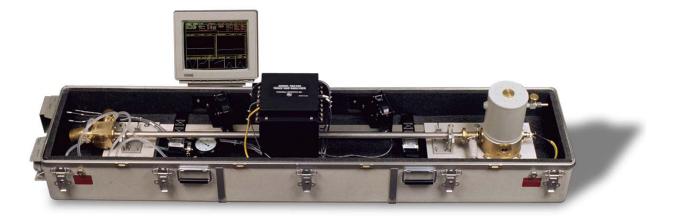
TGA100A Trace Gas Analyzer Overview

The TGA100A Trace Gas Analyzer measures trace gas concentration in an air sample using tunable diode laser absorption spectroscopy (TDLAS). This technique provides high sensitivity, speed, and selectivity. The TGA100A is a rugged, portable instrument designed for use in the field. Common applications include gradient or eddy covariance flux measurements of methane or nitrous oxide and isotope ratio measurements of carbon dioxide or water vapor. The TGA100A concentration measurements can be recorded with a Campbell Scientific datalogger, output as analog voltages, or saved to the hard disk of the optional TGA100A computer.



OV1. System Components

Figure OV1-1 illustrates the main system components needed to operate the TGA100A. These system components include:

- TGA100A Analyzer: The analyzer optics and electronics, mounted in an insulated fiberglass enclosure.
- Optional TGA100A Computer: A desktop computer, supplied as an option for the TGA100A to display data and set parameters.
- Optional Datalogger: Receives concentration data from the TGA100A through the SDM interface cable.
- Sample Intake (15838 shown): Filters the air sample and sets its flow rate.
- Sample pump (RB0021-L shown): Pulls the air sample and reference gas through the analyzer at low pressure.
- Suction hose (7123): Connects the analyzer to the sample pump. Supplied with RB0021 sample pump.
- Reference gas: tank of reference gas, with pressure regulator (supplied by user).
- Reference gas connection (15837 shown): Flow meter, needle valve, and tubing to connect the reference gas to the analyzer.

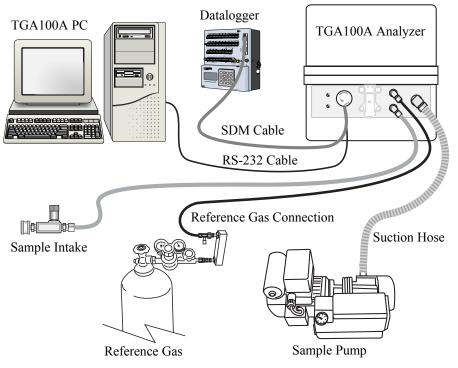


FIGURE OV1-1. TGA100A System Components

OV2. Theory of Operation

OV2.1 Optical System

The TGA100A optical system is shown schematically in Figure OV2.1-1. The optical source is a lead-salt tunable diode laser that operates between 80 and 140 K, depending on the individual laser. Two options are available to mount and cool the laser: the TGA100A LN2 Laser Dewar and the TGA100A Laser Cryocooler System. Both options include a laser mount that can accommodate one or two lasers (up to four lasers can be installed by adding the optional second laser mount). The LN2 Laser Dewar mounts inside the analyzer enclosure. It holds 10.4 liters of liquid nitrogen, and must be refilled twice per week. The Laser Cryocooler System uses a closed-cycle refrigeration system to cool the laser without liquid nitrogen. It includes a vacuum housing mounted inside the analyzer enclosure, an AC-powered compressor mounted outside the enclosure, and 3.1 m (10 ft) flexible gas transfer lines.

The laser is simultaneously temperature and current controlled to produce a linear wavelength scan centered on a selected absorption line of the trace gas. The IR radiation from the laser is collimated and passed through a 1.5 m sample cell, where it is absorbed proportional to the concentration of the target gas. A beam splitter directs most of the energy through a focusing lens and short sample cell to the sample detector, and reflects a portion of the beam through a second focusing lens and a short reference cell to the reference detector. A prepared reference gas having a known concentration of the target gas flows through the reference cell. The reference signal provides a template for the spectral shape of the absorption line, allowing the concentration to be derived independent of the temperature or pressure of the sample gas or the spectral positions of the scan samples. The reference signal also provides feedback for a digital control algorithm to maintain the center of the spectral scan at the center of the absorption line. The simple optical design avoids the alignment problems associated with multiple-path absorption cells. The number of reflective surfaces is minimized to reduce errors caused by Fabry-Perot interference.

