interference completely. Based on that conclusion, and a demonstration in the field, a permanent instrument based on FTIR was requested to replace the NDIR instruments in the field.

FIELD TESTS

Field tests were conducted in all three OPF high bays during waterproofing operations. The FTIR was run from 1600 the day before to 1200 the day following the work which occurred between midnight and 0400. A total of 7 tests occurred over a three month period. The FTIR hardware is shown in Figure 3.

Figure 3, FTIR Hardware Configured for TPS Waterproofing field Tests.



For field tests of the FTIR in support of waterproofing operations, a self contained FTIR Module conforming to specification KSC-DL-3409 was modified by the addition of a gas driven eductor pump (PIAB Model M32) to draw samples from a remote location. The gas inlet manifold incorporated a separate orifice, below the pump, to provide purge gas to the cabinet of the FTIR. The FTIR Module itself is a Midac Model G1001 modified by the addition of an internal power supply (110 VAC in, +/-5 and +/- 12 VDC out) and internal 80486DX33 computer in a 3 slot passive ISA Bus chassis that operates the interferometer, performs the quantitative analysis and reports concentration results in ppm on an RS-232 serial port via an added 9 pin connector (top left corner). Data logging and control are provided by a laptop computer running a generic ASCII terminal program.

CONCLUSIONS FROM THE FIELD TESTS

The field tests demonstrated that the FTIR module is capable of providing long term stable measurements of DMES vapor at less than 0.1 ppm noise. Drift due to temperature change with exhaust fans on was also less then 0.1 ppm. Data logged for periods as long as 24 hours could be plotted and analyzed using spread sheet programs. The operator support required is minimal, and the FTIR Module is capable of restarting itself after power interruption without operator intervention. In one instance, a polymer curing operation was conducted within five feet of the FTIR Module sample point, resulting in very high anomalous readings for DMES, but the auxiliary data (ethanol, methanol and IPA) showed a typical error syndrome in the presence of an unknown vapor. In general, the FTIR demonstrated that it can overcome all of the weakness that caused problems with the NDIR instruments, and with less operator skill required. Based on successful field tests we were asked to build an operational FTIR based instrument to place in each of the three OPF high bays.

DEVELOPMENT OF THE DMES ANALYSIS

The calibration of the FTIR for DMES was approached in stages. A preliminary multi-component calibration was generated to support operations as soon as possible. This method used a spectrum of DMES that had been allowed to react over night with water to produce unknown byproducts, which were assumed to be typical of DMES reactions in the field. This spectrum (labeled DMESD for delta) along with DMES, ethanol, methanol, IPA and MEK formed the preliminary calibration set. Later calibration used neat TMDS in place of "DMESD". While

field tests were in progress, high quality samples of DMES and TMDS were procured and used in the final FTIR calibration spectra.

ANALYTICAL APPROACH

The interference from ethanol in the NDIR tests indicates that the regions selected for DMES analysis also have some absorbance from ethanol. A comparison of the IR spectra, shown in Figure 4, verifies that there are no regions where DMES can be isolated from TMDS and Ethanol. This means that a simultaneous multiple component solution is required to discriminate the DMES vapor from TMDS and ethanol. (Note the x-axis units are cm^{-1} as usual for FTIR work)

