The NanoSpectralyzer®
for carbon nanotube characterization

NS1: Characterization of SWCNTs

NS2 NanoSpectralyzer

Introduction

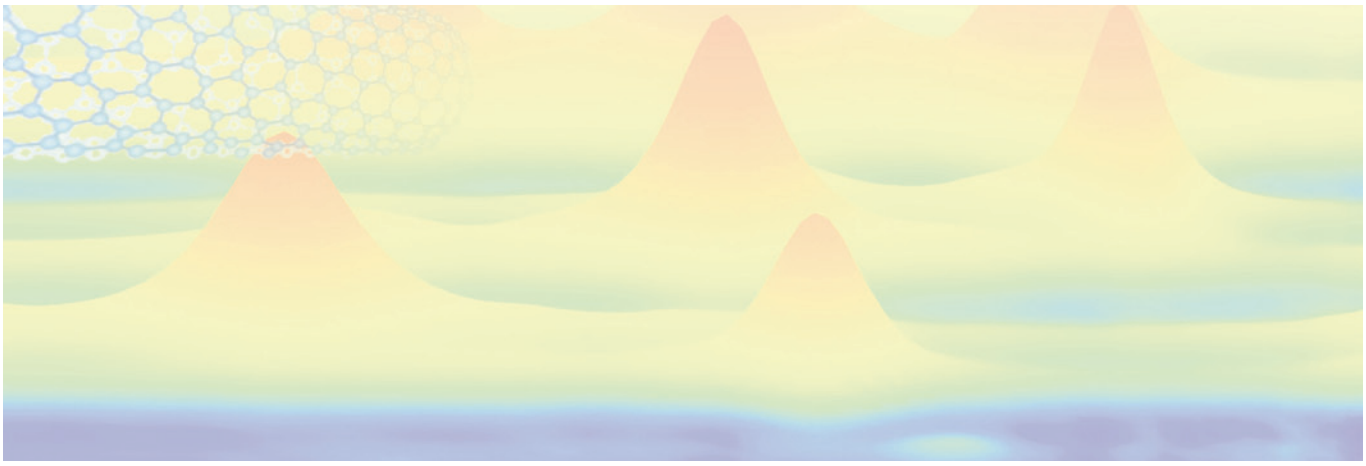
The NS1 and NS2 NanoSpectralyzers® from Applied NanoFluorescence (ANF) are unique laboratory instruments designed to characterize carbon nanotube samples. They contain specialized multi-mode spectrometers integrated with sophisticated computer control and analysis software. The NS1 sensitively captures near-IR fluorescence spectra induced by four excitation lasers, and measures sample absorbance throughout the visible and near-IR regions. The NS2 has all of the NS1 functionality plus Raman spectroscopy. In both instruments, near-IR fluorescence data are automatically analyzed using the latest research findings to give detailed information on sample composition.

Background

Near-IR band-gap fluorescence from single-walled carbon nanotubes (SWCNTs) was discovered at Rice University in 2001. Subsequent research at Rice deciphered the complex pattern of absorption and emission peaks seen in mixed samples. Each distinct spectral feature was securely assigned to a specific nanotube structure. These structures differ in diameter and roll-up angle, and are uniquely labeled by pairs of integers denoted (n,m). Thus, the near-IR emission spectra provide compositional "fingerprints" that allow rapid and convenient (n,m) analysis of bulk SWCNT samples. Near-IR fluorescence is not emitted by the one-third of SWCNT species that have metallic character, or from multi-walled carbon nanotubes (MWCNTs). However, these nanotubes can be detected and characterized by their optical absorption and Raman spectra. Absorption and Raman also offer valuable information about SWCNT samples. General-purpose spectrofluorometers are not optimized for nanotube analysis. Although versatile, they are bulky, slow, insensitive, and give raw data that need careful manual interpretation. In addition, they cannot measure absorption or Raman spectra. ANF has developed the NS1 and NS2 instruments specifically for nanotube analysis. These integrated systems efficiently measure and interpret multi-mode spectral data to provide the best available optical characterization.

Relevant Literature:

M. O'Connell et al., Science 297, 593 (2002).
S. M. Bachilo et al., Science 298, 2361 (2002).
R. B. Weisman and S. M. Bachilo, Nano Letters 3, 1235 (2003).
R. B. Weisman, Analytical and Bioanalytical Chemistry 396, 1015 (2010).
J. R. Rocha et al., Analytical Chemistry 83, 7431 (2011).



