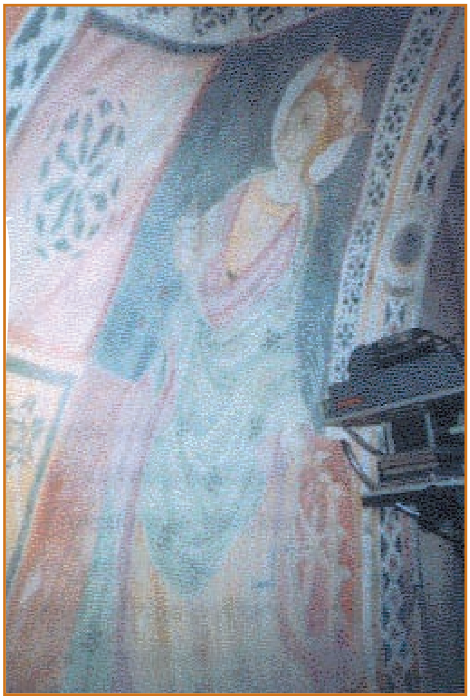
RENISHAW

Spectroscopy Innovations

News from the Spectroscopy Products Division

Issue 6

Art restoration



The need for non-destructive techniques to obtain the chemical information required for art restoration and conservation has led to an increase in use of Raman spectroscopy throughout the art world over the last 10 years. The advantages of Raman microscopy mean that non-destructive and reproducible analyses of tiny particles can be achieved in the laboratory without the need for any sample preparation. In many cases, however, laboratory analyses cannot be performed as the integrity of the work of art has to be preserved, and consequently the removal of even microscopic particles is not permitted. In these cases, the works must be examined *in situ* and the Renishaw RA100 Raman Analyzer is perfect for this task as it can be fitted with a fiber optic probe head (FOPH) that can be used for remote detection up to 100 m from the central spectrometer unit.

In this example, analysis was performed *in situ* on the XII century wall fresco (shown above) in the S. Pietro di Avigliana Church in Turin, Italy. The spectra were collected using a Renishaw System RA100 Raman Analyzer with helium-neon laser (632.8 nm) excitation, connected to a FOPH. The FOPH can fit a wide variety of microscope lenses and an integral camera is used to view the sampling area through the chosen lens. Analyses are fully software controlled and the library search facilities makes comparison of collected spectra with internal library or pre-collected spectra rapid and easy to perform.

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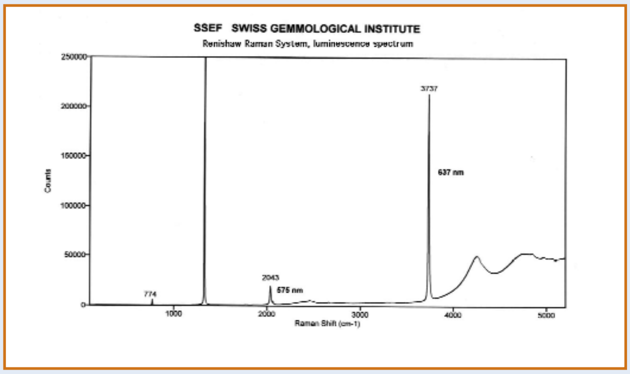
Recognizing GE POL diamonds

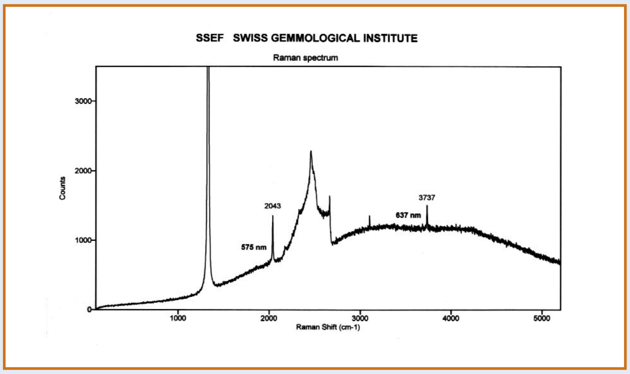
at the SSEF Swiss Gemmological Institute