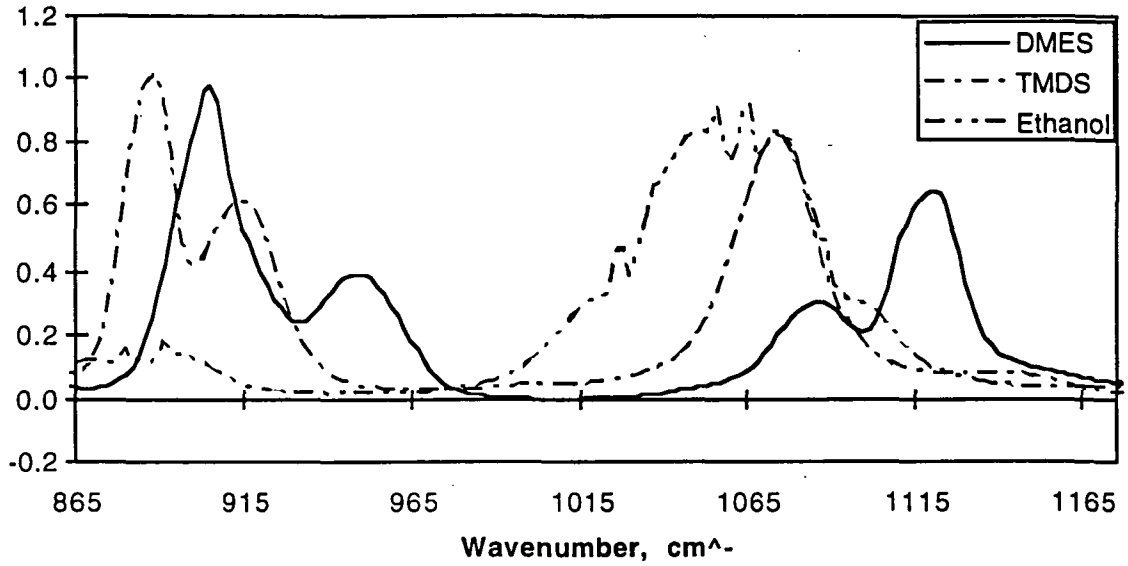


Figure 4. DMES Cart Calibration Spectra. The spectra of DMES, TMDS and ethanol are shown in the region used to calibrate the FTIR Modules for DMES. Note that every point in this region has two or more spectra above zero absorbance.

A brief summary of the analytical approach is given here without proof as it is out of the scope of this paper. The simultaneous Beer's Law solution for the separate components was generated using a locally developed classical least square, multi-component algorithm[5]. The algorithm includes shape vectors for absorbance baseline correction which are used to compensate for the variable thermal environment in the field. The standard form of classical least square problem[6] is formulated to solve the following Beers Law P-matrix expression for multiple component analysis:

$$\mathbf{C} = \mathbf{P}\mathbf{A} \qquad (1)$$

where **C** is the matrix of m unknown concentrations to be measured

P is a matrix which performs the transformation and

A is a matrix of absorbance values at n selected spectral positions.

The matrix **P** can then be determined by solving the matrix form Equation 1 using matrix manipulations to give the standard solution for the matrix **P**:

$$\mathbf{P} = \mathbf{C}\mathbf{A}^T [\mathbf{A}\mathbf{A}^T]^{-1} . \qquad (2)$$

Measured values are then used in the matrices **C** and **A** for known vapor concentrations to calculate **P** from equation 2. Equation 2 can only be solved for [n, spectrum points] <= [m, spectra] so that $[\mathbf{AA}^T]$ will have an inverse. This constraint limits the amount of spectral information that can be used in the quantitative analysis which in turn limits discrimination of spectra and signal to noise ratio.

In order to avoid these limitations, we reformulated the problem in terms of the coefficients of the calibration spectra. This approach is a straightforward application of orthogonal (and arbitrary) functions as basis vectors in a vector space[7]. We defined the following expression for the squared error E:

$$E = \mathrm{SUM}_j \, [\, y_j - (b_1 f_1(x_j) + b_2 f_2(x_j) + b_3 f_3(x_j) + .. + b_i f_i(x_j) + ..+ b_m f_m(x_j) + \qquad \{\text{Calibration Spectra}\}$$

$$+ b_{m+1} + b_{m+2}((x_j - x_c) / n) + b_{m+3}(3/2(x_j - x_c)^2 - 1/2)/ n) \,]^2 \qquad \{\text{Baseline Compensation}\}$$

$$\text{for } j = 1 \text{ to } n. \qquad (3)$$

Where:

m	is the number of calibration spectra
n	is the number of spectrum sample points
y_j	is the measured absorbance value at the jth spectrum sample point
x_j	is the spectrum sample point (wavenumber) of the jth absorbance value
$f_i(x_j)$	is the ith calibration spectrum, sampled at n points, x
b_i	is the ith fit coefficient and
x_c	is a point (may be the center) within the spectral range used for analysis.

The error due to all components is minimized in the classical least square (CLS) sense by simultaneously setting $dE/db_i = 0$ and solving the set of m+3 simultaneous equations in coefficients of the spectra, b_i. The result is a CLS fit of the shape of the unknown spectra to the shapes of the calibration spectra.

