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Detection of diamond in ore using pulsed laser Raman spectroscopy

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Abstract

The viability of using pulsed laser excited Raman spectroscopy as a method for diamond detection from ore, has been investigated. In this method the spontaneous Stokes Raman signal is used as indicator of diamond, and a dual channel system is necessary for correcting for fluorescence of minerals and diamond itself. Various pulsed laser wavelengths from 266 to 1064nm were used, as well as cw lasers for comparison. Wavelength scans of the regions of interest, indicated that pulsed lasers at 532, 355 and 308nm may be used with confidence for this purpose. Mineral fluorescence did not appear to pose a threat to the method, but rather own fluorescence of some types of diamonds. In this respect, pulsed lasers offer a decided advantage above cw, due to non-linear increase of fluorescence with laser power, resulting in superior Raman to fluorescence signal ratios. An apparatus constructed for discriminating diamond from ore was evaluated, and using minerals commonly occurring in diamond carrying ore as well as a wide variety of diamonds, it proved to function effectively. A significant improvement in the capability for diamond detection was found when pulsed lasers at 532 and 308nm were used, in comparison to the 532nm cw laser.

Keywords: Diamonds; Sorting methods; Mineral processing; Raman spectroscopy; Laser excitation

1. Introduction

The method employing the use of the spontaneous Raman signal of diamond (when irradiated with a laser) for extraction of diamond from the diamond carrying ore, seems to offer increased efficiency of extraction over existing methods like the X-ray luminescence method. Various patents have been registered covering the use of lasers for this purpose (see e.g. Bowley, 1990; Donald, 1989; Venter, 1996), while a single research paper has been published (Gudaev et al., 1998), describing the use of a He–Ne laser at 632.8nm for detecting a wide variety of diamonds from a selection of minerals typically present in diamondiferous ore. In all cases the principle of detection employed is the measurement of the spontaneous Raman signal through a narrowband interference filter (typically 0.5 to 1nm) centred on the Raman wavelength, and the simultaneous measurement, on a separate channel, of the emitted radiation through a wide band filter, centred on the Raman wavelength or adjacent to it. With illumination of a diamond by the laser, the channel measuring the Raman signal through the narrowband filter should show an increase relative to the other channel. With illumination of a mineral, no relative increase of one channel above the other will be registered if the luminescence of the mineral is of

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continuum nature over the wavelength interval of the wideband filter. Regarding the diamond's own fluorescence, it is required that it also is a continuum, and not too strong in relation to the Raman emission.

The purpose of the work reported here was to investigate, over the wavelength range 266 to 1064nm, the Raman signal strength in relation to the luminescence signals of typical minerals found in diamondiferous ore, as well as it's strength in comparison with the luminescence of diamond itself. Pulsed lasers at 266, 308, 355, 532 and 1064nm were used, as well as cw lasers at 488, 532 and 632nm. Aspects of the spectroscopy that could possibly aid in the discriminating system were investigated, such as the temporal characteristics of the signals, and the linearity of the signals with laser power. The relative signal to noise ratios expected with pulsed and cw systems was also investigated theoretically and experimentally. The measurements were done in order to arrive at an informed decision regarding the potential of pulsed lasers as sources for diamond detection, the best wavelength for use, and its relative merits compared to cw sources, thus the inclusion of cw sources in the investigation. Paragraphs 3 and 4 give these results.

The following part of this report (Section 5) describes the evaluation of an experimental apparatus constructed for discriminating diamond from ore, using the more promising wavelengths indicated in the preliminary part, also including a cw wavelength for comparison. As for the first part, a large variety of diamonds were used, with particular attention paid to the statistical variations involved.

2. Experimental

2.1. Wavelength scanning measurements

For scanning the luminescence and Raman spectra of the diamonds and minerals, a Kratos 0.25m double monochromator was used to minimize stray light falling on the detector as a result of large amounts of laser reflected light entering the first monochromator. Samples were positioned on the optical axis so that the luminescence could be focused on the entrance slit (0.3mm wide, resulting in a spectral bandwidth of approximately 1nm) of the monochromator by a fused silica lens of 100mm focal length. The laser beam was made incident on the samples with an angle of approximately 30° with respect to the optical axis. The radiaton detector used for all wavelengths except for that exceeding 1064nm, was a Hamamatsu R1477 photomultiplier tube, the output of which was fed directly to a digital oscilloscope (Tektronix 360) in the case of cw measurements. The oscilloscope was connected to a PC with the aid of a GPIB to USB interfacing cable and its associated software, allowing measurements to be registered at a selectable interval. For the pulsed laser measurements, it was necessary to use a modified PMT base to handle the high instantaneous flux of photons, together with a fast response amplifier (Burr Brown model 3554) built into the PMT housing to minimize capacitance between source and amplifier. The modification to the base entailed a resistor chain with 270kΩ across the first dynode and cathode to ensure at least a 150V supply between them. Capacitors of 10nF were placed across each of the last four dynodes (out of a total of 9). The last three resistors of the resistor chain were 150kΩ, 180kΩ and 220kΩ respectively, in comparison with the 100kΩ resistor between the rest of the dynodes, to prevent saturation of the detector and maintain a linear response. Calibrated neutral density filters were used to check linearity of response. For detection of the luminescent radiation above 1064nm, a Hamamatsu G8370 InGaAs PIN photodiode was used, and the gratings of the monochromator replaced with gratings suitable for this region.

For the pulsed laser wavelengths 1064, 532, 355 and 266nm, a flashlamp pumped Nd:YAG (Continuum, Powerlite 9010, with maximum pulse energy of 1.4J at 1064nm and with a fixed repetition rate of 10Hz and pulse length ~ 7–9ns) with the appropriate frequency conversion crystals was used. For the pulsed wavelength 308nm, an excimer laser from Lambda Physik, model 203 MSC, with 300mJ pulse energy, using XeCl gas, with a maximum repetition rate of 250Hz (pulse length ~ 25ns) was used.

