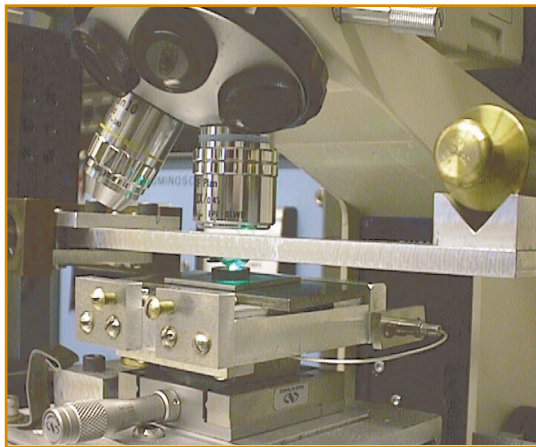


### Raman microscope used for *in situ* tribological studies

There is a need to devise methods to monitor failure of load-bearing contacts in real time. Now, engineers rely on friction, torque, and friction-generated noise to anticipate failure. Unfortunately, failure comes abruptly in many well-lubricated bearings - those that form long-lived contacts with good boundary lubricants or solid lubricants, like molybdenum disulfide ( $\text{MoS}_2$ ). These lubricants sustain steady, low friction coefficients for a long time, then fail rapidly. The difficulty of studying failure of a thin film lubricant is that all the action takes place at a buried interface: thin interfacial films undergo a variety of changes (e.g. thinning, agglomeration, retransferring, oxidation) inside the contact where real-time detection and analysis are very difficult.



NRL micro-Raman tribometer.

Drs. Kathryn Wahl and Irwin Singer at the Naval Research Laboratory in Washington DC have developed an *in situ* Raman tribometer that can watch and monitor chemistry at sliding interfaces in real time. The instrument has been designed and built around a Renishaw micro-Raman spectrometer (with a 514 nm  $\text{Ar}^+$  laser and Olympus microscope with long working distance optics). Optically transparent, hemispherical counterfaces enable visual monitoring of dynamics of liquid and solid lubricants in the contact during sliding. Typically, most *in situ* tribometers have used transparent flat substrates against stationary curved surfaces or rotating spheres; this configuration is advantageous for study of liquid lubricated contacts. However, by using a transparent hemisphere as the stationary counterface, coatings or non-traditional bearing materials can easily be studied since no special coating techniques, machining processes, or substrates are necessary. Some signal loss is to be expected due to the curvature of the ball surface and the need to use a long working distance objective, but the NRL workers have found that the Raman signal from the contact is satisfactory.

*continued on the top of next page...*

### Fast, easy analysis of polymer failures with confocal Raman microscopy

In modern analytical laboratories, investigations of samples should often be done in the shortest time possible, especially when problems in a production process have to be overcome. Consequently, sample preparation should be as simple as possible to save time and money.

Dr. Peter Wilhelm of Graz University of Technology, Austria, reports that Raman microscopy has become a standard tool for polymer characterisation in their laboratory, in addition to electron microscopic techniques (high resolution REM and TEM), and FT-IR microscopy.

Their Raman system is equipped with a HeNe laser (633 nm) and a diode laser (782 nm, for use with fluorescing samples). When analyzing polymer samples (failure analyses, chemical imaging) they benefit from the complementary power of both vibrational spectroscopic methods: infrared (rapid identification, no fluorescence problems) and Raman (better lateral resolution, broader spectral range).

Contaminant inclusions and hazes are common faults with polymer films. FT-IR microscopy has been a useful technique for the identification of organic contaminants. Unfortunately, sample preparation can be laborious, because contaminant inclusions have to be exposed by "digging" within the sample with a scalpel or needle, or by expensive embedding and thin-sectioning.