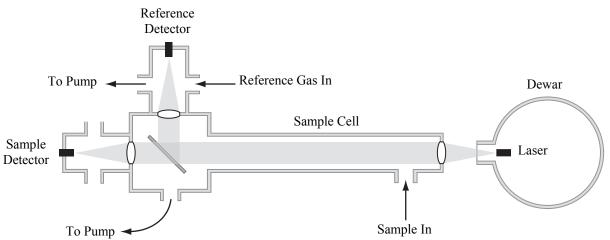


FIGURE OV2.1-1. Schematic Diagram of TGA100A Optical System

OV2.2 Laser Scan Sequence

The laser is operated using a scan sequence that includes three phases: the zero current phase, the high current phase, and the modulation phase, as illustrated in Figure OV2.2-1. The modulation phase performs the actual spectral scan. During this phase the laser current is increased linearly over a small range (typically +/-0.5 to 1 mA). The laser's emission wavenumber depends on its current. Therefore the laser's emission is scanned over a small range of frequencies (typically +/-0.03 to 0.06 cm⁻¹).

During the zero current phase, the laser current is set to a value below the laser's emission threshold. "Zero" signifies the laser emits no optical power; it does not mean the current is zero. The zero current phase is used to measure the detector's dark response, i.e., the response with no laser signal.

The reduced current during the zero phase dissipates less heat in the laser, causing it to cool slightly. The laser's emission frequency depends on its temperature as well as its current. Therefore the temperature perturbation caused by reduced current introduces a perturbation in the laser's emission frequency. During the high current phase the laser current is increased above its value during the modulation phase to replace the heat "lost" during the zero phase. This stabilizes the laser temperature quickly, minimizing the effect of the temperature perturbation. The entire scan sequence is repeated every 2 ms (500 scans per second).

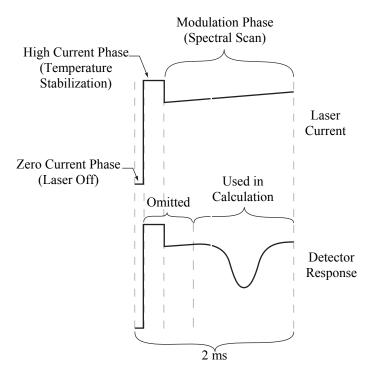


FIGURE OV2.2-1. TGA100A Laser Scan Sequence

OV2.3 Concentration Calculation

The reference and sample detector signals are digitized at 50 kHz (100 samples per scan), corrected for detector offset and nonlinearity, and converted to absorbance. A linear regression of sample absorbance vs. reference absorbance gives their ratio. The assumption that temperature and pressure are the same for the sample and reference gases is fundamental to the design of the TGA100A. It allows the concentration of the sample, C_S , to be calculated by:

$$C_{s} = \frac{(C_{R})(L_{R})(D)}{L_{S} + L_{A}(1-D)}$$

where C_R = concentration of reference gas, ppm

 L_R = length of the short reference cell, cm

 L_S = length of the short sample cell, cm

 $L_A =$ length of the long sample cell, cm

D = ratio of sample to reference absorbance

The trace gas concentration is calculated for each scan, and digitally filtered to a 5 Hz band width and a 500 Hz update rate.

OV3. Trace Gas Species Selection

The TGA100A can measure gases with absorption lines in the 3 to 10 micron range by selecting appropriate lasers, detectors, and reference gas. Lead-salt tunable diode lasers have a very limited tuning range, typically 1 to 3 cm⁻¹ within a continuous tuning mode. In some cases more than one gas can be measured with the same laser, but usually each gas requires its own laser. The laser dewar has two laser positions available (four with an optional second laser mount), allowing selection of up to four different species by rotating the dewar, installing the corresponding cable, performing a simple optical realignment, and switching the reference gas.

The standard detectors used in the TGA100A are Peltier cooled, and operate at wavelengths up to 5 microns. These detectors are used for most gases of interest, including nitrous oxide (N_2O), methane (CH₄), and carbon dioxide (CO₂) isotopomers. Some gases, such as ammonia (NH₃), have the strongest absorption lines at longer wavelengths, and require the optional long wavelength, liquid nitrogen-cooled detectors.