The 532nm cw laser was a diode pumped 5Watt water cooled laser from Spectra Physics (model Milennia). The 488nm cw laser was a line tunable argon ion laser from Spectra Physics (model 2020), supplying approximately 2W. The cw 632.8nm wavelength was supplied by a Spectra Physics model 127 He–Ne laser at approximately 25mW.

A selection of 18 minerals, listed in Table 1, commonly occurring in diamondiferous ore were used to compare its luminescence spectra with that of diamond. The ceramic is included since it is often present in the ore as an added impurity, due to its use in the processing system as liners to prevent wear.

For the wide wavelength region scans initially performed, four diamonds of type Ia, Ib, IIa and IIb were used. For the scans across a narrow wavelength region adjacent to both sides of the Raman shifted wavelength for diamond, a set of 203 diamonds was available, including a wide variety of types. Each of these stones is individually classified according to colour,

Table 1
List of minerals

Amphibole $Ca_2(Fe,Mg)_5Si_8O_{22}(OH)_2$	Kyanite Al_2SiO_5
Barite $BaSO_4$	Olivine $(Mg,Fe)_2SiO_4$
Calcite $CaCO_3$	Pyroxene $(Ca,Mg,Fe,Ti,Al)_2(Si,Al)_2O_6$
Ceramic Al_2O_3	Quartz SiO_2
Chrome diopside $(Ca,Cr)MgSi_2O_6$	Rutile TiO_2
Corundum Al_2O_3	Zircon $ZrSiO_4$
Garnet $(Ca,Fe,Mn,Mg)_3(Al,Cr,Fe)_2(SiO_4)_3$	Black Kimberlite
Ilmenite $FeTiO_3$	Green Kimberlite
Iron oxide $FeO(OH).nH_2O$	Grey Kimberlite

quality, stone shape and impurities. These stones vary from bright white (with no impurities) to darker and black round shaped samples with inclusions.

2.2. Apparatus for sorting diamond from ore

Fig. 1 shows the design of the instrument constructed for evaluation of the laser sorting method, as well as the total experimental system for measurement. The instrument itself consists of a fused silica entrance lens (100mm focal length, 50mm diameter with 35mm aperture) for collimating light emitted by the sample into a parallel beam (necessary for minimizing the angle of incidence onto the filters to follow), a laser radiation blocking filter (long wavelength pass with cut on between the laser and Raman wavelengths), and a beam splitter for splitting the light into two orthogonal arms, each containing an interference filter and photomultiplier (PMT). The beam splitter (a flat piece of fused silica) reflects approximately 8% of the incident light into the channel containing the broadband filter, transmitting the rest to the part with the narrowband filter. Due to the larger transmission band of the wideband filter, the two PMT's receive approximately equal light flux. The peak transmissions of the filters centred on the Stokes wavelength 572.5nm (excitation at 532nm), were 75% for the 1nm and 80% for the 10nm bandwidth filters. The transmissions of the 2nm narrowband and 10nm wideband filters used with 308nm excitation, were 13% and 14% respectively, both centred on 321nm (filters supplied by Omega Optics, Inc.). The cut on wavelengths of the laser blocking filters were 550 and 315nm for 532 and 308nm excitation respectively.

For measurements with the cw laser, the beam of 3.2mm diameter intercepted falling particles on the optical axis with an angle of 30° with respect to it. Signal intensities were measured using R5929 PMT's (Hamamatsu Corporation) with supply voltages of approximately 600V, and registered on two channels of an oscilloscope (Tektronix 360) with a 1MΩ load resistor. Signal levels were sufficient not to need any amplification. The oscilloscope's internal controls allowed measurement of the peak values of the transient signals, which were recorded on a PC with the use of a GPIB to USB interface (National Instruments). The cw laser supplied 2W, resulting in an energy density of $\sim$ 25W/cm^2 incident on the samples. To simulate a particle falling through a laser beam, or a laser beam sweeping over a particle, the laser beam was intercepted by a chopper with a 5mm slit, rotating at a speed resulting in a signal duration of 0.5ms. Although the sampling rate thus achieved was much higher, the interface to the PC

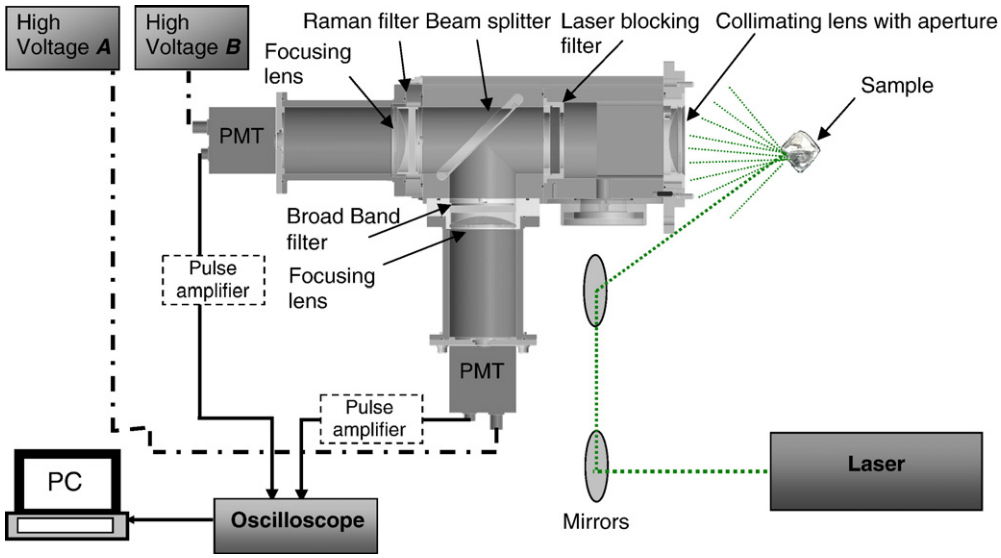

Fig. 1. Design of the experimental measurement instrument.

sampled at a rate of one measurement per second, taking a measurement at random as presented by the oscilloscope.

