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PII: S1386-1425(11)00946-2
DOI: doi:10.1016/j.saa.2011.10.043
Reference: SAA 8827

To appear in: *Spectrochimica Acta Part A*

Received date: 17-6-2011
Revised date: 26-8-2011
Accepted date: 17-10-2011

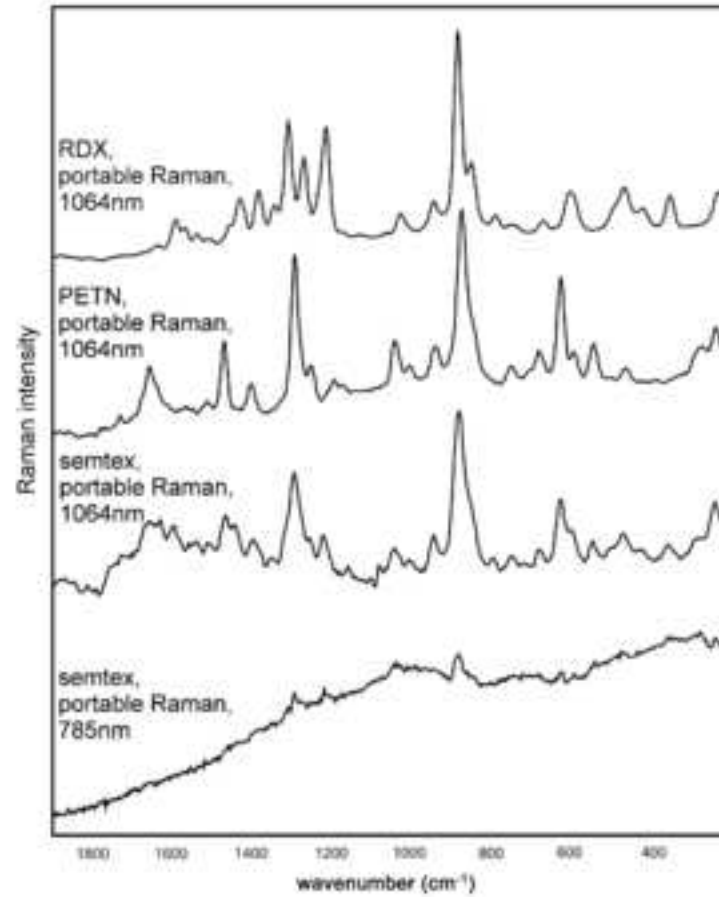
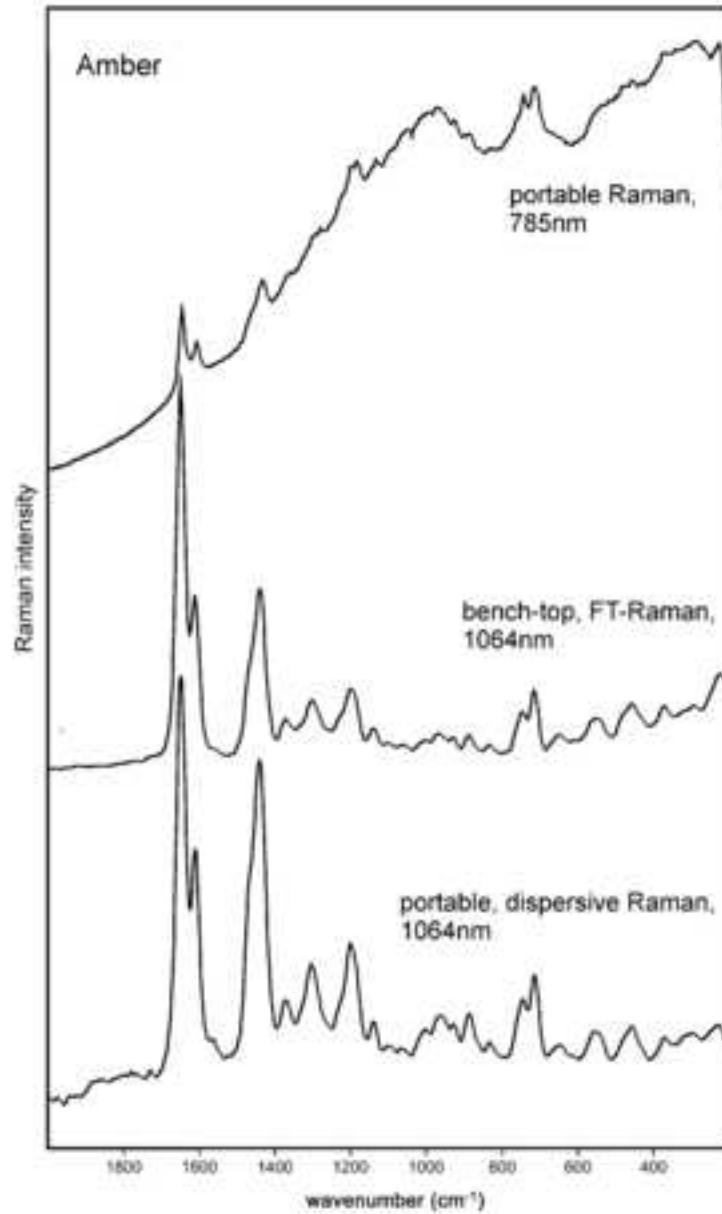
Please cite this article as: P. Víttek, E.M.A. Ali, H.G.M. Edwards, J. Jehlička, R. Cox, K. Page, Evaluation of portable Raman spectrometer with 1064 nm excitation for geological and forensic applications, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2010), doi:10.1016/j.saa.2011.10.043

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Portable Raman with 1064 nm excitation

application in geosciences

forensic application



>portable Raman system with 1064 nm excitation >dispersive system with combined InGaAs and CCD detection >successful application for geological samples and materials of forensic interest >fluorescence dampening

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Evaluation of portable Raman spectrometer with 1064nm excitation for geological and forensic applications

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Abstract

The development of miniaturized Raman instrumentation is in demand for applications relevant to forensic, pharmaceutical and art analyses, as well as geosciences, and planetary exploration. In this study we report on evaluation of a portable dispersive Raman spectrometer equipped with 1064 nm laser excitation. Selected samples from geological, geobiological and forensic areas of interest have been studied from which the advantages, disadvantages and the analytical potential of the instrument are assessed based on a comparison with bench instrumentation and other portable Raman spectrometers using 785 nm excitation. It is demonstrated that the instrument operating with 1064 nm excitation has potential for expanding the number and types of samples that can be measured by miniaturized Raman spectroscopy without interfering fluorescence background emission. It includes inorganic and organic minerals, biomolecules within living lichen and endolithic cyanobacteria as well as drugs of abuse and explosives.