The absorbance baseline (normally zero) of unknown spectra to be analyzed is a source of error that can go undetected and give wrong answers for the vapor concentration as the temperature of the instrument changes. These baseline corrections are embedded in the resulting P-matrix and are reported as "offset", "tilt" and "bend". This approach has been effective over regions of 500 to 1500 cm^{-1}, for moderate changes in temperature and reduces error from this source by an order of magnitude in the library of spectra tested.

Equation 3 gives, after some manipulation, the alternate expression for the P-matrix we are seeking:

$$\mathbf{P} = \mathbf{C}[\mathbf{A}^T\mathbf{A}]^{-1}\mathbf{A}^T. \qquad (4)$$

The result from Equation 4 is identical to the result from Equation 2 IF the inverse, $[\mathbf{AA}^T]^{-1}$, exists. In practice Equation 4 gives good numerical results in Pascal Real precision if $\mathrm{Det}[\mathbf{A}^T\mathbf{A}] >\sim 10^{-7}$ The primary advantages of this alternative formulation are:

- The use of equation 4 allows the use of a large number of spectral points (limited only by computer memory) in **A**, which cannot be done using equation 2. Typically 200 to 1400 data points are averaged into each analysis.
- The matrix inverse computation of equation 5 is done on the inner product $[\mathbf{A}^T\mathbf{A}]$ which is typically 10 by 10 rather than the outer product $[\mathbf{AA}^T]$ which is typically 1000 by 1000 with a very large null space. Computation time is about 10 seconds on a 80486DX50, and the program runs in 640 K of memory for 10 components and 1400 spectral points.

• Baseline compensation is embedded into the P matrix and is part of the simultaneous solution for the unknown spectrum composition. This makes baseline compensation automatic in the analysis using Equation 4. (The form of the baseline compensation function is arbitrary. We selected second order polynomials for our limited spectral region.)

• Other locally developed software allows us to select only the vector of interest out of P and construct customized matrix of coefficients with individually tailored interference rejection capability for each target vapor.

Spectra of DMES, TMDS, Ethanol, Methanol, Isopropyl Alcohol plus three baseline shape functions were included in the calibration. All of the spectral points between 865 and 1175 cm^{-1} were used in the calibration at a resolution of 4 cm^{-1} for a total of 321 points. The program generates an array of 8 (components) by 321 (data points) weight factors that fit the shape of the unknown spectrum to the shapes of the calibration spectra. The calibration spectra were generated at near one absorbance unit. The raw results of measurements are then scaled in a post process against a laboratory standard to produce quantitative measurements of the unknown vapor. The run time analysis program uses the weight factors and scale factors to produce five calibrated, baseline compensated vapor concentration measurements in ppm.

CALIBRATION

The calibration process involves two steps. First spectra of the target materials are generated at about 1 absorbance unit. A high quality, low noise spectrum is produced for each material. Each spectrum is normalized to 1.0 absorbance unit for the highest peak in the region of interest. The set of spectra are cranked through the calibration program to produce the array of weight factors for simultaneous multi-component analysis of the vapors. The second step is to generate a known vapor concentration and measure it using a scale factor of 1.0 and the ratio of the standard to the measurement is calculated (mean and sigma). This ratio then becomes the calibrated scale factor.

The two FTIR Modules to be used in the field were set up to average 16 scans at 1 cm-1 resolution, requiring 55 sec to complete a measurement. Reference spectra were 32 scans. DMES vapor standard concentrations were generated from neat DMES (98%) using a Kin Tek Model 361 vapor generator modified to allow removal of the diffusion source for weighing. Concentrations for DMES, Ethanol (180 proof), Methanol (99%) and IPA (99%) were determined gravimetrically, while TMDS (98%) used an arbitrary scale factor of 100. Based on the repeatability between the two instruments we adopted a single calibration factor for both FTIR Modules.

In addition to the laboratory calibration method, a field calibration method was developed which does not require vapor standard generators or fume exhaust hood. The field calibration method and a comparison of results of the two methods are presented in a later section.