Measurements with the pulsed lasers were made with R1477 PMT's (Hamamatsu), employing the same modified bases as described above for handling the high instantaneous flux of photons generated. Signal levels were so high that PMT supply voltages of approximately 450V were sufficient. In addition, the aperture on the collimating lens was reduced to 12mm diameter (resulting in a f/8.3 aperture) to avoid using too low PMT supply voltages. Laser spot sizes of 5mm diameter were used, with the beam intercepting falling particles again at 30°w.r.t. the optical axis. For both 532 and 308nm pulsed operation, laser beam energies were reduced to approximately 0.4mJ, resulting in an energy density of ~ 2mJ/cm^2 incident on the samples. With a 50Ω load resistor, signal peak values were measured by the oscilloscope and transmitted to the PC. The pulsed lasers were running at a repetition rate of 10Hz, but one measurement each second was taken by the PC as in the cw case.

3. Results of scans at various wavelengths

3.1. Pulsed 1064nm

The four diamonds of type Ia, Ib, IIa and IIb as well as all the minerals were irradiated with pulsed 1064nm at an energy density of 250mJ/cm^2, while the monochromator was scanned from 1100 to 1400nm. The minerals spectra were completely flat, confirming expectations of almost no luminescence in this spectral window. The diamond spectra also showed no broad-band fluorescence, with only very weak Raman signals at 1240nm. Such poor signals relative to those found in the visible and UV, are due to the λ^{-4} dependence of the Raman signal, as well as the intrinsic poor detection efficiency of solid state detectors compared to photo-multipliers. Although it is realised that a commercial sorting apparatus uses this wavelength (cw), results to follow indicate visible and UV wavelengths to be of much higher potential, and no further measurements at 1064nm were conducted.

3.2. Pulsed 532nm

The minerals and four diamonds were irradiated with pulsed 532nm at a density of approximately 15mJ/cm^2, and the monochromator scanned from 540 to 737nm. Only the five minerals calcite, ceramic, corundum, kyanite and zirconium yielded appreciable fluorescence, as shown in Fig. 2. The four diamond types each showed a strong Raman signal at 572nm, with almost no fluorescence, except the type 1b, the spectrum of which is included in Fig. 2.

Scans were repeated over the limited wavelength range of 545 to 605nm (bracketing the diamond Raman wavelength of 572nm), but in this case surveying the set of 203 well characterised diamonds in addition to the 18 minerals. The diamond spectra obtained can be classified in the following categories:

(i) strong Raman signals, superimposed on fluorescence signals ranging from almost zero to strong, i.e. cases representing no threat to a detection scheme in which the Raman signal is to be

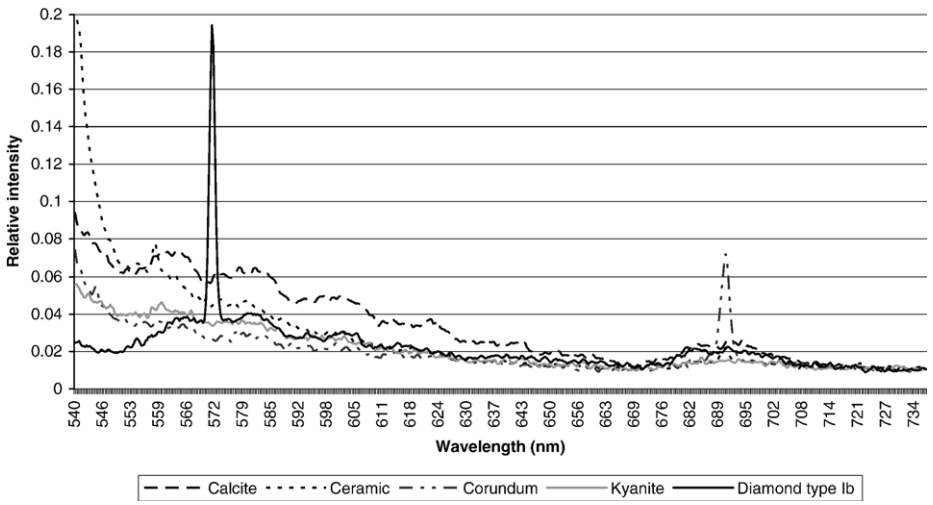

Fig. 2. Spectra obtained with wide wavelength scan for pulsed 532 nm.

discriminated from the fluorescence signal (195 out of the 205 samples);
(ii) weak Raman signals on a strong fluorescence background (3 cases);
(iii) strong Raman signal at 572nm, but accompanied by a similar (yet weaker) signal at approximately 575nm (2 cases);
(iv) weak Raman signal on a virtually zero fluorescence background.

Fig. 3 shows a sample of each of these four types of spectra obtained for the set of diamonds. The fluorescence spectra of all the minerals over this limited wavelength range are low in comparison and smooth, i.e. no peaks in the vicinity of the diamond Raman peak at 572nm (the strongest spectrum, measured for calcite, also shown in Fig. 2).

3.3. cw 532nm

Samples were irradiated with a power density of approximately 7W/cm^2 and the fluorescence recorded. Fig. 4 shows the fluorescence spectra of the minerals calcite, ceramic, corundum and kyanite over the large wavelength span 540 to 696nm, these being the only minerals yielding appreciable fluorescence. For the latter three minerals, the peaks in the region of 690nm observed in the pulsed case with very small intensity, are now present with very large amplitude. The spectra of the four types of diamond over this same wavelength region again show, as in the pulsed case, only appreciable fluorescence for the type 1b, as shown in Fig. 4. The Raman signals of the other three types were strong on a virtually zero fluorescence background. The periodic peaks superimposed on some spectra, also evident in Fig. 2, must be the result of some instrumental effect (probably associated with a periodically varying transmission of the two scanning monochromators in tandem).

The scans over the limited wavelength range around the 572nm Raman wavelength for the set of 203 characterised diamonds and the 18 minerals show more problem cases for the proposed detection scheme than the pulsed system. For the category (ii) above (weak Raman and strong fluorescence background) 10 cases were counted. For category (iii), i.e. a fluorescence peak at 575nm, 13 cases were noted, in some the 575 peak being much stronger than the 572nm Raman peak. For weak Raman as well as weak fluorescence, 14 cases were noted (category (iv)). The fluorescence spectra of the minerals are, as in the pulsed case, of low strength without peaks in the 572nm region. Fig. 5 shows the same spectra with cw excitation as the spectra in Fig. 3 with pulsed excitation.