Keywords: portable 1064nm Raman, biomolecules, InGaAs, fluorescence, drugs, explosives, minerals

1 Introduction

The rapid and nondestructive analysis of organic and inorganic compounds is a major advantage of Raman spectroscopy for forensic and geological field studies. Portability of the instrumentation is vital for several applications, for instance, the identification of street drugs, explosives and other compounds of forensic interest specify a rapid and accurate response for first responders, security and law enforcement [1-4]. Some applications require portable technologies because of the significance of the sample being measured in remote areas. Further, some samples are so large and immovable (e.g. statues and architectural monuments) that benchtop instrumentation is not feasible and *in situ* interrogation is essential [5-7]. Raman spectroscopy has now also been adopted as part of the scientific payload of forthcoming robotic space missions, particularly the European Space Agency's ExoMars mission aimed to search for the signatures of extinct and extant life on the Martian surface and subsurface. The miniaturisation of Raman spectrometers is challenging for such missions because of the payload requirements and rigid performance specifications. For terrestrial purposes, most portable Raman instruments are equipped with a range of diode lasers for excitation, of which perhaps the most popular choice is that at 785 nm (multichannel detection) because of its commercial availability and successful detection of a range of organic and inorganic compounds. Portable Raman instrumentation was recently evaluated for identification of inorganic and organic minerals [8-10]. However, even at 785 nm laser excitation many materials can be compromised by varying levels of fluorescence emission. Further, the background shot noise limit from the fluorescent material can also limit the detection of many materials. In the case of fluorescence interference, a small intensity Raman peak is normally superimposed on a high background, and the noise originates primarily from the fluorescence. The solution arises from choosing a laser wavelength where fluorescence can be minimized or fully eliminated from the Raman spectrum. In general, the fluorescence decreases at longer wavelengths where electronic transitions are not provoked by the exciting radiation. Unfortunately, multichannel detectors in the visible and UV ranges are silicon based and silicon response rapidly falls off (>1000 nm) at longer wavelengths-the photon energy at longer wavelengths is less than the silicon bandgap and the silicon becomes

transparent to the incident photons. The early solution was multiplex detection based on Fourier Transform (FT) Raman spectroscopy coupled with 1064 nm laser excitation laser sources. FT-based Raman instruments have excellent frequency precision, but tend to have lower signal-to-noise than their multichannel counterparts. The multiplex advantage does not apply as the detector noise decreases toward the shot noise limit and can be a disadvantage especially when the spectra become more complex, as is the case for many naturally occurring samples. In contrast, a multichannel system will retain an averaging advantage even with complex spectra, high background or significant detector noise. The last advantage of multichannel detection is that dispersive commercial systems tend to be smaller in size and more robust than their FT-Raman counterparts. These two spectrometer types have had a major influence on the way Raman spectrometers are designed and selected. In general, Raman users that wish to use 1064 nm laser excitation will choose FT-Raman based instrumentation, and users that desire visible or 785 nm laser excitation choose multichannel instrumentation. One goal in the industry was to develop a diode array detector with very low dark and readout noise in the 1000 to 1700 nm range with the sensitivity of multichannel detection and the low fluorescence associated with 1064 nm excitation. Ge and InGaAs arrays are available but have high dark noise compared with silicon CCD detectors. Very few applications utilizing dispersive 1064 Raman systems have been published and specifically for medical purposes [11-13] or detection of explosives [14].

Very few portable Raman instrumentation operating with 1064 nm excitation is currently available on the market. The multichannel detector used here is a combination of InGaAs and the low dark noise capabilities of Si based CCD's. The DeltaNuAdvantage 1064 system used in this work physically varies from the other two dispersive 785 nm portable instruments due to its heavier weight and need for a power connection. The knee-shaped optical head allows for relative flexible positioning of the sample with this instrument.

We present the results of an evaluation of this portable Raman spectrometer (DeltaNu Advantage 1064) using 1064 nm laser for excitation. Several groups of samples were tested with emphasis on application to geosciences (inorganic and organic minerals, biomolecules related to geobiological systems) and also examples of forensic applications (drugs of abuse and explosives) are presented in this study.

2 Materials and methods

2.1 Samples

A pure samples of drugs of abuse, namely cocaine hydrochloride, N-methyl-3,4-methylenedioxy-amphetamine (MDMA) hydrochloride, amphetamine and heroin, were supplied by the Sigma–Aldrich Company Ltd., United Kingdom. A street sample of cocaine hydrochloride and the explosive Semtex were supplied by the Home Office Scientific Development Branch, UK. Pentaerythritol tetranitrate (PETN) and cyclotrimethylene trinitramine (RDX) were supplied by the Home Office Scientific Development Branch.

Minerals were obtained from the Mineralogical Collection of Charles University in Prague and the Mineral Collection of the University of Bradford, comprising, calcite (CaCO_3 , trigonal), aragonite (CaCO_3 , orthorhombic), magnesite (MgCO_3), hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$), huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$), witherite (BaCO_3) mellite ($\text{Al}_2\text{C}_6(\text{COO})_6 \cdot 16\text{H}_2\text{O}$), whewellite ($\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$), fichtelite ($\text{C}_{19}\text{H}_{34}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), cinnabar (HgS), and amber samples from the Baltic sea. Synthetic epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) as well as pure organic standards (β -carotene, mellitic acid, usnic acid) were purchased from Sigma-Aldrich.

As examples of archaeological artifacts, a specimen of wall-painting from King Herod's summer palace in Jericho dating to 10 BCE and pigment on a medieval manuscript were studied.

Biological specimens that are prone to significant fluorescence emission using visible radiation for excitation were provided by lichens of *Acarospora sp.* originating from Signy Island in the maritime Antarctic, harvested at the fringe of the ozone hole where excessively large insolation of UV radiation is experienced. Examples of biogeological specimens were halite from the Atacama desert (Yungay area) and Beacon sandstone rocks from Mars Oasis, Antarctica – both colonised by endolithic cyanobacteria.

2.2 Raman spectroscopic instrumentation

The tested system - Advantage 1064 is a compact Raman spectrometer supplied by DeltaNu (Laramie, WY, U.S.A.). This system is 12" x 8" x 4" (LWH) and weighs 9 kg (see Figure 1). Hence, although it is not hand-held instrument, it is still considered as portable. The instrument has no battery and the power supply has to be provided. It is equipped with a 1064

nm diode laser giving a maximum laser power of 1000 mW at source. This is a dispersive reflective grating system giving Raman spectra in the wavenumber range 200-2000 cm^{-1} . The output optics provides a laser spot size of approximately 100 microns. The knee-shaped optical head was used for all the testing. The multichannel detector is an Intevac Photonics MOSIR 950 camera based on transfer electron (TE) photocathode and electron bombardment (EB) gain technology, benefiting from combined photocathode (InGaAs) and CCD technology. The incident NIR radiation is absorbed by the thin-film surface of the photocathode, electrons are then emitted from the back-side of the photocathode, voltage accelerated and then are detected on CCD. The camera has a working range from 950 to 1650 nm and is thermoelectrically cooled to $-40\text{ }^{\circ}\text{C}$. To cool down the detector, the instrument should be started up several minutes prior the analysis. The instrument is operated by external computer equipped with NuSpec software (DeltaNu) which permits the selection of three steps of operable spectral resolution from 15 to 20 cm^{-1} . The software allows five-step set-up of adjustable laser power from 800 mW to 30 mW. The spectral integration time and the number of accumulations is under full control of the operator. For instrument testing, individual scans of 1 to 10 seconds were accumulated over 10 to 30 scans. The influence of these parameters on spectral data quality was one of the subjects of this evaluation and is discussed further below.



Fig. 1 The compact Advantage 1064 system operated by external computer and equipped by knee-shaped optical head.

To compare the results obtained from the 1064 Advantage system, corresponding measurements on the following Raman spectrometers have also been performed:

Two portable Raman spectroscopic instruments equipped with 785 nm diode laser excitation, namely, the First Defender XL by Ahura (Wilmington, MA, U.S.A.) and the Inspector Raman (DeltaNu, WY, USA). The former instrument weighed 1.8 kg and had a maximum laser output of 300 mW, reducible in three steps. The instrument provides Raman data from a wavenumber range 250 – 2875 cm^{-1} . The instrument is equipped with a rechargeable 7.4 V Internal Lithium Ion Battery allowing about 5 hours of measurement to be undertaken in the field. The second portable Raman spectrometer using 785 nm for excitation is the Inspector Raman by DeltaNu (1.9 kg) equipped with a 785 nm diode laser excitation, with a maximum output power of 120 mW and a thermoelectrically cooled charge-coupled device detector with a wavenumber range of 200–2000 cm^{-1} . This instrument is equipped with the same NuSpec software as the 1064 Advantage system.