In 1999 Lazare Kaplan International (LKI) and General Electric announced a new process that could irreversibly improve the clarity, brilliance, and brightness of colored diamonds. The process involves treatment of near-colorless diamonds at high pressures and temperatures, resulting in colorless diamonds that are indistinguishable by conventional gemmological techniques from their naturally colorless counterparts. Thus, when Pegasus Overseas Ltd. (a subsidiary of LKI) announced in March 1999 that they would market these treated diamonds, they agreed to inscribe the girdles with the 'GE POL' label to distinguish them and prevent them being sold as natural gem quality diamonds by unscrupulous dealers. By summer that year removal of the inscription on some stones had been detected and the jewelry industry and gemmological institutes worldwide sought other methods by which GE POL treated diamonds could be recognized.

Spectra obtained using a Renishaw System RM1000 Raman microscope have been successful in detecting GE POL treated type IIa originally brown diamonds.



Spectrum of a colorless, originally brown, type IIa diamond after GE POL treatment



Spectrum of a type IIa naturally colorless diamond

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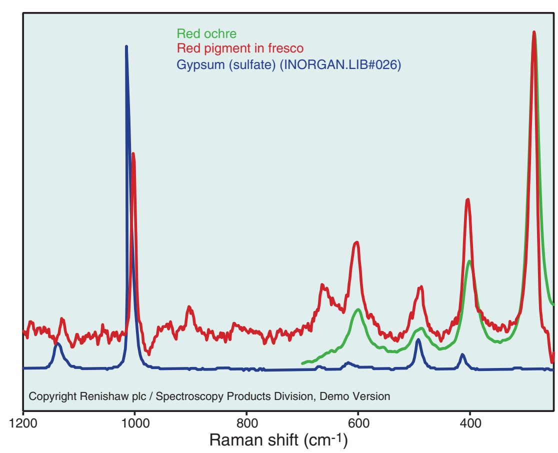
Art restoration *(continued from front cover)*

Many of the pigments on the fresco were examined and this example shows how it was possible to identify a red pigment in the painting by comparing its Raman spectrum with the spectra obtained from standard samples. The Raman spectrum of the pigment contains features from gypsum, which originates from the wall underneath the fresco. Other features in the spectrum match those from a known sample of red ochre and identifies the the pigment as red ochre.



Raman spectra from the red pigment in the fresco, gypsum from the Renishaw minerals and inorganics library, and a red ochre standard.

The success of Raman in pigment analysis and the flexibility of Renishaw's Raman systems has increased interest among art historians who can analyse, for example, gems, corrosion processes, ceramics, marble, and surface treatments with a single instrument.

For more details please contact your local Renishaw representative.

Recognizing GE POL diamonds *(continued from front cover)*

The main feature in the Raman spectrum of pure diamond is an intense peak which occurs at 1332 wavenumbers (cm^{-1}). In natural diamonds, this intense Raman peak is accompanied by higher wavenumber fluorescence bands caused by the impurities present.

By cooling type IIa diamonds to liquid nitrogen temperatures, fluorescent bands at 2043 cm^{-1} (575 nm) and 3737 cm^{-1} (637 nm) can be observed, which indicate the presence of N-V centers (a single nitrogen atom linked to a carbon vacancy). Type IIa naturally brown diamonds display intense fluorescence bands, indicating the presence of a large number of N-V centers (giving the diamond its brown coloration). After GE POL treatment these diamonds are colorless. However, they still have intense fluorescence bands, but the relative intensity of the 575 nm and the 637 nm peaks is the reverse of that observed for the untreated diamonds. This reversal has been found to be characteristic of GE POL treatment (D. Fisher, R. A. Spits, *Gems and Gemology*, Spring 2000, 42). Most naturally colorless type IIa diamonds also show the presence of N-V centers, and by examination of the 637 nm/575 nm peak height ratios in their fluorescence spectra, workers at the SSEF have been able to discriminate between naturally colorless type IIa diamonds and type IIa diamonds rendered colorless by the GE POL treatment.

