Ram-532-NANO™ Portable Raman Analyzers:
Superior Performance for **Carbon Nanotubes** Characterization and Quality Control

INTRODUCTION

Due to their unique electronic, physical and mechanical properties, carbon nanotubes (CNTs) are being increasingly used in the fields of electronics and semiconductors, advanced materials, batteries and capacitors, aerospace and defense. The global CNTs / CNT-based product market is projected to reach 5.64 Billion USD by 2020, with annual growth rate (CAGR) of 20.1% **[1]**.

As commercial CNT production increases, a need to control the quality of produced or purchased CNTs also increases. Raman spectroscopy is one of the most suitable analytical techniques for CNT characterization and/or quality control.

In this Application Note we demonstrate why **Ram-532-NANO™ Series Portable / Handheld Raman Analyzers** (Fig. 1) are preferred options for analysis of carbon nanotubes and other advanced nanomaterials. The superior performance of these analyzers is achieved by combining 532 nm Raman excitation (non-conventional for portable / handheld Raman) with the state-of-the-art methodology to reduce impact of fluorescence on Raman measurements. In addition, the instrument is available in 4 different configurations to best suit your specific analytical needs (Fig. 1).

WHY Ram-532-NANO™ SERIES ANALYZERS? (Shown in **Figure 1** on the next page)

The unique techno-economic benefits of Ram-532-NANO™ Portable / Handheld Raman Analyzers include:

- **~2-fold reduced instrument costs** due to engineering / economic advantages that use of 532 nm light offers.
- **5 and 16 times faster analysis** than that for conventional portable units typically using 785 and 1064 nm excitation, respectively. This is due to Raman signal intensity being inversely proportional to 4th power of laser excitation wavelength (I_{RAMAN} ~ $(1/\lambda_{EX})^4$, where λ_{EX} = **532 nm**, **785 nm**, **1064 nm**).
- **Unmatched** combination of **spectral resolution** (~4 cm^{-1}) and **spectral range** (~120-4000 cm^{-1}) **to enable superior CNT structural characterization.**
- **Automated calculation of CNT structural parameters / physical properties** including: CNT diameter, structural quality (% of defects), CNT type (single-, double- or multi-wall), and conductivity type.
- **No laser-induced damage to carbon nanotubes (or other gentle samples) during analysis.** This is because up to 5-16 fold reduced laser power can be used, compared to conventional 785 and 1064 nm instruments, **without compromising analysis quality**.
- **Ability to measure** advanced materials **'as is'**, **on a slide**, or **through containers:** vials, bottles, jars, Petri dishes, plastic bags, blister packs, etc., **to eliminate any personnel exposure to these materials**, if needed.
- **SERS substrates available**

BioTools
17546 Bee Line Hwy | Jupiter, Florida 33458 | www.btools.com

EXPERIMENTAL

Carbon nanotube samples were analyzed using a **RamTest-NANO™ handheld Raman Analyzer** (BioTools, Inc., Jupiter, FL, USA) shown in **Figure 1-3**. All tests were run in automated mode (requiring no prior knowledge of Raman spectroscopy), where all measurement parameters are automatically adjusted to optimize signal-to-noise ratio and minimize fluorescence, with remaining fluorescence background (if any) automatically subtracted. It should be noted that all **conclusions made here for RamTest-NANO™ unit can be directly extrapolated to all Ram-532™ based BioTools' instruments shown in Figure 1**.

RamTest™ software is CFR 21 compliant and comes with a user-editable database of reference compounds to conform all needs. RamTest-NANO™ software add-on enables calculation / estimate of major CNT structural parameters / physical properties, as well as an option to automatically generate the associated .pdf or Excel report.

Figure 1. Ram-532-NANO™ Series Portable Raman Analyzers show superior performance for carbon nanotube (CNT) characterization (please see text for detail). The following 4 configurations available.

1) Ram-532™ 'as is' – portable Raman spectrometer (top left) – serves as a building block for all the configurations;
2) Ram-532™ with stage – lab-based portable Raman analyzer;
3) RamTest-NANO™ handheld Raman unit; and
4) MicroRam-L532™ portable Raman microscope.
NOTE: Removable attachments enable measurements of liquids and solids 'as is'; on a slide; or through containers: vials, bottles, jars, Petri dishes, plastic bags, blister packs, etc.

RESULTS

Figures 2 shows the Raman spectrum of a carbon nanotube (CNT) sample collected using a 532 nm excitation **RamTest-NANO™ handheld Raman analyzer** (Figure 1-3). All major CNT bands, including RBM, D, G and G' bands, are well resolved and can be used for CNT characterization. Specifically, RamTest-NANO™ software uses these bands to estimate CNT diameter / diameter distribution, CNT structural quality (% of structural defects), CNT type (single-, double-, or multi-wall) and conductivity type.