3.4. Pulsed 355nm

When subjected to a pulsed energy density of approximately 15mJ/cm^2 at 355nm, both minerals and diamonds exhibited slightly enhanced levels of fluorescence in comparison with the pulsed 532nm situation. Scans over a limited wavelength range around the Raman line of the set of 203 diamonds and the minerals revealed that only 3 of the set of 203 diamonds presented potential problems for detection as a result of large

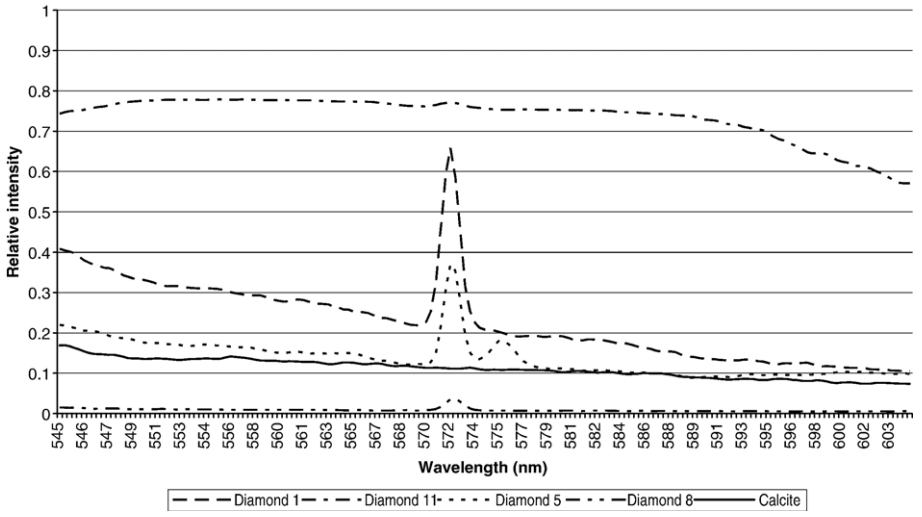

Fig. 3. Spectra obtained with limited wavelength scan for 532 nm pulsed operation, for four different categories of diamond and the mineral calcite (solid line).

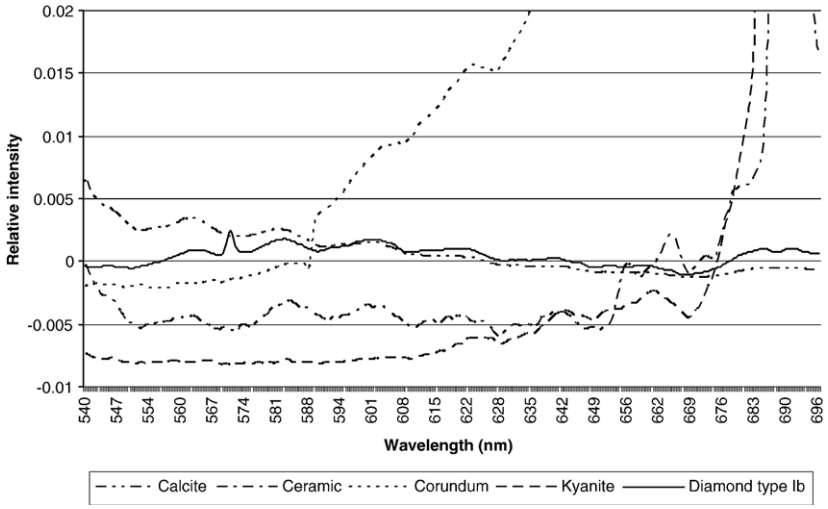

Fig. 4. Spectra obtained with wide wavelength scan for 532 nm cw operation, for the same samples as with pulsed operation (Fig. 2).

fluorescence. Furthermore, only 7 diamonds' Raman signal could be classified as weak, but then also accompanied by weak fluorescence. The fluorescence spectra of the minerals in the vicinity of the diamond Raman peak at 373nm also were smooth without peaks, so that in spite of the higher fluorescence levels, diamond detection at this wavelength looks just as viable as at 532nm (pulsed).

3.5. Pulsed 308nm

Irradiated with an energy density of 7mJ/cm^2 at 308nm, the minerals and diamonds exhibited strong fluorescence in some cases, but rather at longer wavelengths far from the diamond Raman peak at 321nm The narrow wavelength scans (315 to 350nm) of the large diamond set indicated problem cases for only 5 diamonds, where the Raman peak was small in comparison with the fluorescence. The minerals' fluorescence exhibited no spurious peaks in the vicinity of the diamond Raman line. Again, detection with pulsed irradiation at 308nm seems just as viable as with 532 or 355nm.

3.6. Pulsed 266nm

Diamonds exhibit increasing absorption of radiation towards lower wavelengths, until it becomes completely opaque below its bandgap around 225nm. Weak Raman

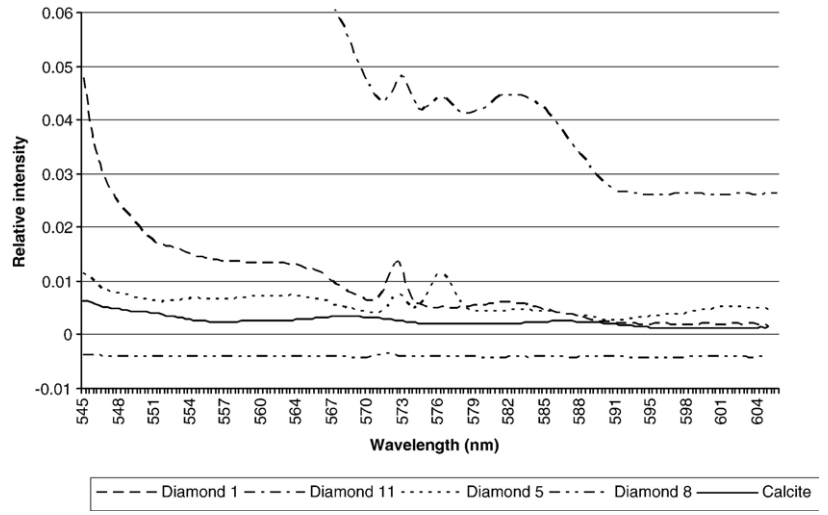

Fig. 5. Spectra obtained with limited wavelength scan for 532 nm cw operation, for the same diamond and minerals as in Fig. 3.