However, opaque samples may now be investigated using the unique confocal optics of Renishaw's Raman microscopes. A dull inclusion in a polypropylene film (see photo) was analysed by a confocal Raman experiment, performed with a Renishaw System 2000 microscope, using a HeNe (633 nm)

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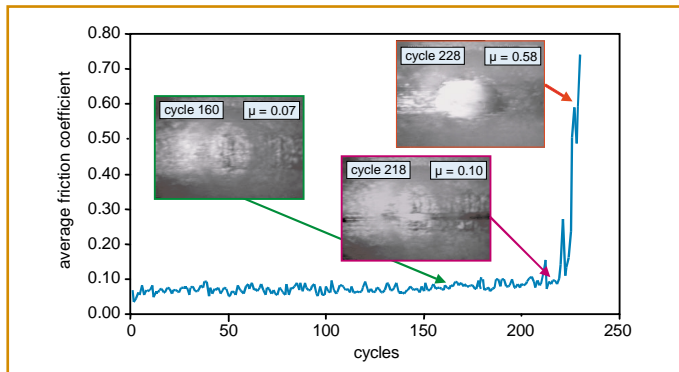
Photograph of a dull inclusion in a polypropylene film

*This edition also contains articles on:*

- novel liquid crystal imaging technology
- full instrument calibration software
- Raman seminars held at Renishaw GmbH, Germany

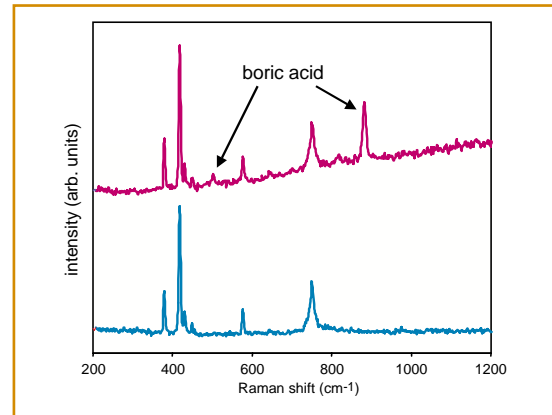
Raman microscope used for *in situ* tribological studies (continued from front cover)

Since the transparent contact must remain stationary during imaging and Raman acquisition, the hemisphere is mounted in a rigid fixture and the friction sensing is done using a quartz piezo crystal under the substrate. The tribometer is controlled with LabView-based software, and the whole instrument retracts away from the spectrometer on a motorized linear translation stage when not in use. Micro-Raman spectroscopy or video of the sliding contact are recorded while friction data are acquired.



Friction test and sliding contact video images through sapphire sliding against  $H_3BO_3$  on Al in air.

The figure above shows results of sliding a sapphire hemisphere against a boric acid ( $H_3BO_3$ ) coating on an Al substrate. The friction coefficient was below 0.1 for more than 200 cycles, after which friction rose suddenly and the contact failed. Micrographs inset into the friction plot are from the video taken during sliding. The contact was fairly featureless until within 20 cycles of failure, when a small bright spot appeared. This spot grew, and at failure, the entire contact area appeared bright. Micro-Raman spectra of the sliding interface before failure showed bands from both the sapphire slider and boric acid (upper spectrum). The bright spot at 218 cycles (pre-failure) and the entire contact at failure showed no boric acid (lower spectrum). Previously, such results could only be inferred from *ex situ* analysis of separated contacts. These experiments establish that the phase actually present in the high stress (~1 GPa) sliding contact is, indeed, boric acid.



Micro-Raman spectra obtained during sliding. Arrows indicate  $H_3BO_3$  (boric acid). Background features around  $400\text{ cm}^{-1}$  as well as  $760\text{ cm}^{-1}$  arise from the sapphire hemisphere.

By combining micro-Raman spectroscopy with traditional friction/torque sensing and, more importantly, contact visualization and image processing, this approach allows investigation of spatially resolved information on both friction and chemistry of the contact. This new system is currently being used to observe debris formation, chemistry, and mobility in solid lubricated contacts as a function of relative humidity, as well as the behavior of mixtures of liquid lubricants in the sliding interface.

Figures courtesy of Dr. S. David Dvorak, ASEE/NRL postdoctoral associate, and Drs. Wahl and Singer. This project was funded by the Office of Naval Research, Material Science and Technology Division.