Micro-Raman analyses of specimens were also performed on a multichannel bench Renishaw *In Via* Reflex spectrometer (Renishaw, Wotton-under-Edge, UK) coupled with a Peltier-cooled CCD detector. Excitation was provided by the 785 nm line of a diode laser.

A benchtop Bruker IFS 66/FRA 106 FT-Raman instrument operating with 1064 nm excitation (Nd^{3+} /YAG laser) was also employed.

Spectral subtraction was undertaken to remove instrumental background exhibiting uniform pattern specific for the 1064 nm data (its role in analyte determination is described in the text). It was performed in the commercially available GRAMS[®] AI (Thermo Electron Corp., Waltham, MA, USA) software by subtraction of the blind measurement spectra using “spectral subtract” function. No other manipulation of data was performed in order to show differences of fluorescence emission between 1064 nm and 785 nm excitation. The importance of fluorescence background for the analyte determination is discussed in the text. Spectral data treatment and stackplot comparisons were made using the GRAMS[®] AI software.

3 Results and discussion

Analysis of polystyrene beads as an ASTM standard calibrant was performed using the 1064 Advantage system. In Figure 2 the observed peak positions are plotted offset against the

certified values. An uncertainty is depicted as ± 2 standard deviations of wavenumbers values as reported by McCreery [15].

3.1 Drugs of Abuse and Explosives

Sample fluorescence is still the main obstacle that limits the use of Raman spectroscopy for the analysis of drugs of abuse and explosives. Many drugs and explosives are comprised as pure components or mixtures. Illicit drugs in particular are diluted or cut at various levels with common household products that exhibit significant fluorescence even under conditions of 785 nm laser excitation. Such excipient compounds include flour, talc, etc. Fourier-transform Raman spectroscopy has been applied for characterization of pure drugs of abuse namely amphetamine, cocaine hydrochloride, and heroin. The technique was also applied for identification of these drugs in cut samples. Although the pure samples give excellent spectra for identification, some cutting agents were highly fluorescent, so preventing the identification of the drugs [16]. Cocaine hydrochloride, MDMA, amphetamine and heroin samples were analyzed as pure samples with excellent spectral quality using portable 1064 nm instrument. Comparison of 785 nm and 1064 nm spectra for a street-grade cocaine sample is presented in figure 3. Despite the presence of some bands attributable to the cutting agent (s), the characteristic cocaine hydrochloride bands can be easily identified. Both 785 nm and 1064 nm excitations allowed acquisition of high quality spectra. However, shifting the excitation to a 1064 nm wavelength has resulted in the dampening of the fluorescence background emission compared with 785 excitation. Despite the fluorescence, the analyte can be easily determined in this case using 785 nm excitation as well, nevertheless this example serves us as prove of elimination of negative effect of the cutting agent on the spectral quality when the 1064 nm system is employed. Its importance may arise with higher content of cutting agent or more appreciable fluorescent cutting agent within real street drugs.

Several common explosives also exhibit fluorescence. Lewis et al. [17,18] analyzed explosives by both FT- and CCD-based Raman spectroscopy in order to determine an appropriate wavelength for constructing a field-usable explosives analyzer. The authors concluded that 1064 nm excitation obviates the majority of fluorescence although longer data acquisition times are required to attain the desired SNR. Also, 785 nm excitation showed a benefit over that at 633 nm for most of the explosives studied, although several samples suffered from similar fluorescence levels with 785 nm and 633 nm excitations [17].

Figure 4 shows the spectra acquired from a Semtex sample using 1064 and 785 nm excitations on portable instruments. This sample is fluorescent using 785 nm excitation, although weak Raman features can be also observed. At 1064 nm laser excitation, the fluorescence background is significantly reduced and the characteristic bands of PETN with minor contribution of RDX can be clearly identified, with significantly better spectral quality compared to 785 nm excitation and including bands of weaker intensity not observed at 785 nm (high quality spectra of RDX and PETN as pure compounds are depicted for comparison).

These two examples show the ability of this 1064 system to acquire good quality spectra from samples that exhibit some degree of fluorescence with 785 nm excitation and with short acquisition times (10 seconds). The rapid acquisition of Raman spectra with sufficient quality is promising for forensic scientists and law enforcement for rapidly identifying unknown samples in the field. Based on presented observations, the technique described here may represent a simple, rapid and reliable nondestructive method for the detection and identification of the drugs of abuse and explosives. Nevertheless, testing of variety of different samples of forensic interest will be another important step for comprehensive evaluation of the instrument in this regard.

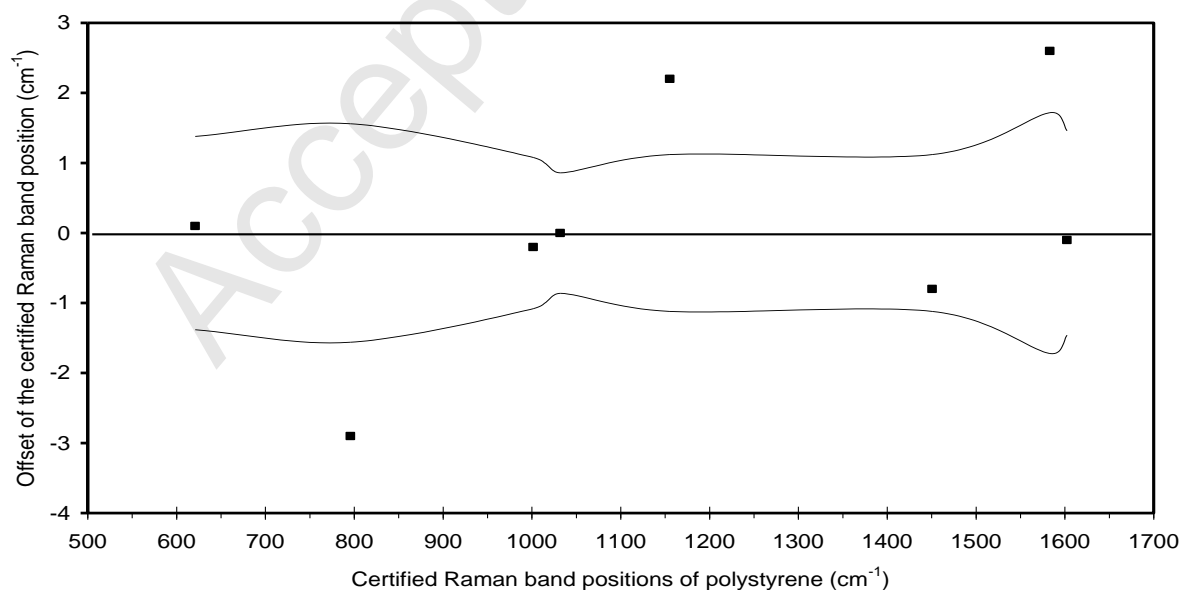


Fig. 2 Offset of the certified band positions of polystyrene as obtained by the 1064 Advantage system. The solid lines represent the $\pm 2 \text{ cm}^{-1}$ standard deviation boundary.