FIELD INSTRUMENTATION FOR DMES

Using an FTIR Module calibrated as described above, a mobile instrument cart was designed to provide a stand alone monitor for use in the OPF. The cart incorporates a six point sample system, two sample pumps, internal zero gas source, instrument purge, and a control computer to automate all of the processes which require operator skill. In addition a field calibration method was developed so that the DMES Cart does not have to be transported to the laboratory for calibration. The DMES Cart begins operation automatically when power is turned on, and provides a graphical user interface and display with password protection for critical control functions.

DESIGN CONCEPT

The DMES Cart was required by the user to sample five fixed locations at distances less than 60 m (200 ft) and one movable sample tube with a movable display. The sample system was to cycle automatically through all six sample points during normal operation. On user command, the sample system was to sample the movable line only, so that a person can walk to different areas of the floor to measure DMES concentrations while reading the movable display. The fixed display was to have two screens, 1) a mimic of the OPF floor plan with readings displayed at each sample location, and 2) a display of six graphs, one for each sample location, of DMES concentration versus time. In order to ensure that instrument drift does not cause false positive readings, a source of zero gas was built into the DMES Cart. A new reference spectrum was to be acquired automatically, or on user

command . The DMES cart requires 120 Volt AC power at less than 10 Amps. and instrument grade air or nitrogen at 350 to 400 MPa (50 to 60 psi) and less than 85 l/m (3 cfm).

SAMPLE SYSTEM

The sample system uses seven Teflon valves with 1/4 inch orifice, one for each of six sample line and one for the zero gas source. The sample manifold is designed for low restriction, low dead volume, and allows for flow to be maintained in unused sample lines to reduce transport time after valve switching. One of two gas driven sample pumps draws the sample through the gas cell while the other draws on the remaining five sample lines. The sample flow is set to 8 liters/minute (0.3 cfm) on the active sample line which results in a pressure drop of 4 Inch water column in the gas cell on a 4 mm ID by 60 m long (1/4 inch ID, 200 foot long) sample line. This flow is a compromise between fast response time and head loss in the gas cell. The head loss is small enough that compensation for pressure in the gas cell is unnecessary.

The sample pumps are gas driven eductor pumps with no moving parts (PIAB model LX10). The gas supply provides drive gas for the sample pumps, zero gas for the built in zero reference and instrument purge for the FTIR. All gas consumption except the FTIR purge is turned off automatically when power is removed from the cart. Reference spectra are acquired automatically under two conditions: 1) every four hours at specified times and 2) any time the FTIR returned a reading less than - 0.1 ppm DMES.

Figure 5, DMES Cart for Operational Support of Shuttle TPS Waterproofing.

Left Front view of the DMES Cart showing the flow control panel, sample manifold (left side), FTIR Module (bottom shelf), control computer (behind right side of flow control panel), keyboard, mouse and monitor. Sample and manifold flows are controlled by valves on the two rotameters. Not visible is the gas supply panel with a quick disconnect for nitrogen supply connection.

The user interface uses screen "buttons" to switch between display modes, with password protection on most functions. The monitor display is the six graph screen. An alternate screen shows measurements located on an outline of the orbiter.

DATA LOGGING

Measured concentrations of DMES, TMDS, ethanol along with baseline offset, date and time are logged in a separate file for each sample location. Log files are tab separated text to be analyzed off line with any spread sheet program. In order to keep log file sizes manageable, a new set of log files is created every day at 1600. This allows one log file to cover one shift of waterproofing operation. In addition certain error conditions are logged in an error file. These conditions include: exceeding the upper limit of concentration, failure to return to zero after a reference spectrum is taken, failure of the FTIR Module to communicate with the control computer, power on reset sent to the FTIR Module, and error condition reported by the FTIR Module internal health checks.

FIELD CALIBRATION

The DMES Cart can be calibrated in the field using a closed loop and recirculation pump. Unions are provided in the sample lines to and from the FTIR for connection of the calibration setup. Zero gas is provided by

the DMES Cart, and liquid DMES is injected using a 1 microliter syringe. The calibration setup permits measurement of the volume of the setup using serial dilution of the vapor in the closed loop, with a typical standard deviation of 1.5 percent of the volume. Accuracy of the calibration is typically within one standard deviation of theoretical concentration. Due to the volatility of DMES, careful technique must be exercised by the operator when using the syringe to achieve repeatable injections. The advantage of this method is that quantities of DMES liquid, and vapor concentrations released into the air are small and fume exhaust equipment is not required.