Spectra were recorded on a Renishaw Raman System 1000 microscope using 514.5 nm laser emission and cryogenic sample cooling to liquid nitrogen temperatures.

Data courtesy of H. A. Hänni, SSEF Swiss Gemmological Institute, Basel.

For further information please contact Ken Williams, Renishaw plc, UK (details on the back cover).

New!

A macro chamber accessory for the Renishaw system RA100 Raman analyzer.

The Renishaw macro chamber accessory makes it easy to analyze solid and liquid samples

- solids
  - bulk
  - in vials
  - card mounted (standard 3" x 2" IR)
  - powders
- liquids
  - in vials
  - in cuvettes
  - in capilliary tubes
  - in custom containers

The Renishaw macro chamber system increases the sampling flexibility of the Renishaw system RA100 Raman analyzer. It consists of a chamber that attaches to the Renishaw fiber optic probe and is supplied with a wide range of sample holders. These permit routine analyses from both solid and liquid samples.

Features

- light-tight enclosed chamber
- class 1 laser safety interlock design
- easy sample loading
- three axis sample manipulator with external controls
- fine focus external control
- sample holders
  - vial/cuvette holder
  - powder holder and powder press
  - capilliary holder
  - solid sample holder
  - microscope slide holder holder
- various lenses available including long working distance lenses

For more details please contact your local Renishaw representative.

Raman helps to develop fuel cells

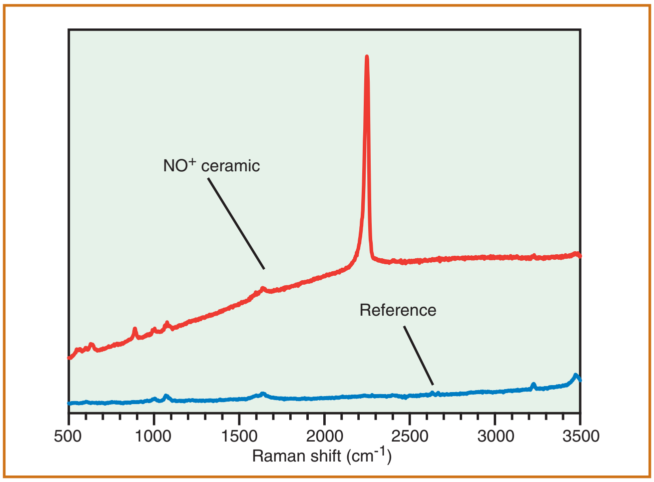
Zero emission engines are a key goal for all major car manufacturers in order to reduce environmental damage and reduce the health risks associated with current levels of exhaust emissions.

Some of the most promising fuel cell materials for these engines are ceramic based solid electrolytes, which also have enormous potential for the production of energy in small home-based power supplies. Cells of this type have been developed and are already highly advanced. However, these solid electrolyte materials can become contaminated with nitrogen oxides (NO_x), which are present in the atmosphere, and cause the fuel cell's performance to deteriorate over time.

The analysis of NO^+ within the solid matrix of these materials is a key process in their development and is currently carried out indirectly, exchanging the NO^+ with hydronium ions (H_3O^+) in dilute acids. The resulting solution contains nitrite (NO_2^-), which is oxidised to nitrate (NO_3^-) if the exchange takes place in sulfuric acid. Consequently, the detection and analysis is based on the application of photometric methods to a dilute solution, an approach which is well known from pollutant analysis in water.

The main disadvantage of this method is that it does not provide direct proof of the inclusion of NO^+ within the matrix, since nitrites and nitrates, which might be present on the surface as impurities, can disrupt the measurements. A method that allows direct measurement of NO^+ in solids would provide more accurate information and be less time consuming. In some cases infrared spectroscopy has already been applied, but the characteristic IR absorption band of the N-O stretching mode is very weak and, in addition, is usually overlapped by CO_2 bands which are already present if the sample has been exposed to air.

