RESEARCH METHOD

STANDARD OPERATING PROCEDURE (SOP) FOR THE FIELD OPERATION OF THE AERODYNE DUAL TUNABLE DIODE LASER SPECTROMETER (TDL)

Prepared by: Joanne Shorter, Mark Zahniser, David Nelson, Scott Herndon Date: May 2001
Reviewed by: Volker A. Mohnen (PMTACS-NY QA Officer) Date: May 22, 2001
Approved by: Kenneth L. Demerjian (PMTACS-NY Project Director) Date: May 23, 2001

Aerodyne Research, Inc.
1. SCOPE AND APPLICATION

1.1 The Aerodyne Dual Tunable Diode Laser Spectrometer (TDL) has been developed for real-time monitoring of atmospheric trace gases. Between two and six trace species can be monitored simultaneously by the TDL instrument. It has a range of applications as both a field and laboratory instrument. It is used to characterize ambient air; to characterize emissions from discrete sources (e.g. vehicles, agricultural sources, landfills) and diffuse sources (e.g. urban areas). In the laboratory it is a tool in the study of chemical reactions, in spectroscopic studies and in the area of industrial monitoring. For ambient measurements the dual tunable diode laser spectrometer can monitor many gas phase molecules. It requires only that the species have a suitable infrared spectrum, i.e. infrared spectrum with discernible features. Suitable species for TDL detection include NO, NO\textsubscript{2}, SO\textsubscript{2}, H\textsubscript{2}CO, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, HNO\textsubscript{3}, and NH\textsubscript{3}. The TDL falls into the category of “new technology” instrumentation and as such “standard” operating procedures have not yet been developed. There are, however, procedures which must be followed to ensure quantitative operation. These procedures are described below.
2. SUMMARY OF METHOD

2.1 The Aerodyne Research Inc. TDL is based on high resolution infrared spectroscopy of gas phase molecules. Ambient air is sampled through an inlet into a 5 l multipass sampling cell with 153 m total pathlength. The sample is maintained at reduced pressure (typically 20 – 40 Torr) by a Busch vacuum pump with a flow rate of ~5 l/sec. This results in a residence time of ~1 second in the cell. The TDL system utilizes infrared radiation from two individually operated lead-salt tunable diode lasers. The lasers follow independent paths through the sample in the multipass cell and then on to separate infrared detectors. The amount of light absorbed by the trace gases in the sample cell is monitored.

2.2 The light from the two lasers detected at the infrared detectors is monitored with a well developed data acquisition system. The data acquisition method is an advanced form of sweep integration which is carried out by a software package developed at ARI, TDLWintel. The program sweeps over the full infrared transition or group of transitions, then integrates the area under the transitions using nonlinear least squares fitting to the known spectral line shapes and positions. Absolute species concentrations are obtained directly, tied to the absolute data found in available databases such as the HITRAN data base [Rothman, 1992]. Calibration gas is not required.

2.3 The concentrations of the monitored trace gases are recorded and stored by the data acquisition and controller computer. The data system provides a real-time display of the collected data.

3. HEALTH AND SAFETY WARNINGS

For normal operation, general good laboratory practices are sufficient.

3.1 The TDL unit requires liquid nitrogen (LN2) for operation. Standard safe handling of this cryogen should be used. Safety glasses and insulated gloves should be worn when handling LN2.

Always secure the LN2 reservoir dewar. If a large spillage of the dewar occurs (e.g. if the dewar was not secured properly and it overturned during mobile operation), evacuate the van immediately and open the doors. Nitrogen could replace the air in the van and cause asphyxiation.

3.2 Eye safety to laser light is not a hazard with the lower power (<1 mW) of the diode lasers.
4. CAUTIONS

During standard operation the entire TDL unit, including optical and electronic units, is housed inside a hard-sided Harding box.

4.1 The TDL unit requires liquid nitrogen (LN2) for operation. Standard safe handling of this cryogen should be used.

4.2 The Harding case housing the TDL is fitted with heat exchangers and fans. The TDL is temperature stabilized by heaters mounted on the bottom of the optical breadboard and on its metallic cover. The temperature of the TDL must be monitored as failures in the heaters can cause temperatures to rise dangerously and potentially damage the system.