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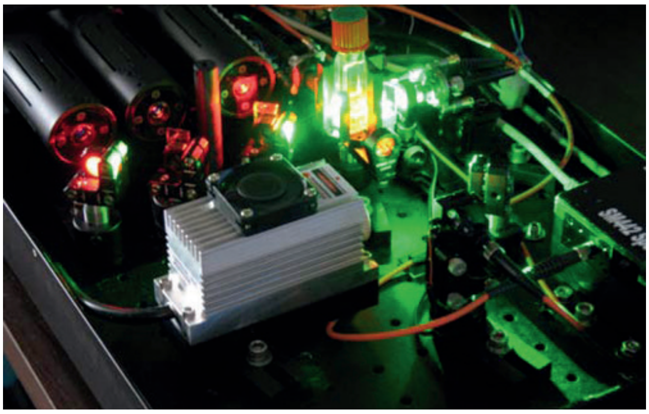
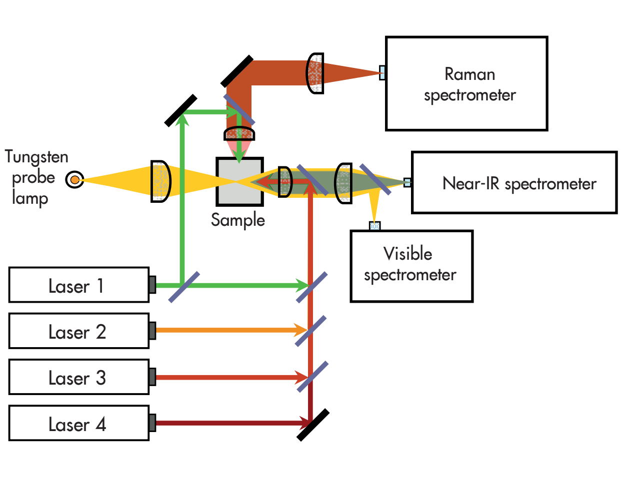
Applications

The NS1 and NS2 are ideal for a variety of applications.

- **CNT Producers** use these instruments to expose changes in product composition while exploring different growth process conditions. Later, during routine production, the NanoSpectralyzers allow rapid monitoring of batch-to-batch consistency and quality. Because the instruments are highly automated, this QC/QA function can be performed by technicians with limited scientific training.
- **Customers who buy nanotubes** use the NS1 and NS2 to assess the quality of incoming CNT material and confirm that it meets their needs.
- **Biomedical & Environmental Researchers** exploit the NanoSpectralyzers' very high NIR fluorescence sensitivity to detect and quantify trace concentrations of SWCNTs in complex surroundings. Major applications include biomedical research involving SWCNTs in tissue specimens, and environmental research that must track the movement and fate of SWCNTs in nature.
- **Nanotube Basic Researchers** find the NS1 and NS2 to be versatile laboratory tools. They allow SWCNT starting materials to be properly characterized, avoiding many experimental pitfalls that can be caused by inconsistent or unknown sample properties. The NanoSpectralyzers also guide and check the sorting of mixed samples into specific structural forms, for example by chromatographic or density gradient centrifugation methods. And they enable sophisticated studies of chemical reactions and physical processes that depend on nanotube structure. Please visit our website for a current list of research publications by NanoSpectralyzer users.



How it Works



NS2 NanoSpectralyzer optical schematic

A small sample of raw carbon nanotubes is first ultrasonically dispersed into an aqueous surfactant solution to individually suspend a portion of the nanotubes. Then a few drops of the dispersion, perhaps containing only nanograms of carbon, are placed into a sample cell.

The NanoSpectralyzer uses four lasers to excite near-IR fluorescence from semiconducting SWCNTs. These laser wavelengths are chosen to match the absorption range of nanotubes in samples grown by common processes such as HiPco or CoMoCAT. As each laser irradiates the sample, sample emission is captured by an efficient optical system, spectrally dispersed in a near-IR spectrometer, and detected by a cooled InGaAs array with 512 elements.

The resulting set of four fluorescence spectra is quickly analyzed by sophisticated fitting software to deduce an inventory of (n,m) species in the sample and their relative concentrations. These results are automatically shown as tables and publication-ready graphs. The fluorescence spectra are complemented by near-IR and (optionally) visible absorption spectra. All CNTs in the sample contribute to these spectra, including nanotubes that are non-emissive because of aggregation, functionalization, defects, metallic character, or multi-walled structure. The data analysis software automatically divides the total emitted fluorescence by the absorption of the excitation beam to display a fluorescence efficiency index. This index is an incisive measure of relative quality for SWCNT samples, reflecting nanotube perfection and disaggregation.