A prepared reference gas having a known concentration of the target gas must flow through the reference cell. The beam splitter directs a small fraction of the laser power through the reference cell to the reference detector. This gives a reference signal proportional to the laser power, with the spectral absorption signature of the reference gas. The reference signal provides a template for the spectral shape of the absorption feature, allowing the concentration to be derived without measuring the temperature or pressure of the sample gas, or the spectral positions of the scan samples.

OV4. Multiple Scan Mode

The TGA100A can be configured to measure two or three gases simultaneously by alternating the spectral scan wavelength between two or three absorption lines. This technique requires that the absorption lines be close together (within about 1 cm⁻¹), so it can be used only in very specific cases. The multiple scan mode is used to measure $\delta^{13}C$ and $\delta^{18}O$ isotope ratios in carbon dioxide or $\delta^{18}O$ and δD isotope ratios in water vapor by tuning each scan to a different isotopomer.

The multiple scan mode may also be used to measure some other pairs of gases, such as carbon monoxide and nitrous oxide, or nitrous oxide and methane, but the measurement noise will be higher than if a single gas is measured. For measurements of a single gas, the laser wavelength is chosen for one of the strongest absorption lines of that gas. Choosing a laser that can measure two gases simultaneously involves a compromise. Weaker absorption lines must be used in order to find a line for each gas within the laser's narrow tuning range.

OV5. User Interface Software

The TGA100A user interface software runs on the optional TGA100A computer or on the user's PC. It displays the data in real time and allows the user to modify control parameters. Normally the trace gas concentration data are recorded by a datalogger, and the PC is required only for setting up the TGA100A. However, the trace gas concentration data can also be saved to the PC's hard disk, making the datalogger unnecessary in some applications.

The real time graphics screen is presented in Figure OV5-1. In the upper left corner is a box which displays the TGA software version, the laser and detector temperatures, and the time. Beneath the time and temperature display is a blank area used for information and error message display. The rest of the top of the screen has five menu columns: run mode, dynamic parameters, detector video, special function enable/disable, and graph selections.

| TGA100 Ver 6.07a | RUN MODE | PARAMETER | DET VID | FUNCTION | GRAPH SELECT |
|---|-----------------|--|--|---|---|
| TEMPERATURES Laser 85.900 K RefDet-20.00 °C SmpDet-35.00 °C TIME: 9:49:47 | Run Run∕Edit | #[3] Mod Current Hi 100.000 Nom 0.500 Lo 0.000 | Magnify MaXdisp DeTrend Folded Absorbn | DataColl[] Gradient[] Laser on[on] | |
| 10 Hz N20 Cone | = 0.3160 ±0 | .00087 ppm | Laser Tem | p = 85.900 | ±0.00053 K |
| | | 0.400 | | | 85.920 |
| | | | | | - |
| | | | | | |
| | | 1 | | | |
| | | -;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;; | | a a cara a ser ser a ser a | - |
| | | | | a da ang katalang katalan kata Katalan katalan k | - All and a second s |
| | | - | | | |
| | | - | | | |
| | | - | | | |
| | | 0.200 | | | 85.880 |
| Detector Sig | nals (mV) | Pressure | | Folded Transm | ittance (%) |
| REF 2.150 SM | IP 37.513 | 3 52.193 1 | | REF 59.260 | SMP 99.801 |
| | | | <u>52,391</u> | | |
| | | | - | | |
| ·.~~~ | | | - | - ::: + | |
| | | 4 | - | - | |
| | | | 50.411 | | |

FIGURE OV5-1. Real Time Graphics Screen

In the middle of the screen are graph 1 and graph 2, used to display userselectable variables. This example shows N_2O concentration in graph 1 and laser temperature in graph 2.

Graph 3 is located at the bottom-center of the screen, and is also used to display user-selected variables. In this example graph 3 shows the sample cell pressure.

At the bottom left corner of the screen are two high speed graphic windows that show the raw reference (REF) detector signal and the raw sample (SMP) detector signal, scaled to match the analog-to-digital converter (ADC) input range.

At the bottom right corner of the screen are two more high speed graphic windows that display processed reference and sample signals. The user may select the type of data to display in these windows using the Detector Video menu or the Quick Keys. The number displayed at the top of these windows is either the transmittance or the absorbance at the center of the spectral scan, depending on the display mode selected. All four of the high-speed graphic windows have three vertical dashed lines. These lines show the center of the spectral scan and the range of data actually used to calculate concentration.

Many of the operating parameters can be edited at the real time screen using the Parameters menu column. Other parameters are available at the Parameter Change menu.