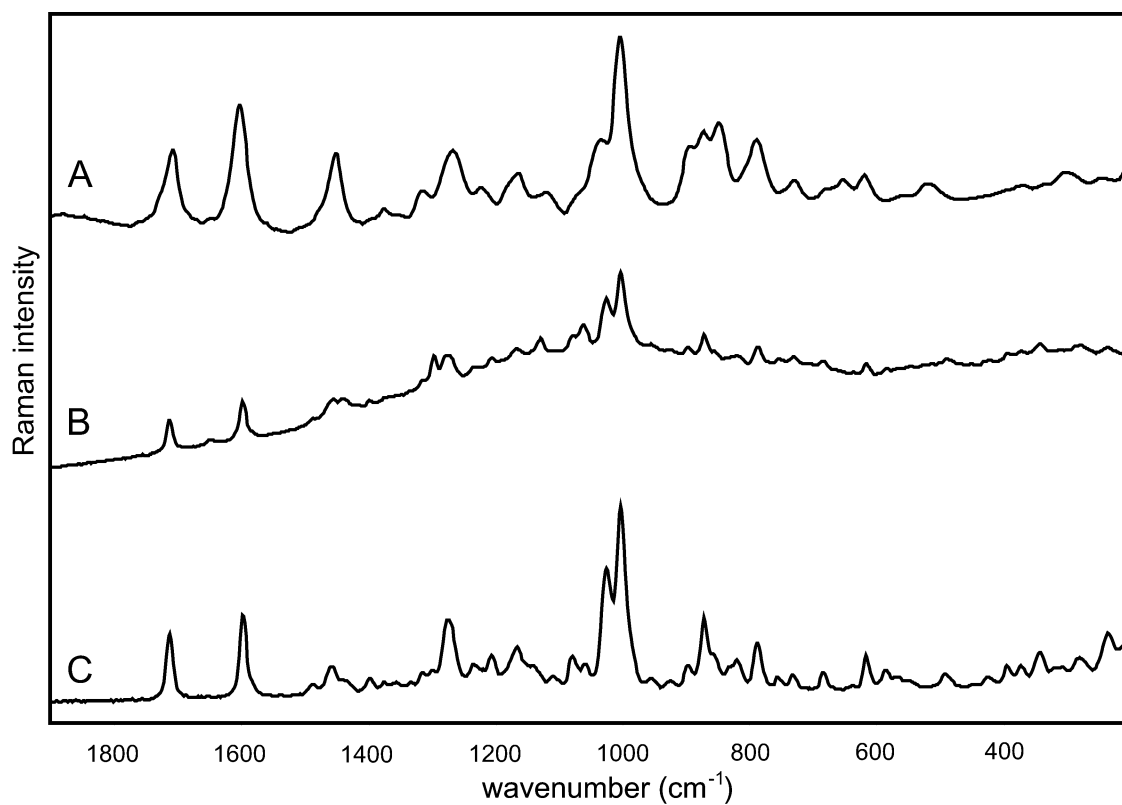


Fig. 3 Raman spectra of drugs of abuse

A: Street cocaine hydrochloride, Advantage 1064 nm, 10 second exposure, 1 accumulation

B: Street cocaine hydrochloride, DeltaNu, 785 nm, 10 second exposure, 1 accumulation

C: Reference cocaine hydrochloride, DeltaNu, 785 nm, 10 second exposure, 1 accumulation

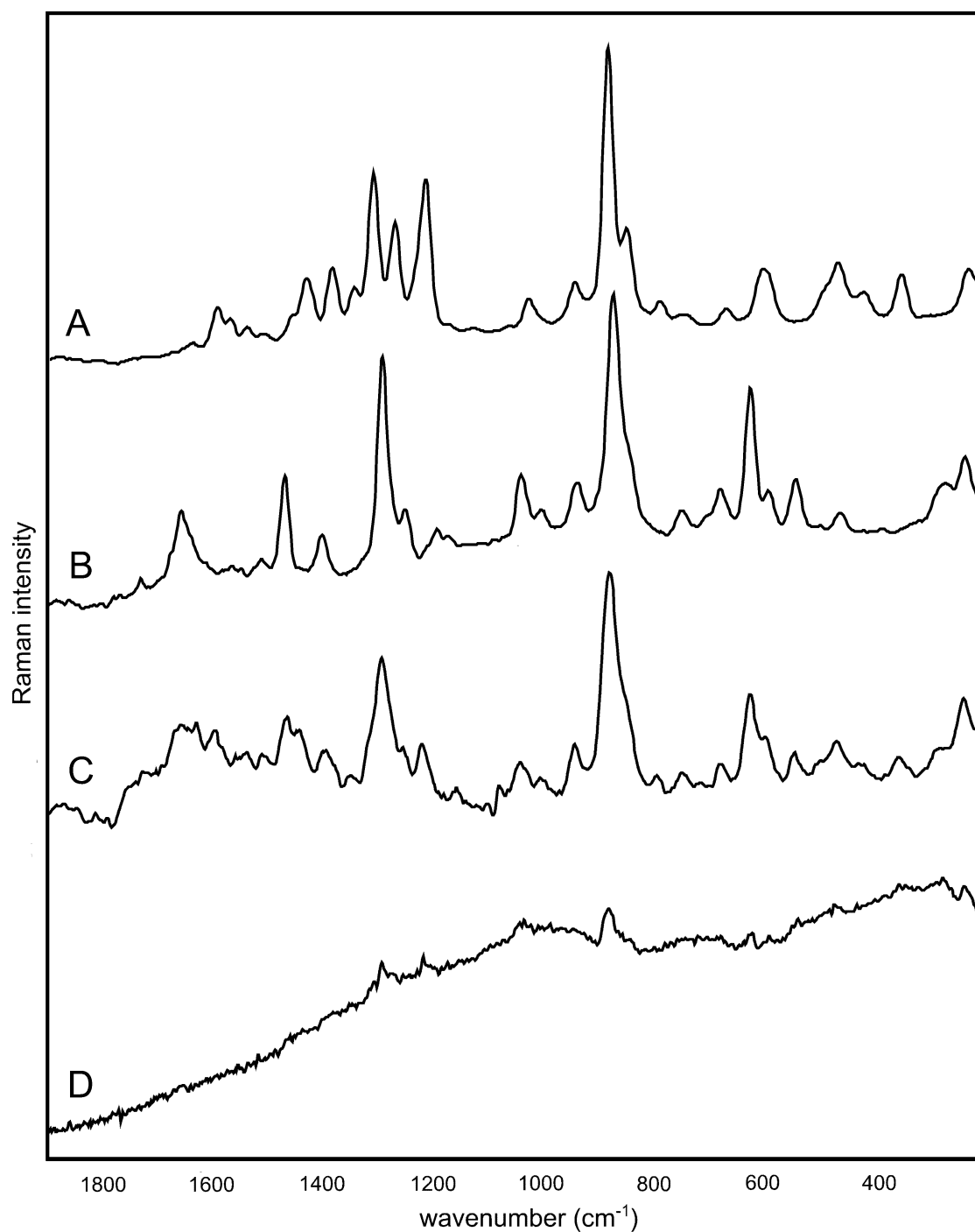


Fig. 4 Raman spectra of the explosives

A: RDX, Advantage 1064 nm, 10 second exposure, 1 accumulation

B: PETN, Advantage 1064 nm, 10 second exposure, 1 accumulation

C: Semtex, Advantage 1064 nm, 10 second exposure, 1 accumulation

D: Semtex, DeltaNu, 785 nm, 10 second exposure, 1 accumulation

3.2 Inorganic minerals

In this section, the potential to routinely detect inorganic minerals is briefly presented to demonstrate the ability of the instrument in this context, although the identification using different wavelengths is in most cases also possible as well. Rapid identification of inorganic mineral components is important for various applications, including geosciences, future planetary exploration or archaeology. We have successfully examined several groups of minerals which are described below. The group of carbonates tested here include calcite, aragonite, magnesite, hydromagnesite, witherite and huntite. It has been proven that successful discrimination between different natural Ca- and Mg- carbonate minerals can be performed by the instrument, with sufficient precision in recording of the ν_1 band wavenumber position as well as the positions of other bands of weak to medium intensity. Sulfate minerals such as gypsum and epsomite have also been successfully examined. All these minerals can be recognized also using 785 nm excitation (both portable and bench-top), although huntite, hydromagnesite and witherite exhibited fluorescence, which was eliminated using the 1064 nm instrument. All band positions are found to occur within 3 cm^{-1} of the standard spectrum obtained on the bench instrument (InVia Renishaw, 785 nm excitation).

