

Nanoscale Photonics Gives Nanolevel Detection.



Key Words

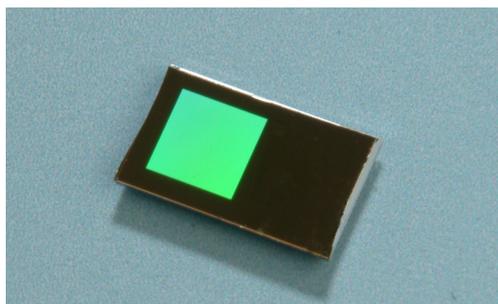
- Trace detection
- Surface enhanced Raman
- Surface science
- Benzoylecgonine
- Nile Blue
- Thiophenol

Combine DeltaNu's portable Inspector Raman™ with Mesophotonic's nanoscale photonic Klarite® crystals and you have a team ready for trace detection and surface science. In 1977 when Professor Richard Van Duyne at Northwestern University [1] and Martin Fleischman at Southampton University discovered anomalously large enhancements from electrochemical roughened surfaces the phrase *nano* had not become the craze that it is today. Now we know that the enhancements are due to nanoscale roughness on the surface. Amazingly these nanostructures have led to tremendous advances in fundamental science and in applications requiring trace detection.



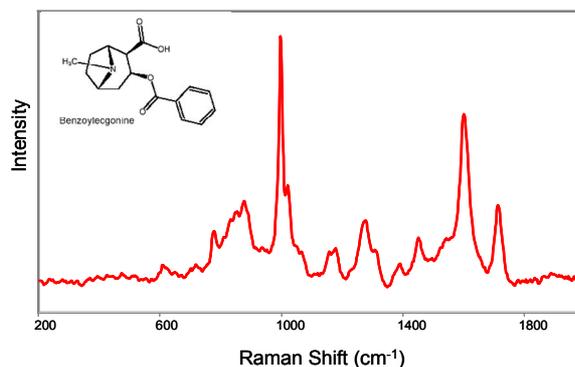
Inspector Raman instrument from DeltaNu

When Surface Enhanced Raman Scattering (SERS) was first discovered the Raman instrumentation was the size of a small car and required more power than a mid-sized car. It also cost about 10 times more than an automobile. Today, DeltaNu has made Raman not only practical with hand-held instruments, but also affordable. In 2004 DeltaNu introduced our Inspector Raman series to offer scientists and nonscientists with a tool to benefit from the many advantages of Raman spectroscopy. Now Mesophotonics is supplying the other half of the SERS equation, SERS Klarite substrates provide microlithographically produced nanostructures for reproducible SERS spectroscopy.



Klarite SERS substrate from Mesophotonics.

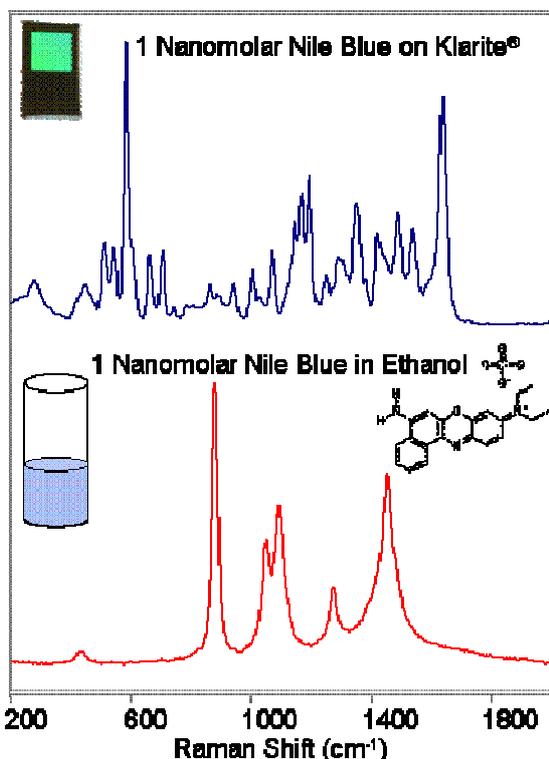
An essential application of SERS is detection of trace materials. Our spectrum of benzoylecgonine illustrates trace detection of the principal metabolite of cocaine. The amount of benzoylecgonine being analyzed is one femtogram or, in nanoterm, one millionth of a nanogram. To put this in perspective, the BBC reported that the Po River in Italy flows with nearly 4 kilograms of this material every day [2]. This spectrum of benzoylecgonine was acquired in 15 seconds with DeltaNu's Inspector Raman and the amount analyzed is 4×10^{18} less than what flows down the Po River every day. The BBC reports that these figures are staggering and that measurement of drug metabolites like benzoylecgonine in rivers could be expanded to heroin and other drugs of abuse.