Table 2. Comparison of FTIR Syringe Calibration to Gravimetric Calibration. The concentrations, error and Std. Deviations are in ppm, The calibration constant is dimensionless.

FTIR Instrument	Calibration Method	Calibration Constant	Predicted Concentration	Measured Concentration	Error	Std. Dev.
FTIR SN 104	Gravimetric	124.75	122.9	123.2	N/A	1.4
FTIR SN 112	Gravimetric	124.75	122.9	122.6	N/A	1.3
DMES Cart 1	Syringe	124.75	129.0	134.4 a	5.4	1.9
DMES Cart 1	Syringe	124.75	116.0	117.0 c	0.9	1.9
DMES Cart 2	Syringe	124.75	129.0	130.0 c	1.1	1.9
DMES Cart 3	Syringe	124.75	129.4	138.4 a	9.0	5.1
DMES Cart 3	Syringe	124.75	117.3	120.8 b	3.5	0.8
DMES Cart 3	Syringe	121.07	117.3	117.3 c	N/A	0.8

a. Error is over about 2 standard deviations. Exceeded linear limit for this instrument. Repeat using 0.9 uL.

b Error is over 2 standard deviations. Reading is in linear range. Adjust the calibration constant.

c Calibration accepted.

The syringe injection and the gravimetric methods for calibration typically agree within 1 or two percent between instruments. Table Three shows a comparison of the five instruments that have been calibrated for DMES, two test instruments and three DMES Carts. The FTIR SN 104 and 112 were calibrated using the gravimetrically determined standard and the average calibration constant was installed in both. The same calibration constant was installed in the three DMES Carts. They were subsequently calibrated using the field calibration method. Cart 1 and Cart 3 appear twice in the table because the first attempt with a 1.0 uL injection produced a concentration error greater than 5 ppm. A subsequent injection of 0.9 uL DMES produced a response within one standard deviation of the predicted concentration. The standard deviations for the test instruments are from the measured values of the standard vapor concentration and result from the noise limits of the FTIR and the stability of the vapor generator. The standard deviation values for the DMES Carts are based on the repeatability of the volume measurement for the test setup. The last standard deviation for DMES Cart 3 is based on the average of 120.8 ppm over three injections of 0.9 ppm DMES with 15 FTIR readings recorded for each injection. The error is reported as N/A after calibration.

DMES CART PERFORMANCE

The DMES Carts were tested to demonstrate performance meets the customers requirements. The tests included low level (<1.0 ppm) measurements for noise performance and high level (>50 ppm) tests for response and recovery times. The required parameters and the measured performance is summarized below.

Table 3. Summary of DMES Cart Performance.

Parameter	Performance Requirement	Typical Performance
Range Min	0.1 ppm	0.09 ppm at 3 standard deviations
Max	100.0 ppm	125 ppm +/- 4.5 ppm at 3 standard deviations
Noise at 0.5 ppm	Less than 0.1 ppm	0.09 ppm at 3 standard deviations
Response time to sample to 90 percent of input	Less than 60 seconds	30 seconds
Recovery Time 80 ppm to <0.1 ppm	Less than 60 seconds	45 seconds
Accuracy at 0.5 ppm	Less than 0.1 ppm	0.09 ppm at 3 standard deviations
Drift in four hours	0.1 ppm	less than noise band after warm-up
Warm up Drift	No Requirement	0.5 ppm during warm-up over two hours