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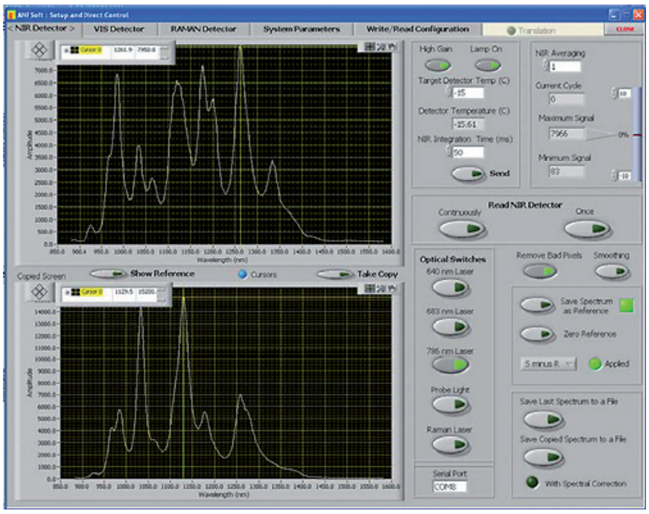
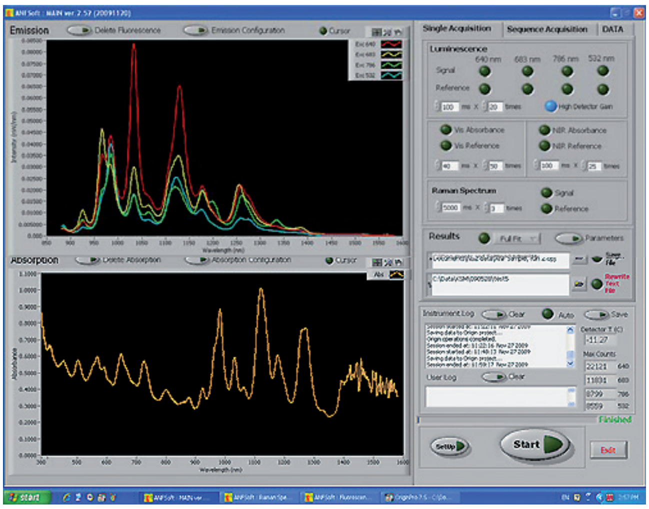
The NS2 NanoSpectralyzer also measures Raman scattering, using an excitation wavelength selected when the instrument is ordered. Raman spectra may show contributions from nanotubes that are semiconducting or metallic, aggregated or disaggregated, pristine or functionalized, single, double, or multi-walled. The NS2 captures RBM, D, G, and G′ bands, which arise from different vibrational modes and reflect aspects of sample structure and condition. Raman data complement the fluorescence and absorption spectra to give more complete sample characterization.



Why use a NanoSpectralyzer instead of separate instruments?

- The multi-mode NanoSpectralyzers save expense, lab space, and time
- Each sub-system of the NanoSpectralyzer is designed for CNT spectroscopy
- All spectra are automatically and quickly measured on a single undisturbed sample
- Integrated analysis software correlates data from different spectral modes, combining all results into a unified Origin project file
- Applications support is provided by expert nanotube scientists



Main control screen

NS1 Measurement Features

- Records near-IR fluorescence, near-IR absorption, and visible absorption spectra
- Four lasers for excitation of SWCNT fluores-cence emission
- Sensitive near-IR fluorescence detection from 900 to 1600 nm
- Rapid absorption spectroscopy from 400 to 1600 nm
- Flexible, integrated data acquisition and analysis software
- Small sample volumes
- Flow cell compatibility
- Kinetics mode for monitoring eluent streams or chemical reactions

NS2 Additional Measurement Features

- Measures Raman spectra of single-, double-, and multi-walled carbon nanotubes
- Covers RBM, D, G, and G′ bands

NS1 and NS2 Convenience Features

- Compact footprint
- Low power consumption
- Uses no cryogens
- Eye-safe CDRH Class 1 laser device
- Low maintenance
- Turn-key system includes computer, soft-ware, installation, training & warranty
- Free software updates for three years