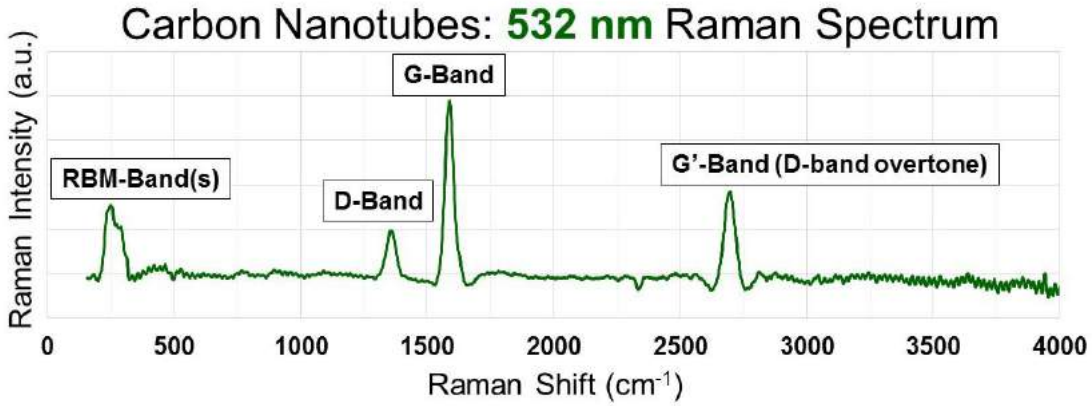

Figure 2. 532 nm Raman spectra of carbon nanotubes (CNTs), measured using BioTools' **Ramtest™-NANO** instrument based on **Ram-532™** spectrometer. This spectrum contains all important CNT Raman bands, which can be used for CNT characterization (please see text for detail).

To compare 532 nm and 785 nm Raman performance for carbon nanotube characterization, Figure 3 shows the 785 nm Raman spectrum of the same CNT sample, as that shown in Figure 2. Specifically, the 785 nm Raman was collected using **Mobile μRaman™ portable Raman Microscope**, based on BioTools' **Ram-785™** Raman spectrometer, in its high resolution configuration (~4 cm^{-1} spectral resolution, and ~200-2000 cm^{-1} spectral range). RBM, D, and G bands of CNTs are well resolved, whereas the G' band is cutoff. To include G' band, the extended configuration of **Mobile μRaman™** or any other **Ram-785™-based instrument**, is recommended for CNT analysis / quality control, if 785 nm excitation is preferred by an end-user over the 532 nm, for any reason (however, please see 'Summary' Section).

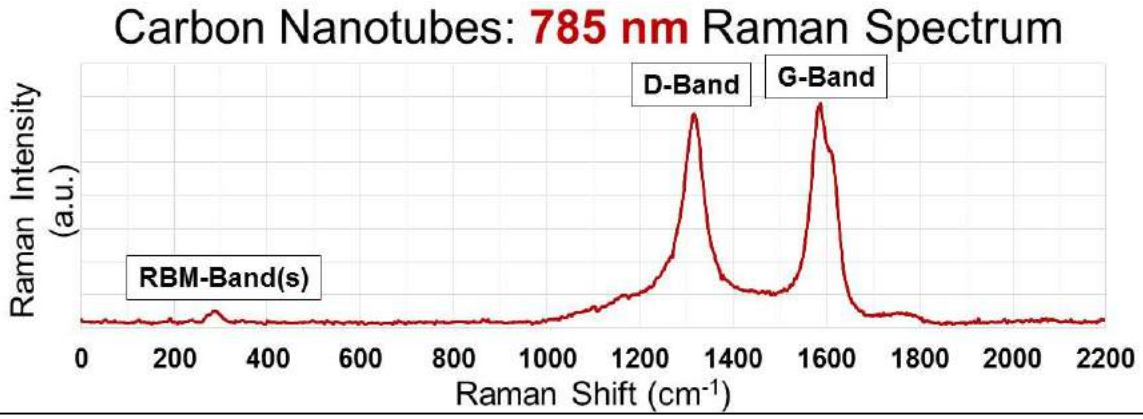

Figure 3. 785 nm Raman spectra of carbon nanotubes measured using BioTools' **Mobile μRaman™** instrument based on **Ram-785™** spectrometer in its high resolution configuration. **NOTE:** Extended range configuration of Ram-785™ recommended to include G' band of CNTs (please see text for detail).

As it can be noticed from Figures 2 and 3, the relative intensity of D-band is significantly higher for the 785 nm Raman spectrum (Figure 3) than that for the 532 nm (Figure 2), even though identical laser powers have been used on both instruments. This may indicate that 785 nm light partially destroys carbon nanotubes, at least at laser power used in this study. Further decrease of laser power helps to reduce the 785 nm laser-induced CNT damage (data not shown). However, it also results in reduction of 785 nm Raman signal and necessity to increase measurement / analysis time.

SUMMARY

BioTools' portable / handheld Raman instruments based on **Ram-532™** and **Ram-785™** Raman spectrometers are generally feasible for CNT characterization. Overall, however, the **Ram-532™ based analyzers** (**Figure 1**), utilizing 532 nm excitation, are likely to be the most suitable option for the task. This is because:

- **532 nm laser of Ram-532™ does not readily destroy CNTs** examined here, whereas 785 nm laser of Ram-785™ must ONLY be used at low power.
- **Raman signal at 532 nm excitation is approximately 5-fold stronger than that at 785 nm**, per unit laser power. (Raman Signal ~ $(1/\lambda_{EX})^4$, where λ_{EX} = **532 nm**, **785 nm**, etc.). Thus, Ram-532™ based units are capable of **~5 times faster analysis and/or improved analysis quality**. In addition, in case of especially gentle samples, the Ram-532™ based analyzers can be used at up to ~5-fold lower laser power than the Ram-785™ based units, respectively, without compromising analysis quality.
- 532 nm Raman provides a superior combination of spectral resolution and spectral range (compared to 785 nm Raman) **to enable superior CNT structural characterization**. This is because higher dispersion of 532 nm light (compared to that of 785 nm) gives engineering advantage in space-limited portable Raman instruments.
- Quantum efficiencies of best in class CCD detectors / optics are greater at 532 nm (compared to 785 nm) to even further increase observed Raman signal in favor of 532 nm excitation.
- In spite of all technical advantages described above, **Ram-532™ based instruments ARE LESS EXPENSIVE** than the units / configurations based on Ram-785™ spectrometers.

REFERENCES

[1] Data obtained from www.marketsandmarkets.com