signals are therefore expected at the Stokes wavelength of 276nm when excited with 266nm, due to absorption of both these wavelengths. Wavelength scans between 274 and 420nm show strong fluorescence from the minerals, with a wide band from 280 up to 340nm in some cases, two of which are shown in Fig. 6 (irradiation density 15mJ/cm^2). Also shown in this figure are the spectra of diamonds type Ia and IIb. The Raman signals of types Ia and Ib are indeed very weak as expected, but contrary to this, the Raman signals of types IIa and IIb are very strong. Due to the risks associated in detection of the type I diamonds, this wavelength is not considered a good choice for an instrument, hence no further measurements were done on the large set of diamonds as was done for the other wavelengths.

3.7. cw 488nm

Samples were irradiated with a density of 7W/cm^2. Scans over the wavelength range 500 to 680nm for the 18 mineral samples and the 4 diamond types showed that the same minerals as at the other wavelengths exhibit strong fluorescence (calcite, ceramic, corundum, kyanite), but that the Raman signal at 522nm of the diamonds are sufficiently strong to be detected above it. Examination of the spectra emitted by the set of 203 diamonds over a smaller wavelength interval, however, indicated that the diamonds' own fluorescence is so strong as to cause severe problems for many of these for detection of the Raman signal above this fluorescence. In 95 cases a very small Raman signal superimposed on a strong fluorescence was noted. It was thus concluded that a detection scheme based on 488nm cw excitation will not be viable.

3.8. cw 632nm

The He–Ne laser supplying only 25mW, the maximum irradiation density that could be used was 0.7W/cm^2. Spectra taken in the region 640 to 734nm showed very strong fluorescence of the minerals corundum, kyanite and ceramic in the region of the diamond Raman peak at 690nm. The Raman signals of all four of the diamond types were very small in comparison, and it is anticipated that a detector with sufficient sensitivity to register the Raman signals of diamonds will be saturated when encountering any of the three minerals mentioned. A commercial instrument using a 632nm cw laser is available, but the comparative measurements of this study indicate improved results to be expected from wavelengths like 488 and 532nm cw, or the pulsed wavelengths 308, 355 and 532nm.

4. Discussion of factors influencing operational parameters of a detector system

4.1. Raman and luminescence signal strengths

The orientation of a diamond in the laser beam has a strong effect on the intensity of the Raman and fluorescence spectra recorded. An experiment with one particular diamond showed a variation of a factor of 10 for four different orientations. This is due to the large refractive index of diamond (~ 2.4) and the many facets of natural stones, refracting both the incident laser beam

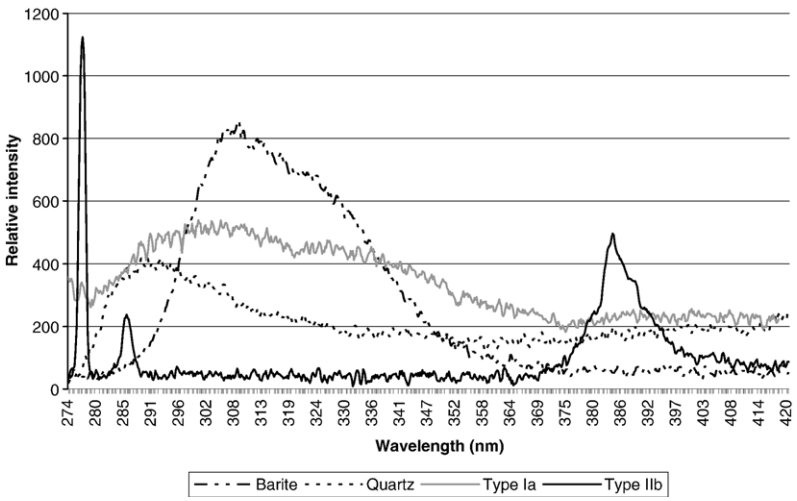

Fig. 6. Spectra obtained with wide wavelength scan for 266 nm pulsed operation.

and the emitted luminescence in various directions. All the measurements reported above were obtained on a single measurement (wavelength scan) for a sample after positioning it in arbitrary fashion in the laser beam. An obvious condition for the proposed method to function properly is that the luminescence of the minerals must not be so strong in comparison with the Raman radiation of diamonds that it saturates the detectors. This aspect could not be accurately evaluated from the measurements due to the orientation effect. Qualitatively it did not appear, however, that problems in this respect will be encountered with any of the wavelengths, pulsed as well as cw, except for excitation with 632nm cw (see Section 3.8).

The wavelength scans of the set of 203 diamonds revealed that the main problem expected in a detector apparatus is rather the insufficient ratio of the Raman signal to that of the diamond's own fluorescence, as shown in Figs. 2 and 4 for some samples. This effect could be accurately evaluated and compared between different excitation wavelengths, since the orientation of a sample in the beam did not change this ratio. The results clearly show that with cw excitation at both 488 and 532nm, this ratio is inferior to that obtained with pulsed lasers (Sections 3.3 and 3.8). Not much difference in this respect was noticed between pulsed excitation at 308, 355 and 532nm.