Cinnabar is a red mercury sulphide mineral which has been used for many hundreds of years as a colouring compound for ancient manuscripts as well as decorative wall paintings. Raw spectra of cinnabar from three types of archaeological and artefact samples (namely, natural efflorescence on the hard rock, pigment from the historical wall painting from King Herod's summer palace in Jericho, the same that was studied previously by Frost et al. [19] and a red pigment on a mediaeval manuscript) are depicted in Figure 5. Two strong Raman bands are observed at $261 (\pm 2)$ and $350 (\pm 2) \text{ cm}^{-1}$ due to the mercury-sulphur stretching and bending vibrations, respectively, in mercury sulphide. The strong spectral background in the case of the native rock sample is ascribed to lower signal scattering intensity compared with the measurements made on the flat surfaces of the other two samples which contained extracted mercury sulphide.

Although spectral data could be obtained at lower wavelength excitation in these cases it is clear that equivalent information is also derived from the excitation at longer wavelength from both geological and archaeological samples of different origin.

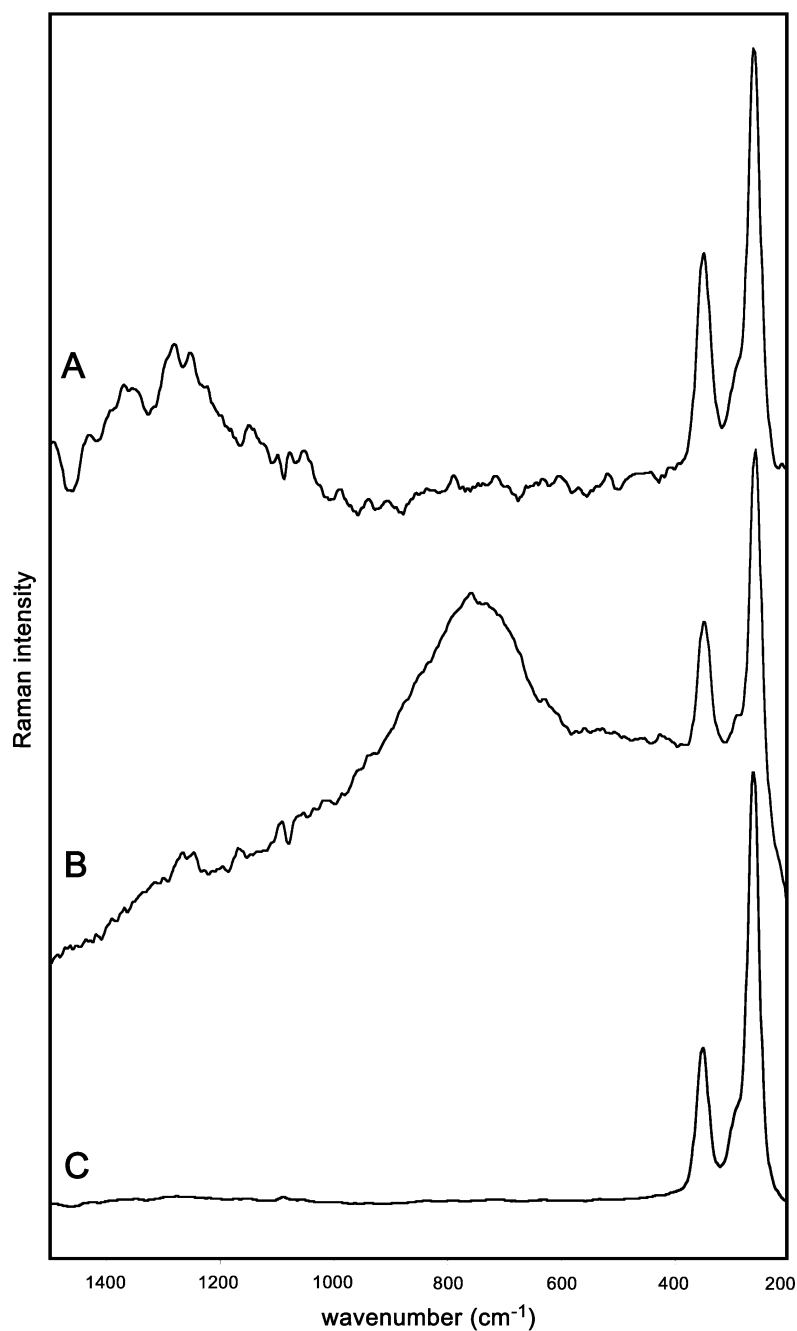


Fig. 5 Spectra of cinnabar of different origin as obtained by the portable 1064 Advantage system – rock sample (A), red pigment in old manuscript (B), pigment on the wall from Herod's palace (C).

3.3 Organic minerals and fossil resin

Organic minerals and fossil resins are a group of organic components in the geological record related to plant metabolic processes, decomposition products from coniferous trees or the

accumulation of fractions generated by natural high temperature distillation from specific precursors [20].

In Figure 6, the spectra of amber from the Baltic sea is depicted. The clear spectrum in the bottom obtained from the DeltaNu 1064 Advantage system can be compared with the spectra obtained from the benchtop FT-Raman instrument using a spectral resolution of 12 cm^{-1} and from the portable Inspector Raman (DeltaNu) equipped with 785 nm excitation. Both Raman instruments using the 1064 nm excitation source exhibited fluorescence free spectra compared with that obtained using 785 nm excitation. The band positions are in good agreement with the measurements reported previously in the literature by Jehlička et al. [21].

Spectra of the three organic minerals studied here – mellite, whewellite and fichtelite- are depicted in Figure 7, obtained using the DeltaNu 1064 Advantage system and DeltaNu Inspector Raman with 785 nm excitation (dotted line). In mellite, a naturally occurring aluminium benzenhexacarboxylate [$\text{Al}_2\text{C}_6(\text{COO})_6 \cdot 16\text{ H}_2\text{O}$], the band positions obtained by both portable instruments fit well with the measurements carried out with the benchtop instrument and published by Jehlička et al. [22].