OV6. Micrometeorological Applications

The TGA100A is ideally suited to measure fluxes of trace gases using micrometeorological techniques. Its rugged design allows it to operate reliably in the field with minimal protection from the environment, and it incorporates several hardware and software features to facilitate these measurements.

OV6.1 Eddy Covariance

The TGA100A's frequency response, sensitivity, and selectivity are optimized for measuring trace gas fluxes using the eddy covariance (EC) method. Its 500 Hz sample rate allows a datalogger to read its concentration data with a maximum timing jitter of only ± 1 ms. A typical eddy covariance system (illustrated in Figure OV6.1-1) includes a TGA100A, a CSAT3 sonic anemometer, and a datalogger.

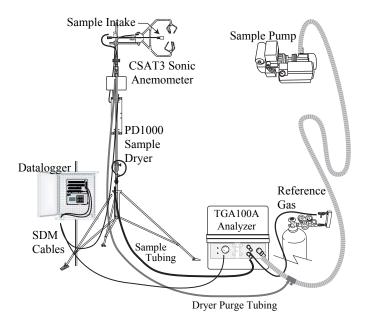


FIGURE OV6.1-1. Example Eddy Covariance Flux Application

The sonic anemometer and air sample intake are mounted on the measurement mast. Tubing connects the air sample intake to the inlet of a PD1000 high flow sample air dryer, which filters and dries the air sample. A needle valve at the outlet of the PD1000 sets the sample flow rate, typically to approximately 15 slpm. The TGA100A analyzer is located near the base of the measurement mast to minimize the length of sample tubing. This minimizes the attenuation of high frequencies in the concentration data caused by tube flow. The sample pump requires minimal shelter and can be located up to 90 m (300 ft) away from the analyzer, connected by 1" ID suction hose.

A Campbell Scientific datalogger collects synchronized data from the sonic anemometer and the TGA100A through SDM interface cables. Analog outputs are available for use with other data loggers. The datalogger records the raw time series data as well as the results of an online EC flux calculation.

OV6.2 Flux Gradient

The TGA100A also supports the measurement of trace gas fluxes by the gradient method. A gradient valve switches the sample between the two intakes, the valid samples from each intake are averaged and the difference is computed. The valve control and the calculations can be performed either by a datalogger or by the optional TGA100A computer and I/O board. The optional TGA100A computer and I/O board provide a convenient user interface, but require shelter from the environment. The datalogger is generally preferred when an instrumentation trailer or other shelter is not available.

Figure OV6.2-1 illustrates a typical gradient application using the optional TGA100A PC and I/O board. Two intake assemblies are mounted at different heights on the measurement mast. Tubing connects each intake assembly to a gradient valve assembly that selects one of the intakes at a time. The air sample from the selected intake flows through the PD1000 high flow sample air dryer, which filters and dries the air sample. A needle valve at the outlet of the PD1000 sets the sample flow rate, typically 5 to 10 slpm. Tubing connects the outlet of the dryer to the TGA100A analyzer, which may be located 200 m (650 ft) or more away. The sample pump requires minimal shelter and can be located up to 90 m (300 ft) away from the analyzer, connected by 1" ID suction hose.

This example shows a gradient flux measurement at a single site. However, the TGA100A can also support flux gradient measurements at multiple sites by installing intake assemblies, a gradient valve assembly, and a sample dryer at each site, and a site selection system near the analyzer. The site selection system connects one site at a time to the analyzer. Normally each site is measured for 15 to 60 min before switching to the next site.

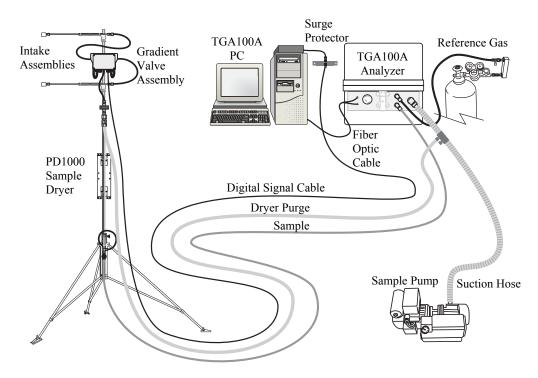


FIGURE OV6.2-1. Example Gradient Flux Application

OV6.3 Site Means Sampling Mode

The TGA100A's site means mode is similar to the flux gradient mode in that it controls switching valves and calculates mean concentrations for each intake. The difference between the two sampling modes is that the gradient mode considers the sample intakes in pairs, switching several times between an upper and lower intake before moving to another site, but the site means mode considers all of the intakes as one group. It cycles through all of the intakes in sequence. Applications for the site means mode include concentration profile measurements and trace gas flux measurements using the mass balance technique. Similar to the gradient mode, the valve switching and calculations can be performed either by a datalogger or by the optional TGA100A computer and I/O board.