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$H_3BO_3$  coating courtesy of Dr. A. Erdemir, Argonne National Laboratories

Fast, easy analysis of polymer failures with confocal Raman microscopy (continued from front cover)

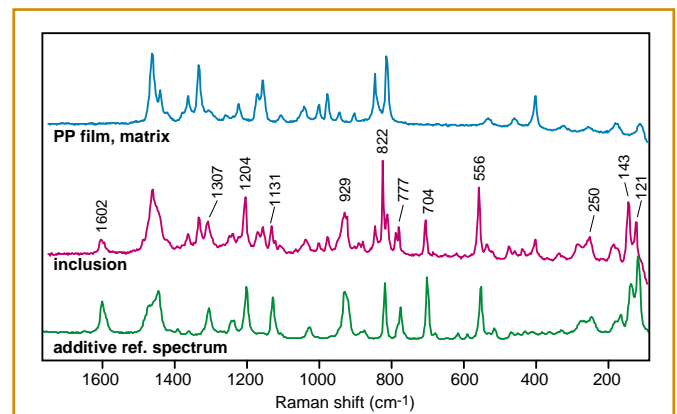
laser as excitation source. The upper spectrum, taken at the surface (above the inclusion) represents a well resolved, undisturbed PP spectrum. By moving the focus down into the PP matrix in steps of  $2\text{ }\mu\text{m}$  in a depth of  $12\text{ }\mu\text{m}$  additional peaks appeared (middle spectrum). By comparing the spectrum with that of a reference sample (lower spectrum) the inclusion could clearly be identified as a bulk of an additive.

For further information please contact:

Dr. Peter Wilhelm, Research Institute for Electron Microscopy, Graz University of Technology,

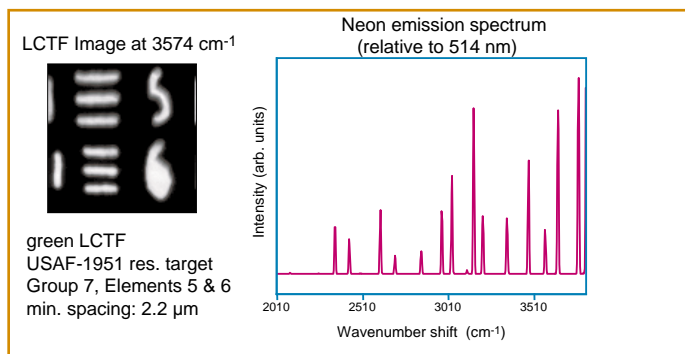
Steyrergasse 17, A-8010 Graz, Austria;

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Raman spectra taken from the inclusion, the matrix, and from a reference sample.

## Novel imaging technology for Renishaw spectrometers



We gave details in *Spectroscopy Innovations 3* of a new Raman imaging system that uses a liquid crystal tuneable filter (LCTF). Some new results are shown to the left; these illustrate the high spatial and spectral resolution of the system.

This system is being developed by Drs. E. Neil Lewis, Pina Colarusso, and Ira Levin of the National Institutes of Health in Bethesda, Maryland, USA, in conjunction with Renishaw and Spectral Dimensions of Olney, Maryland, USA.

The second figure depicts a Raman image at 520  $\text{cm}^{-1}$  of an integrated circuit chip, with image contrast based entirely on the intensity of the strong optical phonon of silicon.

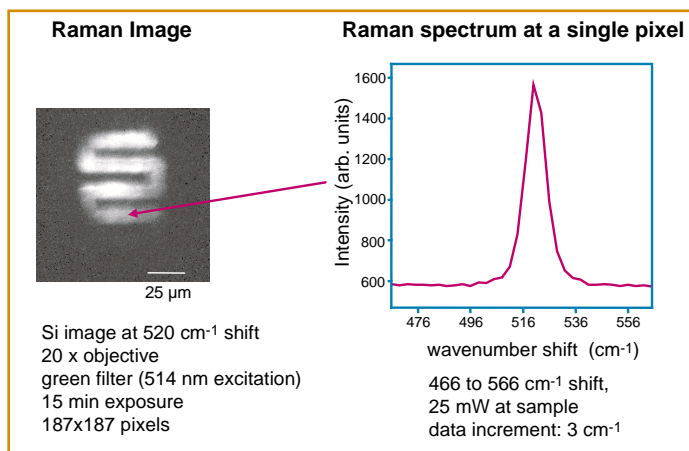
These new Renishaw LCTF imaging systems are already being used by groups at the NIH and Dupont to characterize biological systems and polymer formulations respectively. The higher spectral resolution and full range tuneability, compared to dielectric filter imaging, allows for higher contrast images. Coupled with the new imaging software this is giving users the full Raman picture

For further information please contact:  
Andrew Whitley (USA), or  
Ken Williams (UK)  
Contact details are given on the back cover.