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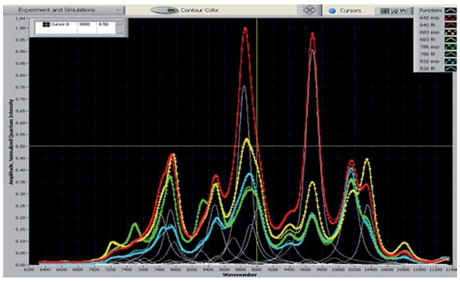
Spectral Modes

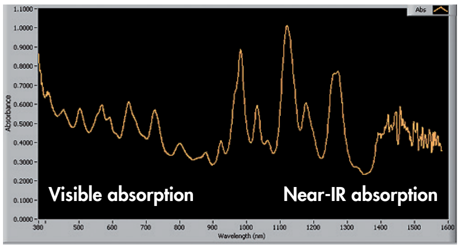
For each data acquisition mode, users can select any or all of the following spectral modes. All data are acquired under program control with a single placement of the sample cell.

Near IR Fluorescence spectra are measured using four excitation lasers. Very weak sample emission can be quickly recorded with high signal-to-noise ratios because of the high excitation powers, the coherently focused excitation beams, the high aperture collection optics, and an efficient emission spectrometer and array detector.

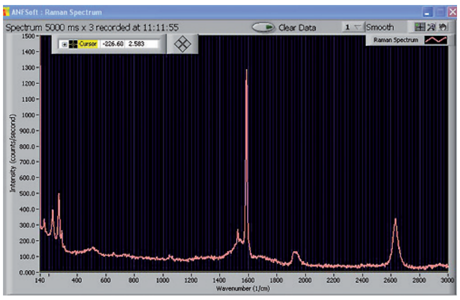


Fluorescence emission spectra

Absorption spectra are measured in single-beam mode using broadband probing light from a stabilized tungsten-halogen lamp. A 2 mm beam diameter permits the use of small sample volumes. The spectral coverage is 900 to 1600 nm in the base model NS1, extended to 400 to 1600 nm in the NS2 and in the NS1 with visible absorption option.



Raman spectra are available only in the model NS2. The Raman excitation wavelength may be selected (on ordering) as 532 or 671 nm, according to the customer preference. The optical configuration has been designed to provide the spectral resolution and range appropriate for CNT spectroscopy.



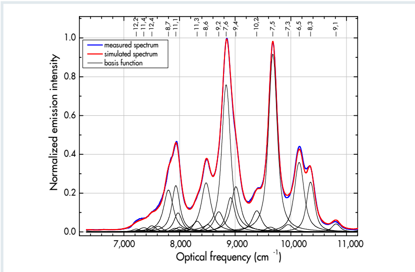
Raman spectrum

Data Acquisition Modes

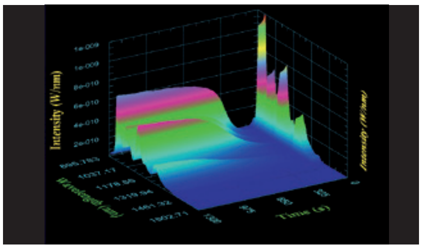
Both the NS1 and NS2 NanoSpectralyzers offer the following selection of data acquisition modes.

Setup Mode allows full manual control of all instrument parameters and displays raw spectra in real time. This is useful for exploratory research applications and for estimating acquisition parameters for new samples.

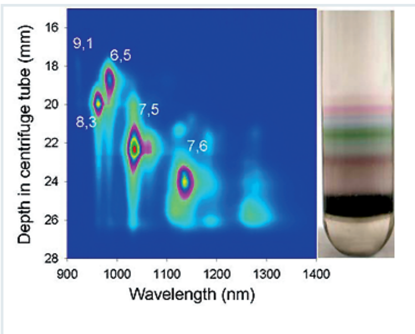
Single Acquisition Mode is used for automated, accurate sample characterization. The user selects the desired spectral modes and acquisition parameters and directs the results to the data analysis routine and/or to an Origin project file.



Time Sequence Acquisition Mode allows any spectral measurements to be recorded as kinetic sequences to measure changes in sample composition or condition. This mode is ideal for studying nanotube aggregation or chemical reactions. If a flowing sample cell is installed, sequence mode also allows the user to monitor eluent streams containing nanotubes. Up to 10 spectra per second can be recorded.