4.2. Saturation of fluorescence

Investigation of the nature of the 575nm peak observed in the luminescence spectrum of some diamond samples (excitation at 532nm) resulted in observation of the effect of saturation of spectral energy levels (see e.g. Alkemade et al., 1982) on the measured fluorescence. Firstly it was ascertained that the peak at 575nm is indeed wideband fluorescence, by scanning over it with a narrow slit on the monochromator. This showed a narrow line for the Raman signal and a wider line, typical of a molecular band system, for the 575nm peak. Next, using pulsed laser excitation at 532nm, this wavelength region was scanned for three different irradiation densities of excitation. Attenuation of the excitation beam to 50% and 25%, resulted in the ratio of the Raman 572nm to fluorescence 575nm peaks to decrease to 6.2 and 3.2 respectively, from the value of 9.2 with the unattenuated beam. Similar results were found for diamond samples with continuum fluorescence near the wavelength of the Raman line (i.e fluorescence not associated with the 575nm band): comparing the Raman line to fluorescence ratio for pulsed and cw irradiation under identical geometries of illumination, the pulsed system yielded a tenfold increase over the cw system. The irradiation density of 30mJ/cm^2 gives approximately 3MW/cm^2 assuming a pulse duration of 10ns, compared to the 7W/cm^2 of the cw beam. The saturation of energy levels being power dependent, it is indeed very likely that no such effect will be seen with cw excitation in comparison with pulsed.

Measurements were also made to investigate the linearity of the minerals fluorescence with incident irradiation density. With pulsed excitation at 532nm, non-linearity was shown to differing extents for the 18 samples, calcite, garnet and iron oxide showing the strongest non-linearity (graphs not shown).

This effect of saturation of fluorescence of both minerals and diamonds with pulsed irradiation suggests a distinct advantage of using pulsed rather than cw lasers in a detection apparatus.

4.3. Comparison of cw and pulsed signal detection

The characteristics of a photomultiplier tube (PMT) as an amplifier of the primary electrons generated by incident radiation is so ideal ("noiseless amplification") that the situation of a shot noise (or quantum noise) limited signal to noise ratio can be readily achieved. The general expression for the size of the shot noise signal strength is given by Bachor and Fisk (1989) as

$$\Delta I = \sqrt{2e.I.\delta f}$$

where δf is the (electronic) frequency interval over which the fluctuations are integrated (= bandwidth of measurement), and e is the electronic charge. If the signal itself is the only source of noise in the measurement, the signal to noise (SNR) ratio is given by

$$\mathrm{SNR} = I/\Delta I = k\sqrt{I} \quad \text{with } k = (2e.\delta f)^{-0.5}$$

Very high gains in SNR can be obtained with pulsed measurements and a gated detector over cw measurements if the dominating source of noise is not signal related, such as background radiation or dark current. In the preliminary measurements reported here, however, it was found that the Raman signal strengths were of such magnitude that the condition of signal dominated noise is easily achieved. This will be even more the case in a final detecting apparatus where filters instead of a monochromator with its large losses are used. The SNR with both pulsed and cw systems will thus be directly proportional to the square root of the signal, or $\sqrt{I}$, where I is the total signal due to Raman and luminescence

contributions. In both cases(cw and pulsed) the signal I is proportional to the product of the laser power and the time duration of the signal, i.e. to the number of photons generated. The gain with a pulsed system over cw thus is

$$G = \sqrt{\frac{Et}{E_0 T}}$$

where E and E_o are the laser irradiation powers (W/cm^2) of the pulsed and cw systems respectively, and t and T the respective time durations of the signals. It is important to note that a single measurement of signal is under discussion, i.e. no average measurements. Both measurements require the evaluation of a pulsed signal, the duration of which is determined by the laser pulse duration in the pulsed case, and the time spent by the particle in the laser beam in the cw case.

Using the values approximately equal to those in the measurements reported here, i.e. E = 15mJ/cm^2 and t = 10ns for the pulsed laser, and E_o = 10W and T = 3ms for the cw system (approximate time spent in beam by particle after falling through 100mm), the gain obtained in the equation above is G = 0.7.

A set of measurements was made at 532nm to arrive at an experimental comparison between pulsed and cw operation. Using the type Ia diamond as sample, 60 single pulse measurements for both pulsed and cw systems were made, using a 1nm bandpass on the monochromator and − 800V supply on the PMT, and measurement electronics best suited for each system. The signal was dominated by the Raman contribution, i.e. the diamond fluorescence was low in comparison. The same irradiating conditions were used as previously, i.e. 15mJ/cm^2 for the pulsed and 7W/cm^2 for the cw system. The time duration of the signal in the cw case was limited to ~ 3ms by using a chopper in the irradiating beam. The relative standard deviation (standard deviation as percentage of the average signal) of the two sets of signals were almost equal, confirming the theoretical result derived above that there is no real advantage of one system above the other for the particular laser powers chosen. A relative advantage will thus rather be established by other conditions pertaining, e.g. ratio of Raman to fluorescence signals as discussed in Section 4.2 above.

4.4. Indicated preferences for a detector system

Regarding the wavelength of pulsed lasers for use in a detection apparatus, the results clearly indicated disadvantages for use of wavelengths in the infrared or low UV. For 1064nm excitation, the two sources of poor performance are the λ^{-4} dependence of the Raman signal, and the relative inefficiency of solid state detectors compared to photomultipliers. PMT's suitable for use at the Stokes wavelength of 1240nm are now available (Hamamatsu Corporation), but were not available in the laboratory for evaluation. At 266nm high absorption of radiation is expected to result in poor detection of some diamond types. The wavelengths 532, 355 and 308nm seem equally suited for a detection apparatus, not taking practical constraints like repetition rate, beam size and quality into consideration.

The use of 532nm appears the best for use in cw lasers among the three wavelengths tested, results indicating less problems to be expected from fluorescence. Using 632nm, strong fluorescence by some minerals at the Stokes wavelength, as well as poor laser power will limit performance. With 488nm excitation, strong fluorescence of diamond itself, overwhelming the Raman signal, argues against use of this wavelength.

The non-linearity of diamond fluorescence with laser power indicates a distinct advantage of using pulsed lasers instead of cw. The ratio of Raman to fluorescence signals are up to 10 times higher with a pulsed laser at 532nm, reducing the effect of fluorescence interference on detection. In addition, minerals fluorescence was also found to saturate to some extent with pulsed laser excitation, facilitating discrimination of diamond from minerals.