4.3 Verify that the modulation waveform in TDLWintel will not damage the laser. The selected modulation waveform must not exceed the acceptable range of input voltage for the laser.

4.4 Verify that the temperature of each of the lasers is stable. There should be an approximately constant heater output at each laser.

4.5 Avoid oil contamination of multiple pass cell. Never pump on the cell without a flow of at least 1 lpm when using an oil sealed mechanical pump. Always vent the cell from the inlet side; never from the pump end.

4.6 Read the TDLWintel manual.
5. INTERFERENCES

The TDL draws on the high resolution spectroscopy of trace gases. At reduced pressure lines can be chosen for monitoring such that interferences can be identified.

5.1 Spectroscopic simulations based on available databases, such as the HITRAN database, are performed in advance of field deployment of the instrument to aid in the choice of spectral region for monitoring. If it can be identified using these simulations, the interference can either be included in the spectral fit or another spectral region can be chosen. If included in the fit, the second species will not interfere with the monitoring of the trace gas of interest.

5.2 Optical fringes are a known source of interference particularly when studying species at very low levels. The source of these fringes are typically from the multipass cell and can be on the order of $1 \times 10^{-4}$. Background subtraction techniques are employed to minimize the effects of fringes on the signals. Thermal control of the optical table and its components stabilize the fringes, minimizing their drift, thus allowing for more successful background subtraction. Automatic background subtraction is employed during field studies, in which a zero air is flushed through the system at a set time interval determined by the stability of the fringes (typically 30 minutes or less). An averaged background spectrum is saved and is used to eliminate both fringes and other possible interferences (for example, electronic noise) from subsequent experimental spectra. A ratioing technique is utilized. If a specific gas species at a constant mixing ratio is considered an interference, it may included in the background gas and thus be eliminated from spectra via background ratioing.

5.3 Very high levels of radio transmission signals have been seen to interfere with the operation of the diode laser temperature sensors inside the dewar. Changes in the laser temperature result in large drifts in its frequency.

6. APPARATUS

6.1 The Aerodyne Dual Tunable Diode Laser Spectrometer is a custom built optical system which couples mid-IR lead-salt lasers with a multipass astigmatic Herriott cell designed at ARI (ARI patent), and a highly developed windows-based data control and acquisition system (TDLWintel). The cell design provides maximum pathlength in minimum volume by using an area-filled spot pattern on astigmatic mirrors. The cell can be coated with a fluorinated siloxyl coating if it is to be operated with “sticky” gases, such as NH$_3$ and HNO$_3$. In addition, special attention must be given to the inlet lines and line losses must be quantified.
6.2 The entire TDL optical and electronics system, with the exclusion of the computer monitor, keyboard and mouse, and the vacuum pump, is mounted on a 2’x4’ breadboard which is housed in a hard shelled Harding case [size 30” x 54” x 30”]. The Harding case is kept closed during normal operation. The weight of the system is 140 kg. The complete system uses 1.3 kW of power (including pump).

6.3 The sample cell is evacuated to 20-40 Torr with a 5 l/sec Busch vacuum pump.

6.4 The TDL system consists of optical and electronic subsystems.

The optical system includes a LN2 cooled dewar housing (Infrared Labs) for the Laser Components diode lasers (up to 4 lasers on each of the two mounts in the dewar) and up to four infrared detectors (Kolmar Technologies); a custom built multipass cell (5 liter volume, 153 m pathlength) with a Baratron 0-1 atm pressure gauge and thermocouple; and reflective optics. A helium neon laser serves as a trace visible laser for alignment purposes. The visible and infrared beams are coaligned by means of pinholes.

The electronic system includes a Laser Components Inc. Dual laser controller [L5830], a fast computer (PC compatible, running Windows 95 or Windows 98) running ARI copyrighted software, TDLWintel, and utilizing a National Instruments data acquisition board (PCI-6110E), which digitizes the detected laser signals and sends analog ramp and shutoff signals to the laser. Data are processed and displayed by TDLWintel, and data files are stored on the PC.