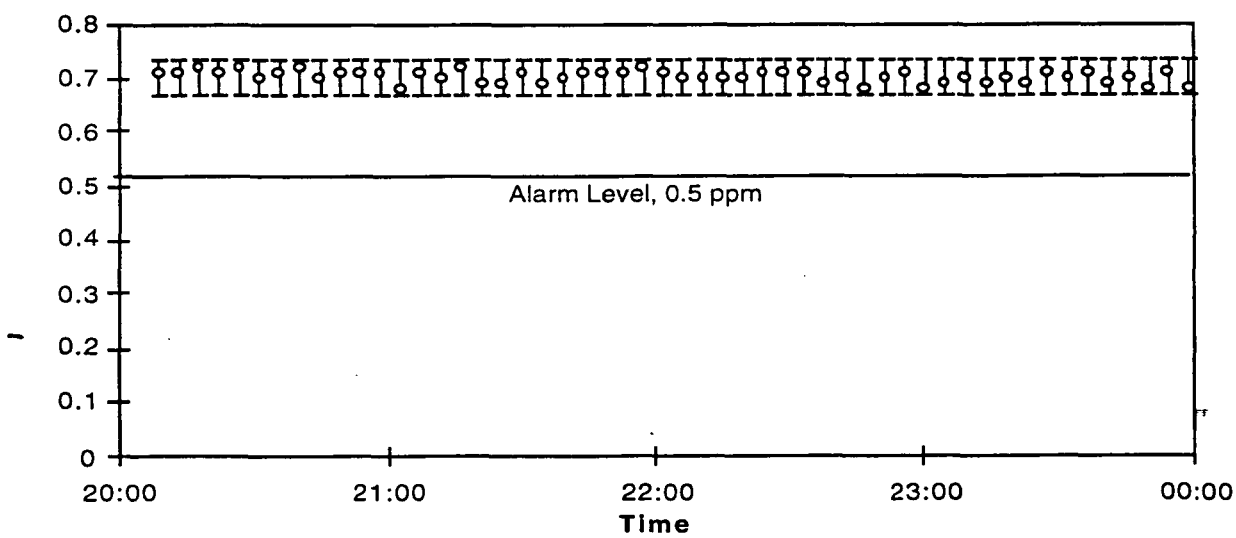


Figure 6. DMES Cart Number 2 Noise Performance. The data points were sampled from 200 feet of 1/4 inch ID Teflon tube over a four hour period. The error bars are three standard deviations of the data over the four hour period. The sample spacing in time is approximately five minutes, the time to sample all six lines.

CONCLUSIONS

The single wavelength NDIR instruments tested are not capable of measuring DMES vapor at 0.5 ppm under conditions found in the OPF after Shuttle TPS waterproofing operations because interfering reaction products can not be discriminated. As a result, work time was unnecessarily lost due to false positive measurements indicating unacceptable levels of DMES. Laboratory and field tests with a multiple component analysis method operating on an FTIR instrument demonstrated the capability to measure DMES in the presence of the same interferences. The FTIR methods developed at the TVDL. were demonstrated to be easy to use in this new application. An instrument cart using the FTIR instrument, multiple component analysis method, a sample manifold and control computer was designed and placed in the OPF to provide reliable DMES measurements.

The process and tools (both hardware and software) used to develop analytical procedure for DMES can be applied to any vapor for which we can get an IR spectrum. The calibration and run time software are being applied to ammonia monitoring for the Space Station Processing facility at KSC. The hardware has been tested in field conditions and has met or exceeded performance requirements.

---

[1] C. Schwindt and C. Mattson, "Computer Program Suite for the Calibration and Operation of a Fourier Transform Infrared (FTIR)-Based Vapor Monitoring Instrument". Reference Number K-11699 and K-11705 (NASA Tech. Brief to be published)

[2] Johnson, Richard E. and Ford, Douglas I., LeTourneau University, Longview Texas.

[3] Manufacturers Safety Data Sheet for DMES, Aldrich Chemical Co., Milwaukee, Wis.

[4] Manufacturers Safety Data Sheet for TMDS, Aldrich Chemical Co., Milwaukee, Wis.

[5] C. Mattson and c. Schwindt, "Correction of the Infrared Baseline Using Shape Parameters" NASA New Technology Report available electronically at http://technology.ksc.nasa.gov/WWWaccess/93report/instf/inst22.htm.

[6] "Fourier Transform Infrared Spectrometry", Girths, Peter R. and dE Haseth, James A., John Wiley & Sons. (p366)

[7] Any good text on math methods of theoretical physics, for example: "Mathmatics of Classical and Quantum Physics", Byron, F. W. and Fuller, R. W., Addison Wesley Publishing Company. Chapter 4, "Vector Spaces in Physics".