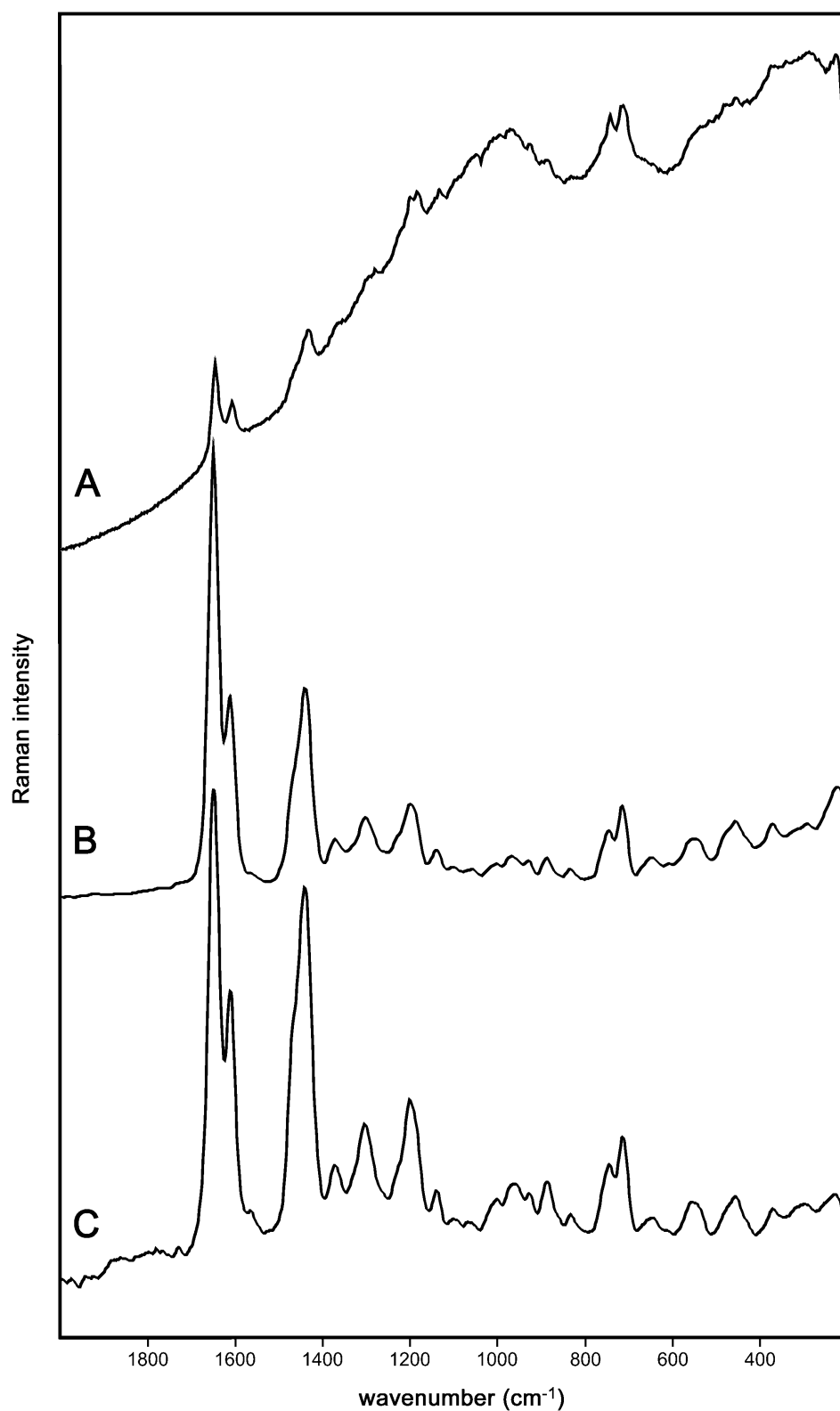


Fig. 6 Comparison of the spectra of Baltic amber as obtained by portable Raman spectrometer equipped by 785 nm diode laser (A), bench FT-Raman instrument (B) and portable instrument using 1064 nm excitation (C).

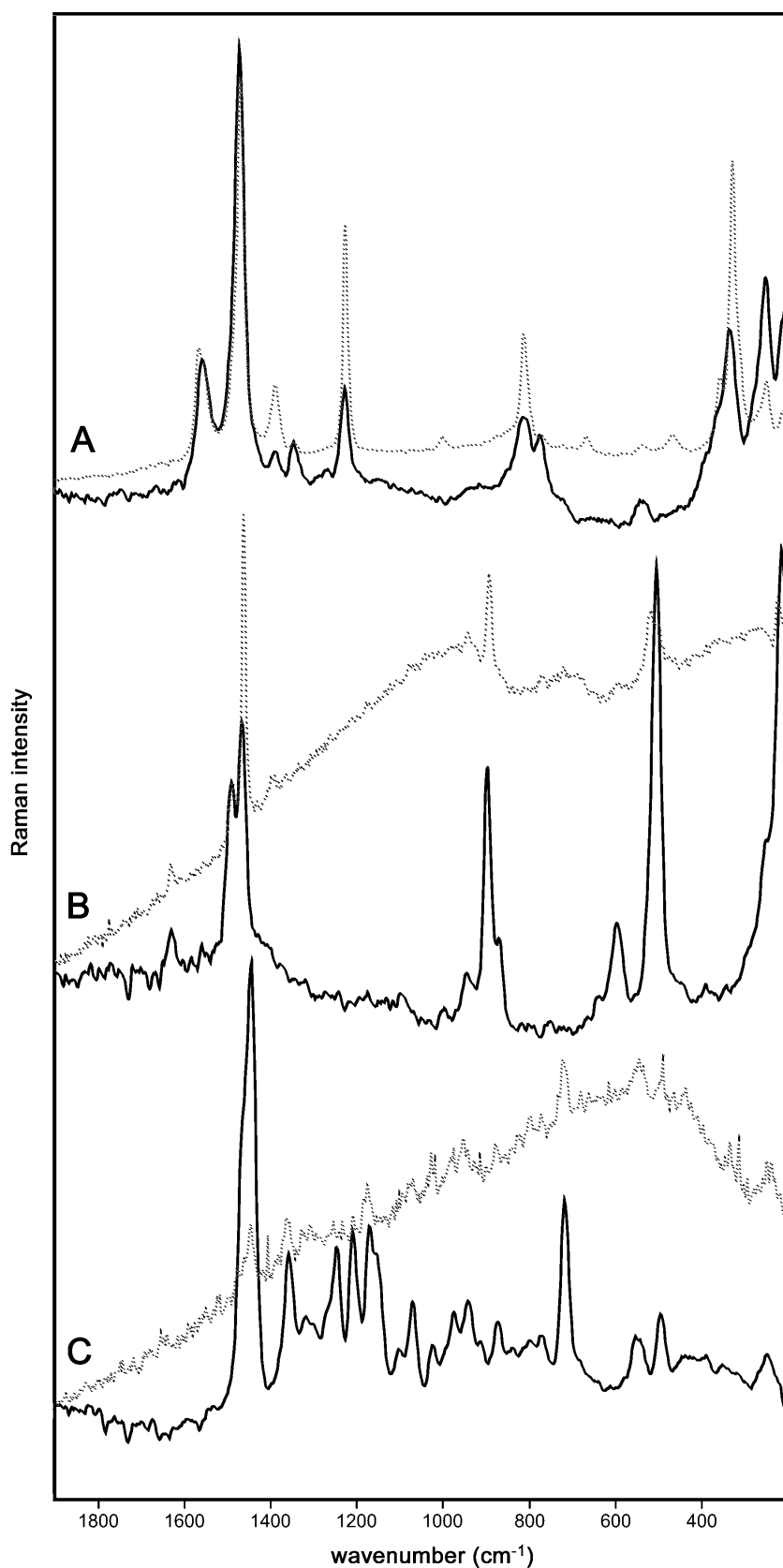


Fig. 7 Raman spectra of three organic minerals: mellite (aluminium benzenehexacarboxylate) (A), whewellite (calcium oxalate dihydrate) (B) and diterpenoid mineral fichtelite (C). Spectra from the 1064 Advantage system are compared to the spectra obtained by the portable instrument with 785 nm excitation (dotted line), which have fluorescence background in the case of whewellite and fichtelite.