The computer interfaces with the dual controller via two Measurement Computing, Inc. boards (CIO-DIO24/CTR3). A slow (ks/s) data acquisition board (Measurement Computing, Inc. PN: CIO-DAS08-AOH) is used to monitor ambient temperature and pressure. These parameters are necessary for proper spectroscopic analysis.

Background subtraction is performed with an automatic solenoid valve (General Valve) mounted in the input stream to switch in background air (“zero air”). Valve control is performed through the TDLWintel program. Liquid nitrogen autofill of the dewar is also controlled by this program.
7. INSTRUMENT CALIBRATION

7.1 Trace Gas Mixing Ratios:
The TDL uses a data acquisition method, an advanced form of sweep integration, which is carried out by an ARI copyrighted software package, TDLWintel. In this method, the TDL program sweeps over the full spectral transition or group of transitions, then integrates the area under the transitions using nonlinear least squares fitting to the known spectral line shapes and positions. At the beginning of each scan the software turns the laser on and its frequency is swept across the desired transition frequency using a software generated voltage ramp. At the end of the scan the laser current is dropped below threshold to determine the detector voltage corresponding to the absence of laser light. The sweep rate can be as fast as 20 kHz for a 150 point spectrum. This sweep rate is fast enough to strongly suppress the effects of 1/f noise. Spectra are coaveraged in a background process while maintaining a 100% duty cycle. The resultant spectrum is fit to a set of Voigt line shape functions which are determined by the pressure and temperature. The baseline is treated as a slowly varying polynomial, typically of third order.

Absolute species concentrations are returned from the nonlinear least squares fits. Calibration with known concentrations of trace gases is not required. The species concentrations are tied to absolute spectroscopic data such as the HITRAN database. The pressure and temperature of the sampled gas is monitored continuously. This is necessary since the line shapes functions, known from theory, use these parameters. This is particularly important for applications where the ambient pressure and temperature may vary rapidly.

If a spectral region has been determined to contain contributions from other modes, the zero light level for the spectral feature might not be determined during the “shut off” period of the current ramp. There are two alternate options for determining the zero light level. The first option is to look at a “black” (totally absorbing) line in the mode. The “black” portion of the line can be used to manually determine the zero level. The second option is to use a calibration gas.

TDLWintel normally operates with “spectral calibration”. However, Gas calibration may be instead chosen. This method relies on calibration gases as concentration standards. TDLWintel has a automatic procedure for implementing gas calibration. (see TDLWintel manual)

7.2 Baratron calibration: The 0-1 atm baratron requires occasional calibration. A dry pump capable of sub-mtorr evacuation (e.g. a molecular drag pump system) is used to zero the Baratron and a mercury wall barometer at atmospheric pressure sets the span.
7.3 **Reference Cells:** A 5 or 10 cm reference cell is placed in the reference path of each of the two lasers beams. They are used for spectral identification during setup and reference locking a laser position during monitoring.

### 8. SAMPLE COLLECTION

8.1 Ambient air is sampled through an inlet connected to tubing, which should be kept as short as practicable. PFA ¼” tubing is used to minimize wall interactions. The latter should be quantified for “sticky gases, such as ammonia and nitric acid. In general 1/4” tubing will not be used for sticky gases, instead a specially designed inlet will be utilized.

8.2 Fill LN2 before start of measurement period. Typical hold time of dewar is 15 hours with 2 lasers running at 20% heater output.

8.3 Open 2 versions of TDLWintel (1 for side A and a second for side B). Turn on the heater and current of each laser with TDLWintel interface.

8.4 Check line positions with reference cells. Atmospheric species can also be used to verify the frequency.

8.5 Confirm that menus have correct information (HITRAN files, peak positions, etc.) and that correct fit markers are in place.