The temporal characteristics of the pulsed signals did not indicate a viable additional means of discrimination between diamonds and minerals. Some minerals exhibited fluorescence signals longer in duration than the excitation pulse at some wavelengths, but this phenomenon was not general enough so as to warrant its use as supplementary means of discrimination.

5. Evaluation of sorting apparatus

The apparatus for sorting diamond from ore described in Section 2.2 was evaluated, choosing the operating modes 532nm cw, 532nm pulsed and 308nm pulsed for use, and using the set of 18 minerals as well as the characterised set of 203 diamonds.

5.1. Measurement procedure and data analysis

The measurement procedure for each of the three modes of operation (532 cw, 532 pulsed and 308 pulsed) was the same. The 16 minerals and a selection of 36 diamonds (from the set of 203) were each subjected to a large number of measurements (between 30 and 40), in order to establish a sound idea of the standard deviation of the signal ratio for single measurements on such

samples. Single measurements only are considered in this work, since a particle usually is subjected to a single measurement for evaluation in a sorting system. The 36 diamonds have been identified as potential "problem cases", and the particular diamonds selected, with the aid of the results reported in Section 3. These diamonds were chosen from the characterised set of 203 diamonds to represent the following three categories of samples:

(i) diamonds exhibiting a fluorescence peak at 575nm;
(ii) diamonds with weak Raman signals and low fluorescence;
(iii) diamonds with weak Raman signals superimposed on strong fluorescence.

Following immediately on this, the rest of the set of 203 diamonds was subjected to a number of 10 measurements each, in order to establish an average value only of the ratio of the two channel intensities. For all measurements, the samples were positioned on the top end of a graphite rod (6mm diameter), which was rotating slowly in order to expose a different facet of the sample to the irradiating beam for each measurement.

For each of the three measuring modes, the two channels (Raman and broadband) were first balanced to give a ratio near to 1, using the mineral calcite, before performing the rest of the measurements and calculating the resulting ratios of narrowband to wideband channel signals. For good performance this ratio should be in the vicinity of 1 for the minerals, with an enhancement in value for the diamond samples. The results of the more extensive measurements on the minerals and 36 selected diamonds were evaluated to arrive at a sorting criterion, i.e. the value of the narrow to broadband signal ratio that can be used best for discriminating between diamonds and minerals.

The approach in this study was to use the selected 36 diamonds, mostly of poor quality and representing the worst scenario regarding detection, for arriving at a sorting criterion, and then analyse the situation to find a recovery figure for each mode of operation (532 cw, 532 pulsed and 308 pulsed).

5.2. Minerals

As stated previously, the mineral calcite was used to balance the two channels to give a ratio of approximately one before the measurements on the other samples, for each mode of operation. For 532nm cw operation, all the other minerals gave ratios of one or less, with an average standard deviation of 0.055. An almost identical result was found for the pulsed 308nm mode of operation. For pulsed 532nm, however, results were less satisfactory: for the two minerals olivine and corundum, ratio values of 1.83 and 1.48 were measured respectively, and an average standard deviation for all minerals of 0.088.

For all three operating modes, mineral ratios were in some cases significantly lower than one (in the region of 0.8). The reason for this, as well as the reason for the high values of the two minerals with 532nm pulsed, could not be found, as the wavelength scans of the luminescence over the relevant spectral regions did not reveal any spectral features except a smooth continuum.

For 532nm cw operation, the standard deviations of the individual minerals were clustered near the average, except for four which gave standard deviations near to 0.1. For 308nm, values were more uniform, with only one outlier with a value of 0.1. For 532nm pulsed, the values of standard deviation were spread across the range of 0.02 to 0.1, with one value as high as 0.12. From these figures, it appears safe to take as a general upper limit the value of 0.1 for the standard deviation of mineral ratios. Hence it is concluded that mineral ratios will lie with 95% confidence below the value of 1.2, and this value of the ratio of Raman to broadband channel signals can be used as a sorting criterion for diamonds from ore.

5.3. Group of 36 selected diamonds

This group of diamonds, selected to represent potentially the samples with the least chance of detection, was used to evaluate and compare the three modes of operation with each other, having made a sufficient number of measurements on each sample to arrive at reliable figures of reproducibility of measurement. Table 2 below summarises the results found for this group, giving the average figures of merit for the group of 36 diamonds.

The values of standard deviation were not uniform at all, varying from 3 to 40% relative. Furthermore, there is almost no correlation between the standard deviation values of cw and pulsed 532nm cases, indicating that poor values of reproducibility cannot be blamed on particular types of diamond. A correlation coefficient of 0.55 was found between the standard deviation values of the pulsed 532 and 308nm cases.

In order to give the reader an idea of the numbers involved, the values obtained for 12 diamonds are given in Table 3. The first two in the table were selected on grounds of their characteristic of a rather narrow fluorescence peak at 575nm (excitation at 532nm) which may disturb the ratio values, the third is characterised by very strong fluorescence with a strong Raman signal

Table 2
Average values of ratio and standard deviation for the selected set of 36 diamonds

Mode	Ratio	Standard deviation	Relative standard deviation
Cw 532	1.67	0.24	14.6%
Pulsed 532	3.27	0.39	11.9%
Pulsed 308	2.23	0.27	12.3%

superimposed, while the remaining 9 showed weak Raman signals on strong fluorescence (selections made according to the wavelength scans reported in Section 3). Also given in the first column, are the relative commercial values of the diamonds, where the value of 100 indicates the best quality stone in the collection. This measure of stone quality was also used with the set of 36 diamonds to check for correlation between this figure and the values of standard deviation. Negative values of correlation coefficient were found (− 0.2 to − 0.3), indicating the expected tendency of poor quality stones to be responsible for poor reproducibility of measurement. This is, however, not a strong correlation, as can also be noted in Table 3.