Trace spectra of 1 femtogram of cocaine metabolite benzoylecgonine recorded in 15 seconds.

While the enhancement of benzoylecgonine is amazing, additional enhancements can be achieved with resonance Raman scattering. Molecules absorb radiation due to electron promotion between molecular states. A photon is absorbed when the energy required to promote an electron matches the energy of the incident photon. When Raman spectroscopy is performed under this condition it is called resonance Raman scattering. Typically, when the absorbance is strong, the resonance enhancement can be several orders of magnitude. DeltaNu's analysis of Nile Blue on a Klarite substrate shows what we can see with 5 second acquisitions and about 6000 molecules. Nile Blue absorbs light at 785 nm and when excited with 785 nm excitation from the Inspector Raman one observes very large enhancements. In fact, Shuming Nie and his group observed single molecules of rhodamine 6G under similar conditions [3]. Along side our SERS spectrum from a Klarite substrate we show a spectrum of nanomolar Nile Blue in ethanol. All you see is a nice spectrum of ethanol.

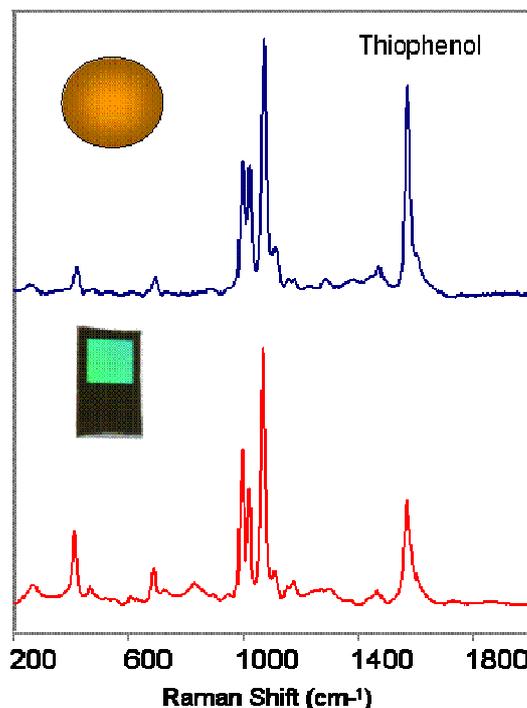
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Raman spectra of 1 nanomolar Nile blue on Klarite and of 1 nanomolar of bulk solution recorded with Inspector Raman showing the distinguishing features of Nile blue can only be seen on the SERS substrates.

In addition to trace analysis SERS provides fundamental information about molecules on metal surfaces. In the early 1980's Professor Alan Creighton at the University of Kent formulated a method to determine a molecule's orientation with respect to a surface from its SERS spectrum [4]. The method utilizes the directionality of the electric fields responsible for the SERS effect. In 1991 Professor Keith Carron further developed Creighton's method by including the dielectric constant of the surrounding medium [5]. Professor Carron used thiophenol as his surface probe molecule. We have repeated this work with the portable Inspector Raman. The spectrum below shows the spectrum of thiophenol on a spherical nanoparticle in a colloidal gold suspension and on a Klarite substrate. The

differences seen in the intensity of certain Raman bands acquired from a spherical particle and from a Klarite are predictable from theoretical descriptions of SERS and the unique cavity structure of the Klarite design.



SERS spectrum of thiophenol on gold colloides and Klarite substrates.

Further details of the Inspector Raman instrument, Klarite substrates and additional applications notes are available from www.mesophotonics.com and www.deltanu.com

References

- 1 Jeanmaire, D., Van Duyne, R., *J.Electroanal. Chem.* 1977, 84, 1.
- 2 <http://news.bbc.co.uk/1/hi/world/europe/4746787.stm>
- 3 Nie, S. and Emory, S. *Science*, 1997, 275, 1102
- 4 Creighton, J., *Surface Science*, 1983, 124, 209.
- 5 Carron, K. and Hurley, L., *Journal of Physical Chemistry*, 1991, 95, 9979.

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Tel: +1 307 745 9148
Email: DrRaman@deltanu.com
Web: www.deltanu.com



mesophotonics

Tel: +44 23 8076 3752
Email: sales@mesophotonics.com
Web: www.mesophotonics.com