Spatial Profiling Mode is used with the vertical translation option to quickly identify the layers containing sorted SWCNTs in density gradient centrifuge tubes. After an unfractionated centrifuge tube is placed into the NanoSpectralyzer, spectra are automatically measured as a function of depth in the tube. The spatially resolved spectral data are displayed as contour or surface plots.



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Spectral Analysis

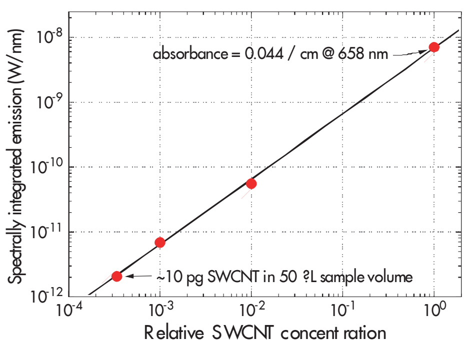
Sets of near-IR fluorescence spectra measured from SWCNT samples are automatically interpreted by a sophisticated program that is part of the NanoSpectralyzer software. This program uses templates that contain detailed spectral data on dozens of semiconducting (n,m) species. By accurately simulating the measured spectra, it then finds the set of (n,m) concentrations that account for the observed fluorescence data.

Although this analysis is based on emission data from four discrete excitation wavelengths rather than a conventional excitation scan, it provides equivalent results. This is because the NanoSpectralyzer analysis takes advantage of the extensive spectral data known for SWCNTs.

To allow accurate analyses with different surfactant coatings, which slightly alter SWCNT spectra, the NanoSpectralyzer is supplied with additional templates containing appropriate spectral parameters.

Quantitation

High NIR fluorescence sensitivity makes the NanoSpectralyzer particularly well suited for SWCNT trace detection. Spectrally integrated NIR emission is automatically computed and displayed along with the sample's fluorescence efficiency index (described in How it Works). As illustrated in the adjacent graph, the NanoSpectralyzer provides a dynamic range of ~10^5 and detection limits in the picogram range.



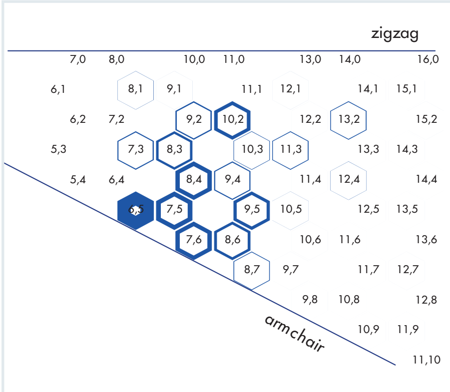
ANFSoft : Fluorescence Power and Efficiency				
Excitation (nm)	640 nm	785 nm	532 nm	671 nm
Total Power (nW)	38.10093	20.37163	22.45301	13.38291
Efficiency (nW cm)	70.11062	58.57185	49.83078	26.84586

See Schierz et al, Environmental Science and Technology 46, 12262-12271 (2012)

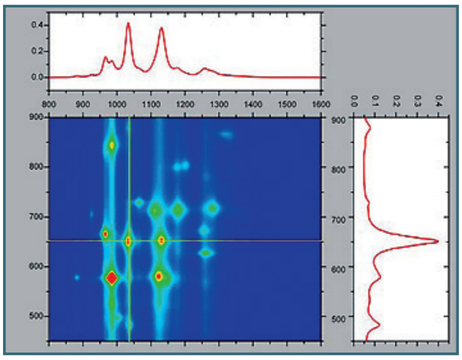
Presentation ready Graphs

Spectral data and analysis results are automatically compiled into an Origin project file and converted into publication-quality graphs.

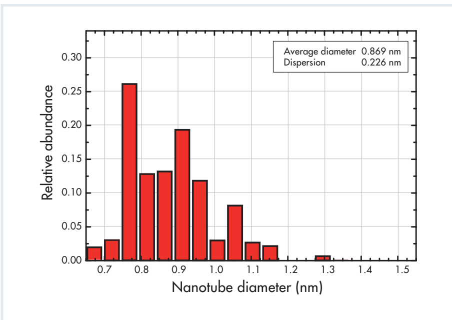
The graphene sheet plot displays the abundances of different (n,m) species in an SWCNT sample. The relative abundance deduced for each species is indicated by the thickness of its hexagonal border. Results are displayed with and without fluorimetric efficiency corrections.