Whewellite [$\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$] is the most common oxalate found in sediments and coal-bearing series. The spectrum is fluorescence – free at 1064 nm contrary to the data obtained by a portable instrument with 785 nm excitation although this excitation also allows mineral determination. The observed band positions correspond well to the data provided previously by other authors [10,20,23,24]. It should be noted that the instrument background is not dependent on the analyte electronic state (as for fluorescence background), however its importance for the identification of analyzed compound depends on the signal intensity. This is illustrated in the figure 8, where the importance of background subtraction is evident from the example provided by the whewellite spectrum.

Fichtelite ($\text{C}_{19}\text{H}_{34}$) is a monoclinic diterpenoid containing molecules of three non-linearly fused, six membered rings in a chair conformation, with an axial methyl, an angular methyl and an isopropyl group attached to the rings. This hydrocarbon occurs dispersed with other terpenoids in slightly carbonified *Pinaceae* wood remnants, usually in peat. As depicted in Figure 7, the fichtelite spectrum is significantly clearer with sufficient determination of bands of weak to medium intensity when 1064 nm excitation is employed, contrary to 785 nm data with huge fluorescence. The band wavenumber positions are in good accordance with the data published by Jehlička et al. [25], where detailed vibrational assignments are given.

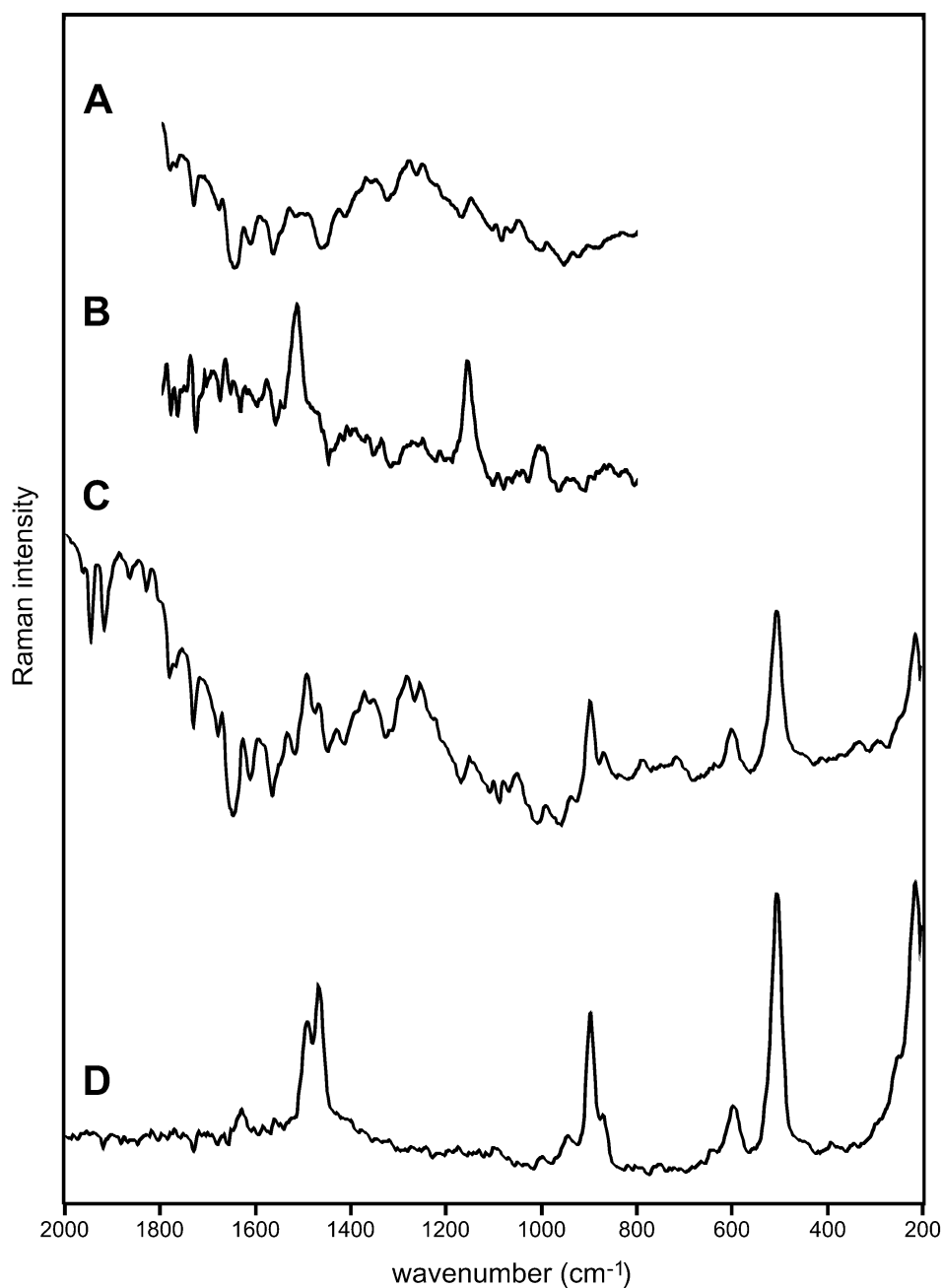


Fig. 8 Example of the instrument spectral background and role of its subtraction for compound identification (spectral subtract function of Grams software, without baseline correction). Upper two spectra: 100 mg kg⁻¹ of β-carotene in halite matrix – raw (A) and after background subtraction (B). Lower two spectra: whewellite – raw (C) and after background subtraction (D).

3.4 Biomolecules

Three different biomolecules were analyzed in the form of pure powders - β -carotene, mellitic acid, usnic acid (Figure 9). These molecules can be considered as potential biomarkers for Earth-based studies as well as for astrobiological research on the planetary bodies in our Solar System (namely, Mars) [26-33]. Clear bands of all studied biomarkers were obtained, with band wavenumber positions being in good accordance with those reported in the literature [22, 28, 30, 34]. For a low concentration of analyte, the background subtraction can be crucial for compound identification as shown in the example of β -carotene measured at a concentration of 100 mg kg^{-1} (100 ppm) in admixture with halite (see figure 8). Portable Raman spectrometers using both 785 and 1064 nm excitation sources were recently evaluated for detection of β -carotene and mellitic acid in varying concentration levels in halite by Víték et al. [35].

