

**WELCOME** to the first issue of Spectroscopy Innovations, the newsletter from the Renishaw spectroscopy group. After launching the first Raman imaging microscope 5 years ago, Renishaw spectroscopy has now grown into a successful business with an ever increasing number of products and customer base. This newsletter is intended to be a regular update on Renishaw spectroscopy activities worldwide and is written for our existing customers and future new customers. It will focus particularly on new applications and products.

### Patents granted

Renishaw has been granted several key patents for its technology by the European and US Patent Offices. European Patent No 0543578 and US Patents Nos 5,442,438 and 5,689,333 relate to Renishaw's use of a holographic filter at a low angle of incidence as a beamsplitter, a key element of Renishaw Raman systems. This has the dual purpose of injecting the illuminating laser light into the optical path, and rejecting scattered light of the laser wavelength from the resulting Raman spectrum.

Professor David Pitt, Managing Director of Renishaw's Transducer Systems Division, commented: "The patented holographic filter arrangement is a result of the collaboration over several years between Renishaw and Leeds University. This technology is vital for the exceptionally high light throughput of our systems, and is crucial for customers who need to see Raman bands as close as 50 cm<sup>-1</sup> from the laser."

"Renishaw has further patents covering direct 2D imaging using a tunable filter, and for our 'easy confocal' technology", added Professor Pitt. "In addition, we have patent applications relating to our extended scanning technique which gives a complete spectrum from 50 cm<sup>-1</sup> to 9000 cm<sup>-1</sup>, (using a 514 nm laser) with a high spectral resolution. The combination of these innovative technologies gives our customers unprecedented advantages in terms of high performance, high throughput and ease of use."

### New worldwide Raman offices

Renishaw has recently enlarged the marketing teams in several worldwide subsidiaries, recognising the need to strengthen considerably the sale, marketing and support of spectroscopy products in a fast growing worldwide Raman market. Those countries with increased support are:

- Renishaw Inc with four offices in the USA
- Renishaw GmbH in Germany, Austria and the Netherlands
- Renishaw S.A. in France and Belgium
- Renishaw SpA in Italy and Switzerland
- Renishaw's representative office, Beijing in China

The addresses of Renishaw's subsidiaries around the world are shown on the back page.

### Record annual results for Renishaw plc

Renishaw's annual turnover for the last financial year (July 1996 - June 1997) increased from £81.4m from the previous year's £77.1m. Particular growth was recorded in scales, CMM and spectroscopy products.

Announcing the results, Chairman David McMurtry said "I am pleased to report a group profit before tax for the year ended 30<sup>th</sup> June 1997 of £18.0m (including £1.9m profit on the sale of property) which compares with £20.1m in 1996."

"Turnover rose to £81.4m from the previous year's £77.1m, although the marked appreciation of Sterling during the year reduced turnover in Sterling terms by £6.7m, when compared with 1996 exchange rates. Significant turnover growth was achieved in the USA and Japan, despite these exchange rate movements, and in the UK where turnover rose 25%. Profit after tax was £13.4m (1996 £15.9m) giving earnings per share of 18.4p (1996 21.9p after adjustment for the one for five capitalisation issue)."

"Operating profit was £14.2m (1996 £17.6m) after taking account of increased research and development expenditures. At exchange rates comparable to the previous year, operating profit would have been over £4.5m higher."

"Although the appreciation of Sterling has caused extra pressures, the Group is in a very strong position, both in terms of the growing product range and its resources, with net cash balances in excess of £30m in spite of increased capital and research expenditures and we remain confident of the longer term growth. .... the Board believes that at current exchange rates, the Group will show an improvement in trading profits over last year."

A full report on Renishaw's results can be found at Renishaw's World Wide Web site at:

<http://www.renishaw.com>.

*This edition contains articles on:*

- Leica • UV microscope
- DLC analyser • Photodynamic Therapy
- Diamond film analysis

# NEW

# PRODUCTS AND SERVICES

## Renishaw and Leica combine forces

Renishaw is pleased to announce that it is joining with Leica, world leaders in microscopy, to market a new micro Raman system. The new Raman system combines the recently launched Leica DMLM microscope with the patented Raman imaging spectrometer from Renishaw\*. The combined system allows both spectroscopic measurement and chemical imaging of samples of less than 1 micron. Amongst several unique features is the ability to perform confocal Raman microscopy without the need of a traditional, unstable pinhole.

An essential requirement of a micro Raman system is a high quality optical microscope. The Leica DMLM has many qualities that make it an ideal platform for Raman microscopy, such as its high optical quality and a patented high stabilisation system\*\* which adds to its high mechanical stability. The Leica DMLM gives access to a large range of standard microscope accessories as well as encoder motorised stages and heating and freezing cells.