The deduced (n,m) distribution is also displayed in the form of an excitation-emission contour plot. This plot is synthesized from the four measured emission spectra and the parameters deduced from spectral analysis.



The diameter distribution of a SWCNT sample is automatically computed from the (n,m) distribution and converted into a histogram plot. The first and second moments of the diameter distribution are also computed and displayed on the plot. Results are shown with and without corrections for (n,m)-dependent fluorimetric efficiencies .



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What's included with the NanoSpectralyzer?

The NS1 and NS2 are complete turn-key instruments built from stable, high quality components to provide reliable long term operation with no user adjustment. Each system comes with:

- An integrated optical system containing four lasers and three spectrometers (two in the NS1)
- Full custom software for instrument control, data acquisition, and spectral analysis
- A licensed copy of OriginLab Origin, a leading program for data analysis and scientific graphics
- An interfaced desktop computer system with pre-loaded software
- On-site installation and training
- A one-year parts and labor warranty
- Free software upgrades for three years
- Expert applications support

Product List

NS1 NanoSpectralyzer	
NS1 base system	includes 4 excitation lasers 900 – 1600 nm range for fluorescence and absorption
Visible absorption option	extends absorption spectral range to 400 – 1600 nm

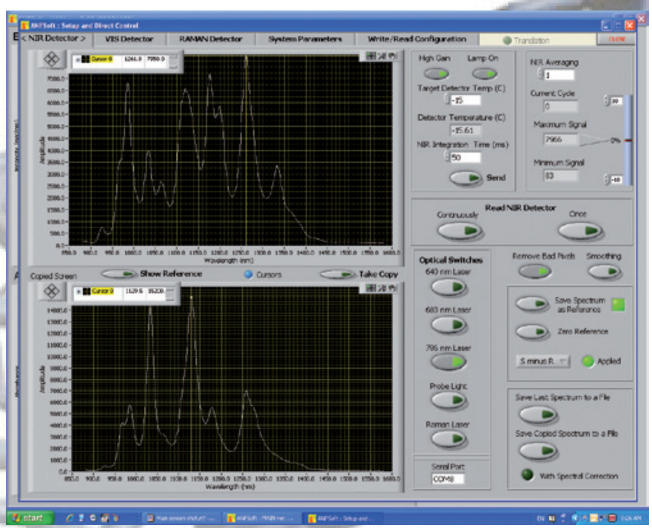
NS2 NanoSpectralyzer
includes all functions of NS1 plus visible absorption option and Raman spectroscopy (532 or 671 nm)

NS3 NanoSpectralyzer (New)
modular system with 5 lasers allows customization for versatile characterization of nanomaterials

NM1 Near-Infrared Fluorescence Microscope (New)
modular system with 5 lasers allows customization for versatile characterization of nanomaterials

Options	
Vertical sample translation stage	allows rapid, automated fluorescence mapping of DGU centrifuge tubes
Reduced sample volume capability	permits measurements on 50 microliter samples
Flow cells	allow spectral monitoring of eluent streams
Extra NanoSpectralyze software license	for spectral data analysis on a second stand-alone computer

Specifications	
Fluorescence excitation laser λ	532, 638, 671, and 785 nm
Fluorescence geometry	High numerical aperture epifluorescence
Fluorescence spectral range	900 –1600 nm
Near-IR detector type	512 element TE-cooled InGaAs array
*Raman excitation laser λ	532 or 671 nm (choose when ordering)
*Raman spectral range	150 to 2900 cm^{-1} shift
*Raman spectral resolution	4 cm^{-1}
*Raman detector type	2048 pixel back-thinned Si CCD
Absorption light source	Stabilized tungsten-halogen lamp
Absorption spectral range	400 – 1600 nm
Absorption spectral resolution	5 nm (NIR), 1 nm (vis)
Absorption ceiling	3 AU (NIR and vis)
Visible detector type	3648 pixel Si CCD
Absorbance noise (rms), near-IR	<2 x 10^{-4} AU at 0 AU for 10 s integration
Absorbance noise (rms), visible	<5 x 10^{-4} AU at 0 AU for 10 s integration
Minimum sample volume	120 µL
Data acquisition time (typical)	2 minutes for full set of spectra
Power consumption	75 W (excluding computer)
Main Optical Module dimensions	310 x 465 x 195 mm
System weight	22 kg (excluding computer)
*Raman available only with NS2	



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