Raman spectroscopy, however, provides clear and unambiguous evidence for the presence of NO^+ in a solid. The spectra show a strong Raman peak at 2250 cm^{-1} which is assigned to the N-O stretching mode. The figure shows a typical Raman spectrum of a compressed pellet of a solid host containing NO^+. The spectra were recorded using a Renishaw System 1000 microscope with 514 nm laser excitation.



Raman spectra of a NO^+ containing ceramic and the corresponding reference material containing no nitrosium ions.

In conclusion, Raman spectroscopy is a rapid and effective direct method for the detection of nitrosium ions (NO^+) in solid matrices and neither the presence of NO_2^-/NO_3^- nor CO_2 contaminants affect the Raman measurement.

For details please contact S. Maraun,[1] U. Simon,[1] A. Hürland,[2] R. Moos,[2] and C. Plog.[2]
[1]Institute für Anorganische Chemie, Universität Essen, Schützenbahn 70, D-45127 Essen.
[2]Dornier GmbH, Abt. FT4/SC, Posfach 1420, 88039 Friedrichshafen.

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Conferences

Some of the many conferences we will be attending throughout 2001:

February 19 - 23

American Academy of Forensic Sciences (53rd Annual Meeting)

Seattle, Washington, USA.
http://www.aafs.org

March 4 - 9

The Pittsburgh Conference (Pittcon 2001)

New Orleans, LA, USA.
http://www.pittcon.org

September 2 - 7

European Conference on Diamond and Related Materials (Diamond 2001)

Budapest, Hungary.
http://www.elsevier.nl/locate/diamondconf

Newly refurbished demonstration room

Renishaw UK has recently refurbished its spectroscopy demonstration room. In this view you can see a system 2000 fitted with the microscope enclosure.

For full details of the microscope enclosure and other accessories, please contact your local Renishaw representative and ask for for an options and upgrades brochure.

Renishaw worldwide companies with spectroscopy support

Renishaw GmbH
Karl-Benz Strasse 12,
D 72124 Pliezhausen,
Germany.
Tel +49 712 79810
Fax +49 712 88237

Renishaw S.p.A.
Via dei Prati 5, 10044 Pianezza,
Torino,
Italy.
Tel +39 11 966 10 52
Fax +39 11 966 40 83

Renishaw S.A.
15 rue Albert Einstein,
Champs sur Marne,
77437 Marne la Vallee,
Cedex 2,
France.
Tel +33 1 64 61 84 84
Fax +33 1 64 61 65 26

Renishaw Inc.
USA - Main Office
5277 Trillium Boulevard,
Hoffman Estates, IL 60192, USA.
Tel +1 847 286 9953
Fax +1 847 286 9974
email raman.usa@renishaw.com

Renishaw K.K.
Across City Nakano-Sakaue,
38-1, Chuo 1-chome, Nakano-ku,
Tokyo 164-0011, Japan.
Tel +81 3 5332 6021
Fax +81 3 5332 6025

Renishaw (Hong Kong) Ltd
Unit 4A, 3/F, New Bright Building,
11 Sheung Yuet Road,
Kowloon Bay, Hong Kong.
Tel +852 2753 0638
Fax +852 2756 8786

The Peoples' Republic of China
Room 2302, Silver Tower,
No 2 Dong San Huan North Road,
Beijing 100027.
Tel +86 10 6410 7993
Fax +86 10 6410 7992

If you or any of your colleagues would like to be added to our mailing list or if you have any queries or comments about our spectroscopy products, please contact us at any of the addresses above or simply email us at raman@renishaw.com.

Your local Renishaw spectroscopy agent or distributor is:

Renishaw plc, Spectroscopy Products Division,
Old Town, Wotton-under-Edge,
Gloucestershire GL12 7DW, United Kingdom
Tel +44 (0) 1453 844302 Fax +44 (0) 1453 844236
email: raman@renishaw.com
http://www.renishaw.com