Figure OV6.3-1 illustrates an eight-level vertical profile using the optional TGA100A PC and I/O board. The eight intake assemblies are arranged vertically on a single measurement tower. These intake assemblies include a filter to remove particulates and a critical flow orifice to set the sample flow (typically less than 1 slpm). A separate tube connects each intake assembly to the site selection system, which selects one of the intakes at a time. All of the unselected intakes are connected through the bypass tube to the 1" suction hose leading to the sample pump, keeping air flow at all times in all intake tubes. The flow from the selected intake goes through a PD625 low flow sample dryer to the TGA100A analyzer. A second PD625 is used to provide dry air to purge the sample dryer.

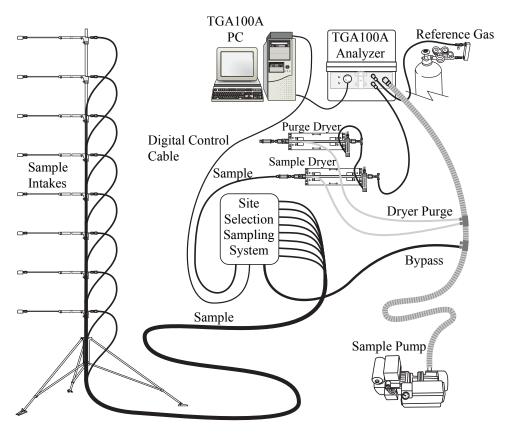


FIGURE OV6.3-1. Example Profile Application

OV6.4 Absolute Concentration / Isotope Ratio Measurements

The TGA100A can be configured for highly accurate measurements of trace gas concentrations by performing frequent calibration. The TGA100A has a small offset error caused by optical interference. This offset error changes slowly over time, with a standard deviation roughly equal to the short-term noise. Offset errors have little effect on flux measurements by either the gradient or eddy covariance technique, but may be important in other applications. For measurements of absolute trace gas concentration, the offset error can be removed by switching between a nonabsorbing gas (e.g. nitrogen) and the sample, using the gradient mode of operation.

Applications such as isotopic ratio measurements require the highest possible accuracy. This is achieved using a frequent two-point calibration to correct for drift in the instrument gain and offset. High accuracy requires the flow rate for the calibration gases to be the same as for the sample air. Even though the sampling system can be designed so that calibration gases flow only when they are used, frequent calibration (every few minutes) consumes a large amount of calibration gas if high flow rates are used. The site means sampling mode is normally used because it works well at low flow rates.

Figure OV6.4-1 illustrates a typical CO_2 isotope application. It is similar to the site means example above, but it includes two intakes connected to calibration tanks. A tank of nitrogen or CO_2 -free air is also shown connected to the analyzer to purge the air gap between the laser dewar and sample cell. This purge is required for CO_2 isotope measurements because of the high ambient concentration of CO_2 and the need for high accuracy.

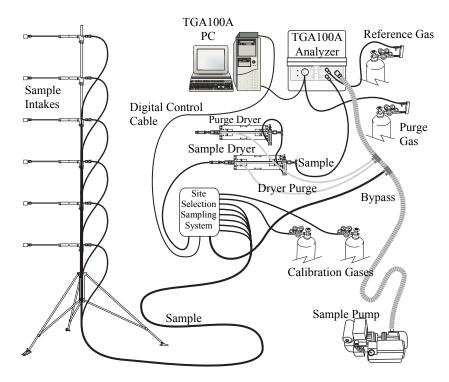


FIGURE OV6.4-1. Example CO₂ Isotope Application

OV7. Specifications

OV7.1 Measurement Specifications

The preliminary frequency response and noise specifications given in this section are based on performance of the TGA100, which has a 10 Hz update rate. The TGA100A has a 500 Hz update rate, which should give improved performance.

| Sample Cell Volume: | 480 ml |
|---------------------|--------|
| Update Rate: | 500 Hz |
| Band width: | 5 Hz |

The TGA100A frequency response is determined by the time required to flush the sample cell. The frequency response was measured at 14.4 slpm flow rate and 50 mbar sample pressure (4.8 actual l/s) by injecting approximately 1 μ l of N₂O into the sample stream. The resulting time series and frequency response graphs are shown below (TGA100 data are shown, with a 10 Hz update rate).