5.4. Full set of diamonds

The ratios of Raman to broadband channel signals measured for the whole set of 203 diamonds provided the average ratios of 5.31, 2.91 and 2.97 for 532 pulsed, 532 cw and 308 pulsed operation respectively. A very high correlation was found between ratio values with pulsed and cw 532nm operation (correlation coefficient of 0.91), and reasonable correlation of 0.56 between pulsed 532 and 308nm operation. Good correlation was found between the commercial values and the ratio values for all three modes of operation: correlation coefficients of 0.55, 0.6 and 0.45 were calculated for 532 pulsed, 532 cw and 308 pulsed modes respectively. Table 4 gives the distribution of values for the three modes of operation.

Table 3
Ratios and standard deviations of 12 diamonds

Relative value	Pulsed 532		cw 532		Pulsed 308	
	Ratio	Standard deviation	Ratio	Standard deviation	Ratio	Standard deviation
6.7	3.324	0.224	1.675	0.046	2.813	0.200
7.8	3.016	0.236	1.287	0.046	2.780	0.230
24	1.967	0.207	1.430	0.108	2.468	0.251
0.16	2.382	0.122	1.020	0.107	1.431	0.084
0.26	4.037	0.344	1.276	0.258	1.999	0.147
0.26	4.261	0.513	1.114	0.089	1.458	0.201
0.9	4.502	0.467	2.043	0.326	1.903	0.292
1.3	2.300	0.665	1.066	0.033	1.405	0.130
0.25	1.960	0.149	1.053	0.028	1.501	0.179
11.5	1.995	0.458	1.198	0.106	2.902	0.564
8.7	2.139	0.234	1.342	0.157	1.464	0.304
0.85	2.300	0.575	1.266	0.180	2.787	0.638

Table 4
Distribution of ratio values for the three modes of operation

Interval	Number of cases		
	cw 532	Pulsed 532	Pulsed 308
1–1.2	12	0	1
1.2–1.5	35	0	5
1.5–2	28	19	29
2–3	49	31	68
3–5	50	52	95
5–7	29	45	5
>7	0	56	0

The predominance of values higher than 2 for the 532 nm pulsed case favours this mode of operation. The 47 cases with values lower than 1.5 for the cw system, on the other hand, leaves a question mark for this mode in view of the sorting criterion of 1.2 suggested by the mineral ratios. Of these 47 cases, 23 were included in the set of 36 selected for extensive measurements.

5.5. Detection power of the different modes

The lowest ratio measured for the 532 nm pulsed mode was ~1.6. Assuming the average relative standard deviation of ~12% as given in Table 2 as generally applicable, it can be calculated that the minimum value of the 95% confidence level interval lies just above 1.2, the value of the sorting criterion suggested. Since the relative standard deviations of the other two modes are almost the same, it is reasoned that the ratio values for these modes must exceed the value of 1.6 in order to provide an equal detection power. The distribution of values in Table 4 shows, however, that with 532 cw operation, 47 ratio values were lower than 1.5, and for 308 nm pulsed operation 6 values were found lower than 1.5. Of the three modes investigated, the 532 nm pulsed mode thus clearly seems the best for use in a detection system like the one described.

6. Conclusions

The wavelength scans with the monochromator using different excitation wavelengths, indicated improved discrimination abilities at wavelengths in the visible and upper UV regions (308 to 532 nm). Poor signal strength at 1064 nm and absorption of radiation at 266 nm inhibit detection. These scans also revealed increased Raman to

fluorescence signal ratios with pulsed lasers as sources in diamonds exhibiting enhanced levels of fluorescence, presumably due to saturation of fluorescence. The expected improved detection efficiency with pulsed lasers resulting from this observation, was confirmed by the measurements with the apparatus developed for sorting diamonds from ore: ratios of narrowband to broadband channels were approximately a factor of two higher with pulsed operation.

The method of discrimination employed proved to be working reasonably well, especially with the use of pulsed lasers, and the apparatus designed and constructed for the measurements also functioned properly. The difference in wavelength regions covered by the two detector arms ensured higher relative signals on the narrowband (Raman) channel when diamonds are irradiated. The success of this principle is largely dependent on the quality of the filters used, i.e. the interference filters mentioned, but especially the low wavelength cut-off filters used for eliminating laser radiation from entering the apparatus. These proved to function exceptionally, even in the UV (excitation at 308 nm, detection at 321 nm, with cut-off filter edge at 315 nm). With both pulsed operating modes, signal sizes encountered were unexpectedly high, ensuring that the shot noise contribution to signals was minimized.

Slightly inferior results were found with pulsed 308 nm excitation than with 532 nm pulsed. The ratios of Raman to broadband channel were generally found lower at 308 nm, this being ascribed to the $\sim 2\times$ higher bandwidth of the 321 nm narrowband filter. The excimer laser with its rectangular beam pattern allows a relatively higher processing capability than a laser with circular beam, as can be deduced with calculations similar to that in the previous paragraph, due to better overlapping of the rectangular beam with itself. The use of excimer lasers in practice, however, will probably be limited by the fact that they are operating only at relatively low repetition rates (<1 kHz). Although providing high pulse energy and average powers, large spot sizes have to be used at low repetition rates, resulting in problems such as identification of the position of the particle detected, an optical system for handling the emitted radiation, and possibly the worst, dilution of the Raman signal given by a diamond with fluorescence signals of several mineral particles also present in the laser beam.

The processing capacity of the laser based detection system was investigated and calculations regarding this laser method point at very high capabilities, e.g. the use of a feeder belt of 1 m wide running at 1.59 m/s, for a pulsed laser at 10 kHz. An advantage of a factor 2 is deduced from the expressions for a cw laser of the same power, based on the assumption that equal light fluxes are received by the detection system. This will probably not materialise in practical operation, since the limited detection capability of a cw system relative to a pulsed system will require larger light flux to make the method competitive, if possible at all.

In summary, discrimination of diamonds from diamondiferous ore with a pulsed laser detection apparatus, proved to be a very viable method. Detection of the poorest quality of diamonds seem possible, and very large throughputs are indicated by calculations.

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