RENISHAW

Leica



\*Renishaw Patents Europe 0543578, 0542962, 0404901 United States 5442438, 5194912, 5510894, 5689333 \*\* Leica Patents Germany DE 195 30 136 C1, European, US and Japanese pending

## Renishaw announce new UV Raman system

The wavelength range over which Renishaw Raman microscopes can be used has recently been extended into the ultra violet. The new Raman microscope system uses ultra-violet laser excitation (a wide range of excitation wavelengths are possible such as 229, 244, 325 nm). It is the first commercial high optical throughput UV Raman system, employing laser-blocking filters and a single diffraction grating (rather than an inefficient double- or triple-grating design) to give unprecedented throughput and signal-to-noise values.

UV excitation has many benefits. For example, the resultant Raman scattering occurs at a shorter wavelength than most fluorescence, and therefore is not masked [out]. As a result highly fluorescent samples (e.g. biological systems) can be studied successfully. In addition, most molecules have absorption bands in the UV and, with the appropriate selection of excitation wavelength, will give resonantly enhanced Raman scattering. The resonance can be used to boost sensitivity, and preferentially study just one component of complicated multi-component samples.

Typical application areas include biochemistry (distribution of material within cells), materials science (direct measurement of the hydrogen content of hard carbon films), and forensic science (detection of traces of explosive on fabrics). The instrument has already enabled breakthroughs in understanding diamond-like-carbon films, allowing previously unobtainable data on chemical bonding effects to be related to the friction and wear properties of the films.

## DLC analyser

Renishaw is already the major supplier of Raman equipment to the DLC industry and we have recently announced a new quality control system for diamond-like-carbon (DLC) coatings facilities. DLC has become the material of choice in many areas where smooth wear-resistant coatings are required. For example, these materials are used extensively to protect the platters of computer hard disc drives against damage from contact with the read-write heads. Traditionally these coatings have been tested using wear and scratch testers. This has proved very time consuming, with long lead times of up to several days, making these methods unsuitable for routine use. A method for non-destructive rapid analysis was required.

Renishaw now satisfies that requirement with its new DLC analyser. It uses the technique of Raman spectroscopy, in which Renishaw are world leaders, to determine rapidly a range of important parameters of DLC films. These parameters are:

- film thickness
- hydrogen content
- nitrogen content
- chemical bonding of the carbon

The measurements are performed:

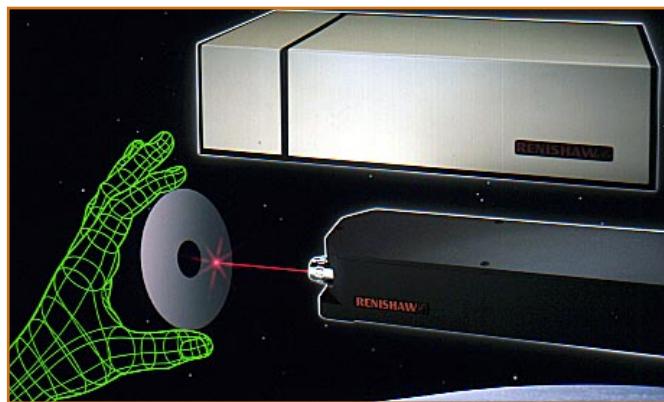
- in air
- with no sample preparation
- with DLC on a wide range of substrates (e.g. aluminium, ceramic, glass)
- on samples ranging in size from 1  $\mu$ m to over 150 mm
- with Class 1 laser safety
- without sample damage
- with typical data acquisition times of 10 seconds

Using Renishaw's unique PASS software the instrument can be semi-automated to give a simple pass/fail message during production or, if required, can give full details of parameters for use in process development.

# D APPLICATIONS

The system has true process architecture for sampling at the process line, rather than at a remote station. It is fully modular, with separate control unit, laser, computer and sampling station. Armoured fibre optic cables of up to 50 m length can be run between up to four sample stations and a central base unit. This allows the computer and lasers to be isolated from the main production line, an especially useful capability for clean room production facilities.

With this new DLC analyser, Renishaw provide a unique tool for DLC characterisation in industry. Now coatings can be analysed rapidly at the production line, allowing users to improve further product quality and yields.