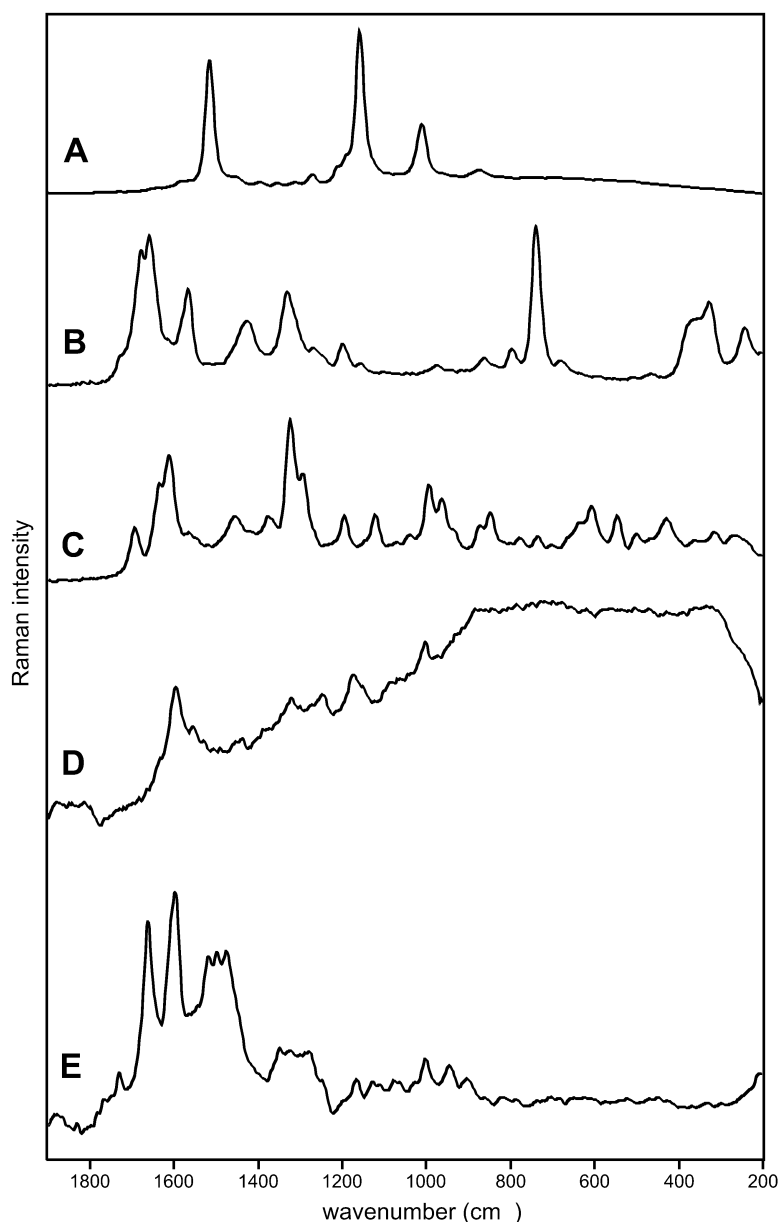


Fig. 9 Spectra of three types of pristine biomolecules – β -carotene (A), mellitic acid (B) and usnic acid (C), and spectra of obtained from natural specimens – namely epilithic lichen *Acarospora sp.* (D) containing rhizocarpic acid, whewellite, weddellite, β -carotene and the endoevaporitic cyanobacterial colonization from Atacama desert (E) with signatures of scytonemin, carotenoid and chlorophyll (the region between $300 - 900 \text{ cm}^{-1}$ corresponds to oversaturated fluorescence).

A considerably more difficult task for mobile Raman instrumentation is the identification of biomolecules incorporated within the organic/inorganic matrix in biogeological specimens. In this study we have examined the ability of the portable 1064 nm system to detect organic compounds in a) highly coloured epilithic lichens on a rock surface from the Antarctic and b)

layers of endolithic colonization in rocks from extreme terrestrial hot and cold desert habitats in the Atacama Desert and Antarctica.

The Raman spectroscopic identification of biomolecules in various species of lichens has been published by Edwards et al. [28,36]. A Fourier—transform Raman spectrometer using 1064 nm excitation was used since the fluorescence emission from the excitation at lower wavelengths swamps the Raman signals and renders identification difficult if not impossible; such specimens, therefore, represent a challenge for portable instrumentation, which hitherto has failed to record Raman data from these systems. Using the DeltaNu 1064 Advantage system, it was important to realize that the significantly large laser power used could be potentially sufficient to thermally degrade or burn the sensitive biological samples being interrogated. Nevertheless, it was possible to balance between laser power necessary to record Raman signal and simultaneously not thermally damage the sample. Good quality spectra of the *Acarospora sp.* epilithic lichen (Figure 9) was obtained, showing the strong features of rhizocarpic acid which are typically characteristic for this species [37-39] at 1663 and 1597 cm^{-1} as well as bands of the metabolic products, calcium oxalate monohydrate and dihydrate at 1497 and 1478 cm^{-1} . The contribution of carotenoid pigment to the lichen pigmentation is reflected by the Raman spectral features observed at 1518, 1165 and 1002 cm^{-1} .

It was found that it was generally much more difficult to use mobile Raman instrumentation in a macroscopic mode for the identification of the endolithic microbial colonization using both 1064 and 785 nm excitation; this is attributed to the need for a Raman microscope to target the minute colonies of microorganisms at the micrometer scale. Biocolonised zones of Beacon sandstone from Antarctica were not successfully identified by both 785 and 1064 nm excited portable systems. However, using the portable system equipped with 1064nm excitation, satisfactory signal from the dark colonization layer containing dense cyanobacterial pigments in the halite from the Atacama desert was obtained (Figure 8). The features at 1596, 1555 and 1173 cm^{-1} indicate the presence of scytonemin, a UV protective pigment, developed by cyanobacteria as part of the survival strategy in harsh UV radiation conditions. The band at 1321 cm^{-1} is a combined signal of scytonemin and chlorophyll. Other bands due to a carotenoid are present at 1528, 1153 and 1002 cm^{-1} . These spectral signatures are in good agreement with the measurements obtained using the benchtop Renishaw InVia instrument, equipped with the 785 nm excitation [40].

4 Conclusions

It was demonstrated that dispersive 1064 nm laser excitation coupled with transfer electron (TE) InGaAs photo-cathode and electron bombardment (EB) CCD technology can rapidly and successfully analyze samples with sufficient spectral quality using 1064 nm laser excitation. Examples of analysis of street-grade illicit drugs and plastic explosives show dampening of fluorescence background compared to 785 nm excitation. Its importance for compound identification depends on the intensity of fluorescence emission. It may not be compromising for the compound determination, however it may vary with different cutting agents and its content. Further effort should be focused on forensic application of the instrument and its comprehensive evaluation within this regard. Organic and inorganic minerals could be routinely identified, including minerals that exhibit significant fluorescence using 785 nm laser for excitation. Selected biomolecules in pure state as well as within organisms in 2 types of geobiological system were successfully identified, after finding of optimal laser power and position of the laser spot. The important issue to be addressed when performing analysis of compounds sensitive to thermal damage is an optimal setting of laser power and integration time to obtain good Raman signal response and simultaneously avoid burning the sample. Sample positioning can be also significant from this point of view, when analysing such complex bio-geochemical systems as endolithic or epilithic communities (lichens, cyanobacteria etc.) within rocks. The inherent spectral background, which cannot be eliminated by higher number of accumulated spectra is one of the weak points of this instrument. However, this can be successfully subtracted from the spectra when needed using GRAMS© AI software and its automatical elimination will be possible within further stage of development.

For application in geosciences, 785 nm excitation remains an universal excitation source capable to excite many compounds of inorganic and organic origin with further sufficient spectral quality. However there are special cases of minerals and bio-geochemical systems fluorescing at 785 nm wavelength. In these cases the system tested here can be beneficial, as demonstrated on the examples of organic mineral hartite, epilithic lichen *Accarospora* sp. or specific type of endolithic cyanobacterial colonization.

Although for some applications especially where higher spectral resolution is needed, benchtop FT-Raman instrumentation remains the instrument of choice; the portability and rapidity of analysis are significant advantages of the 1064 DeltaNu Advantage system. For applications where rapid analysis is needed for interrogation of samples which fluoresce at

lower excitation wavelengths, the employment of the dispersive 1064 nm system tested here can possess some new possibilities.

Acknowledgments

We are grateful to Jacek Wierzchos from whom the colonized halite sample from the Atacama Desert was obtained. This work has been supported by the Grant Agency of Charles University in Prague, grant No. 83007, by Czech Science Foundation (Project 210/10/0467) and a grant MSM0021620855 from the Ministry of Education of the Czech Republic. Also, the authors would like to thank the Egyptian Government for providing the financial support to Esam M. A. Ali, and the Home Office Scientific Development Branch and the Forensic Science Service, UK, for providing the drugs of abuse and explosive samples.

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