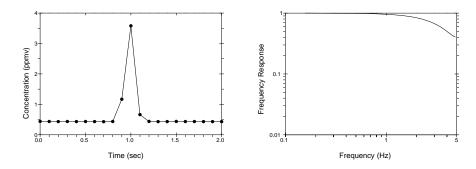


FIGURE OV7.1-1. Time Series (left) and Frequency Response (right)

The typical 10 Hz concentration measurement noise is given as the square root of the Allan variance with no averaging (i.e. the two-sample standard deviation. This is comparable to the standard deviation of the 10 Hz samples calculated over a relatively short time (10 s). The typical 30-minute average gradient resolution is given as the standard deviation of the difference between two intakes, averaged over 30 minutes. Values shown in Table OV7.7-1 are for ambient concentrations.

| Gas | | Wave number (cm ⁻¹) | 10 Hz Noise (ppbv) | 30-min Gradient Resolution (pptv) |
|------------------|-----------------|------------------------------------|-----------------------|--------------------------------------|
| Nitrous Oxide | N_2O | 2208.575 | 1.5 | 30 |
| Methane | CH_4 | 3017.711 | 7 | 140 |
| Ammonia | NH_3 | 1065.56 | 6 | 200 |
| Carbon Monoxide | CO | 2176.284 | 3 | 60 |
| Nitric Oxide | NO | 1900.08 | 13 | 260 |
| Nitrogen Dioxide | NO_2 | 1630.33 | 3 | 60 |
| Sulfur Dioxide | SO_2 | 1366.60 | 25 | 500 |

TABLE OV7.1-1. Typical Concentration Measurement Noise

Typical performance for isotope ratio measurements is given in delta notation. For example, the $\delta^{13}C$ for CO₂ is given by:

$$\delta^{13}C = \left(\frac{R_s}{R_{VPDB}} - 1\right) \times 1000$$

where R_s is the ratio of the isotopomer concentrations measured by the TGA100A (${}^{13}CO_2/{}^{12}CO_2$) and R_{VPDB} is the standard isotope ratio (${}^{13}C/{}^{12}C$). $\delta^{13}C$ is reported in parts per thousand (per mil or ‰). The 10 Hz noise is the square root of the Allan variance with no averaging. The calibrated noise assumes a typical sampling scenario: two air sample intakes and two calibration samples measured in a 1 minute cycle. It is given as the standard deviation of the calibrated air sample measurements.

TABLE OV7.1-1. Typical Isotope Ratio Measurement Noise

| Gas | Isotope Ratio | Wavenumber | | |
|----------------|----------------|-------------|-----|-----------|
| | | (cm^{-1}) | (‰) | Noise (‰) |
| | $\delta^{13}C$ | 2293.881 | 0.5 | 0.1 |
| Carbon Dioxide | | 2294.481 | | |
| | $\delta^{18}O$ | 2308.225 | 2.5 | 0.5 |
| | | 2308.416 | | |
| | $\delta^{18}O$ | 1500.546 | 2 | 0.5 |
| Water | | 1501.188 | | |
| | δD | 1501.813 | 10 | 2.5 |
| | | 1501.846 | | |

OV7.2 Physical Specifications

Analyzer

| 211 cm (83 in) |
|------------------|
| 47 cm (18.5 in) |
| 55 cm (21.5 in) |
| 74.5 kg (164 lb) |
| |

Optional Cryocooler Compressor

| Length: | 31 cm (12 in) |
|---------|-----------------|
| Width: | 45 cm (18 in) |
| Height: | 38 cm (15 in) |
| Weight: | 32 kg (71 lb) |

Power Requirements

| Analyzer: | 90-264 Vac, 47-63 Hz, 50 W (max) 30 W (typ) |
|------------------------------------|---|
| Optional Heater: | 90-264 Vac, 47-63 Hz, 150 W (max) |
| Optional PC: | 115/230 Vac, 50/60 Hz, 150 W |
| Optional Cryocooler Compressor: | 100, 120, 220, or 240 Vac, 50/60 Hz, 500 W |
| RB0021-L sample pump: | 115 Vac, 60 Hz, 950 W (other power options are available) |