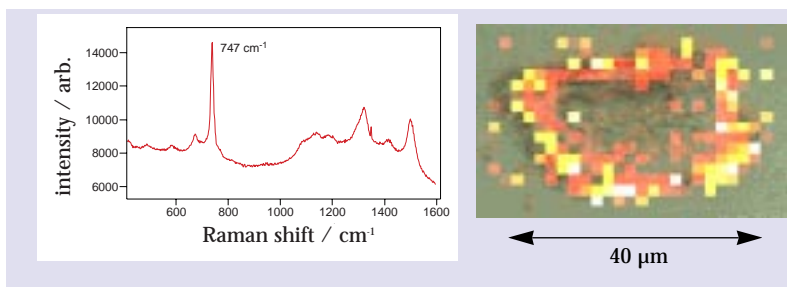


## Photodynamic Therapy

Recent results have been announced from Dr Mark Stringer's lab. in the Department of Medical Physics, University of Leeds, where Raman spectroscopy has been applied to research in photodynamic therapy (PDT). Journal of Raman Spectroscopy 28, 641, 1997.

PDT is a developing method of cancer treatment which involves the administration of a photosensitive drug followed, after a time period that allows selective accumulation within the tumour, by irradiation of the treatment site with light of an appropriate wavelength. Light absorbed by the photosensitiser leads, via a process of molecular energy transfer, to the generation of highly reactive oxygen radicals that can initiate tumour destruction. Zinc pyridinium phthalocyanine (ZnPPc) is one of several promising new photosensitiser agents that have been developed by the Leeds PDT group. Localization of ZnPPc within individual cells has been studied by Raman mapping, using a 782 nm diode laser. This wavelength brings two main advantages; firstly the intensity of fluorescence from cell constituents and sensitiser is minimized. Secondly, and more significantly, as 782 nm is beyond the chromophore absorption band of ZnPPc, this wavelength does not initiate photodynamic activity and does not, therefore, perturb the system under investigation.

The above illustrations show (left) a spectrum of crystalline ZnPPc (782 nm, 5 mW at sample), and (right) an image of a human endothelial hybridoma cell (EAhy 926) with a Raman map (step size: 2 mm) of the major sensitiser peak superimposed. In this example the cell was incubated in the presence of ZnPPc for 60 s. Results indicate that the intracellular distribution varies with incubation time, and that zinc phthalocyanines with different substituent groups show different patterns of uptake.

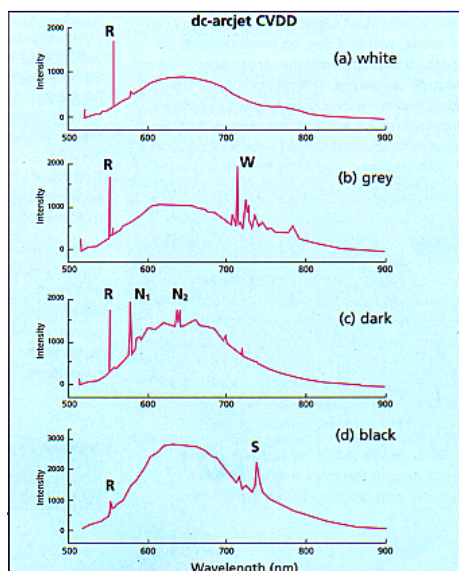


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For further information please contact Dr Mark Stringer, Department of Medical Physics, University of Leeds, Leeds General Infirmary, LS1 3EX, UK. email: m.r.stringer@leeds.ac.uk

## Combined Raman and photoluminescence of diamond films

Raman and photoluminescence spectra from samples of dc-arcjet CVD Diamond.



A study of diamond films at 4K using a Renishaw Raman system and an Oxford Instruments Microstat cryostat has been reported by Professor J.W. Steeds of the Department of Physics, University of Bristol, UK. A variety of diamond films were studied, ranging in thickness from 200 to 380 μm. The films were prepared by dc-arcjet chemical vapour deposition (CVD) by Norton Diamond Films. Cooling the samples to 4 K considerably simplifies the photoluminescence spectra, leaving the Raman signal largely unchanged. Spectra were acquired using the Renishaw 'extended scanning' facility, which allows combined Raman and photoluminescence spectra to be obtained from 500 to 900 nm in one shot, without the need for step and stitch techniques.

The data reveals that the photoluminescence spectra are very sensitive to impurity type and quantity. Tungsten impurities (W) are revealed by a series of peaks above 700 nm, nitrogen vacancy complexes by the well known peaks at 575 nm (N1) and 639 nm (N2) and silicon (Si) by the large peak at 737 nm.

The spectrometer was coupled to an Olympus microscope, and used an argon ion laser (514 nm). A sample spatial resolution of about 2 μm was achieved within the cryostat. Oxford Instruments Microstat cryostats are available through Renishaw.

This work has been reported by Professor J. W. Steeds, who is at the Department of Physics, University of Bristol, UK. email:m.j.pendrey@bristol.ac.uk



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