Figures are presented courtesy of Drs. E. Neil Lewis, Pina Colarusso, and Ira Levin at the National Institutes of Health in Bethesda, Maryland, USA.

We would like to apologize to Drs. Lewis, Colarusso, and Levin; we accidentally omitted text giving credit to them for the second figure when it appeared in *Spectroscopy Innovations 3*.

Image of a resolution test target, and a spectrum from a Ne lamp.

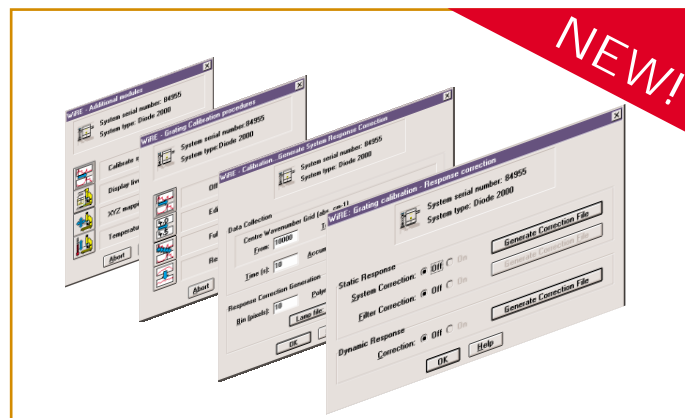


Raman image of a test sample (left), and a spectrum taken from one point (right)

## Full instrument calibration software

Renishaw has recently introduced software which, for the first time, allows full Raman instrument calibration. Calibration of the spectrum intensity (y-axis) is now possible, with measurement of the instrument response and automatic instrument response correction fully integrated into the software. Together with the existing spectrum position (x-axis) calibration, this allows a Raman System to be fully characterized. Data is then directly transferable between different instruments of both the same model type but also between completely different models (e.g. between a Renishaw Raman Microscope System 1000 and a System 100 DLC Analyzer).

For more details contact your local Renishaw company or distributor.



Raman seminars at Renishaw subsidiaries worldwide

We are holding a series of Raman application seminars at Renishaw's subsidiary sites around the world.



Attendees at the first meeting at Renishaw GmbH

The first meeting was held recently in Germany, at Renishaw GmbH in Pliezhausen, south of Stuttgart. Ten participants from a range of industrial and research facilities in Germany and Austria attended seminar presentations by Dr Ralph Lehnert (Renishaw GmbH) and Dr Ian Wilcock (Renishaw plc).

Please contact your local representative (or Ian Wilcock) if you are interested in attending one of the meetings.

## Reorganization!

**RENISHAW®**   
Spectroscopy Products Division

Observant readers will have noticed that we are no longer the Spectroscopy Group of Renishaw's Transducer Systems Division!

Renishaw plc had a major reorganization at the start of the year. The Spectroscopy Products Group has grown rapidly since the launch of its first Raman spectrometer in 1992, and has now become a separate Division.

This has brought a few minor changes to our contact details (see below), including a change in our general email address.

Spectroscopy Products Division contains the same personnel as before, and its network of agents and distributors remains unchanged.

## Meet the UK Renishaw spectroscopy group

We are pleased to welcome Dr. Mike Claybourn to the UK marketing group as a product support engineer. Mike was at ICI for many years, where he was a senior research scientist specializing in the spectroscopy of polymers; he has published over 40 papers and is the author of *Infrared reflectance spectroscopy of polymers* (ISBN 1-890086-03-7).



Mike installs his first Renishaw instrument, a System 100 DLC Analyzer, in the clean room of a major hard disk manufacturer.

## Renishaw worldwide companies with spectroscopy support

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