8.6 For each of the laser systems, if a fingerprint fit is used, verify that the tuning rate is appropriate. The tuning rate is typically set by means of an etalon during initial characterization of the laser. If the features in the spectral fit do not line up with their corresponding features in the reference spectrum, the tuning rate can be manually adjusted. This is done by fitting a reference spectrum and varying the tuning rate parameters until corresponding features line up in the spectra. The tuning rate parameters can be found under the Edit menu. A second option for correction of the tuning rate is to use the “tuning rate from single peak” routine in TDLWintel to recalculate the tuning rate (see TDLWintel manual for details).

8.7 Turn on Busch pump and verify that the pressure is 20-40 Torr in the cell.

**Turn on Procedure:**

1. close main valve
2. open small vent valve
3. push “on” switch on pump
4. close small valve
5. open main valve
6. verify that ventilation fans are turned on

Pump shut-down procedure:
1. close main valve
2. push “off” switch
3. open vent valve

8.8 Set-up automatic reference locking (“rlk4”). The frequency of invoking reference locking feature depends on the laser stability. Typical time interval is 1 to 3 minutes. (see TDLWintel manual)

8.9 Set-up automatic background subtraction in field 3 (“ab3”). The frequency of invoking background subtraction depends on the stability of the fringes as well as how often one is willing to have measurements interrupted briefly (~20 seconds). Typical time interval during mobile measurements is 30 minutes. (see TDLWintel manual)

8.10 Note laser temperature and current setpoints, and detector levels in an electronic notepad file. A new file should be opened each day.

8.11 Start streaming the fits and collecting mixing ratio data. Turn on data saving (“wd” button toggles the write to disk option) and RS232 data transfer (“RS” button toggles the RS232 output option). The latter starts transfer of time stamps and concentrations to the Datalogger computer.

9. DATA MANAGEMENT

9.1 Concentration data are saved to the TDL computer by invoking the “wd” button in TDLWintel. When it is on and the program is in stream mode, the molecular concentrations which are returned from the spectral fits are written to a file with the extension “*.str”. A time stamp is also written for each measurement.

9.2 Concentration data are also exported to a Datalogger computer via an RS232 cable when the “RS” button is invoked in TDLWintel.

9.3 Individual spectra may be saved to the hard disk at any time. When saved they are written to the default data directory, with the extension “*.spe”. The file names are encoded with the year, date, hour, minute and second that the file was opened. This is true for stream data as well as spectral files.
9.4 There is a “save every” option (“SE” button), which when selected, every spectrum that is analyzed is also saved to disk in a spectral file with extension “.spe”. There is also a special save every option that saves the average of the last 20 spectra whenever 20 new spectra have been collected and analyzed.

9.5 Once fit parameters, laser settings, current ramp conditions, etc. for a monitoring a particular species have been determined, the configuration file is saved in a separate folder. This allows easy switching between different lasers or modes for a single laser. The configuration file is used to store the startup conditions and preferences for TDLWintel. Among other things, it includes the laser settings (temperature and current setpoints), current ramp, and fit parameters.

9.6 Hit files are used to store the spectroscopic information required to fit a single species. These files are usually saved under the Hit folder in the working folder. They must end with the “*.hit” extension. The files follow the format of the widely used HITRAN data base.

10. TROUBLESHOOTING

This instrument is designed to run with minimal intervention by a trained operator. Since this is a “research –grade” instrument, problems that might arise will require specialized diagnostics from the trained operator. Some routine checks of instrument performance include the following: vacuum pressure, diode laser stability (i.e., stability of a spectral line position), verification of automatic reference locking and background subtraction; liquid nitrogen fill and temperature at designated locations.

11. QUALITY CONTROL

11.1 The identification and peak position of the trace species of interest must be verified daily using spectra from either a reference cell or ambient air if the species is in sufficient abundance in ambient air (examples include CH4 and N2O).

11.2 The data analysis is a primary spectral method based on Beers Law. It measures absolute molecular concentrations provided the appropriate absorption coefficients are provided. Well recognized and characterized spectral databases provide this information.

11.3 Make a copy of the raw data on an independent data storage device at least once a day.
11.4 Document all irregularities of the measurements and the instrument performance in the electronic records. The electronic files must also be backed up daily onto an independent data storage device.

12. REFERENCES

See also www.hitran.com