

Study of Raman Spectroscopy to detect the Underlying Substance Concealed below Diffusely Scattering Medium

Xiaohua Zhang*, Ji Zhang, Haifeng Zhang, Jianxin Lu, Leijian Wang, Yongsheng Xu
China Institute of Atomic Energy, Beijing, China
Email: *xhciae@126.com

Received 2013

ABSTRACT

Measurement and comparison of NaNO_3 powder concealed in opaque and semi-transparent plastic bottles are carried out through conventional Raman spectroscopy and spatially offset Raman spectroscopy individually. The action mechanism why the spatially offset Raman spectroscopy can effectively detect the medium concealed in the non-transparent bottle is analyzed. The spatially offset Raman spectroscopy breaks through the detection neck of the conventional Raman spectroscopy (the detection depth is small and cannot detect the ingredient of the subsurface under non-transparent medium), and the measurement and identification of the substance concealed in the non-transparent medium (opaque/semi-transparent plastic) bottle have been realized.

Keywords: Spatially Offset Raman Spectroscopy; Opaque/sub-transparent Plastic Bottle; Ingredient of the Subsurface; Diffuse Scattering

1. Introduction

Raman spectroscopy is a measurement method based on the inelastic scattering through interaction between light and matter. It can test samples noncontactly and non-destructively, and offers a substantially higher degree of chemical specificity, so this technique is one of the research focuses of analytical science. To conventional Raman spectroscopy adopted generally, the sampling depth is only limited in the area no more than several hundred microns of depth [1], or subsurface in transparent medium. However, diffusely scattering surface layers are frequently encountered in many medical and biological applications, such as food products, colloids, polymers, catalysts, powders in general, coating technology, dermatology applications involving the detection of cancerous tissue, biochemical identification for medical studies, and noninvasive authentication of pharmaceutical products. Such samples are often highly heterogeneous and can be made of various layers, each having a different chemical make-up. The major goal for analytical science is to provide a method capable of determining the chemical composition of subsurface layers in turbid media in a non-destructive way, by which the sample can be authenticated or the disease can be diagnosed. If the conventional Raman spectroscopy is employed, the fluorescence and Raman spectra of the target are collected simultaneously, whereas the Raman spectrum of the sub-

surface is relatively very weak, and it is often interfered seriously or even overwhelmed by the fluorescence and Raman spectra from the surface layer, so it becomes extremely complicated or even impossible to separate the spectrum of the surface and the one of the subsurface. In the face of these emerging challenges, a new technique based on Raman scattering, spatially offset Raman spectroscopy (SORS), which is capable of retrieving the subsurface concealed by opaque or sub-transparent diffusely scattering medium, is discovered by the workers of Rutherford Appleton laboratory [2]. And it has been used in the fields such as researches and applications of authentication of the packed pharmaceutical products [3-5], disease diagnoses [6-8], anti-smuggling [9], airport screening for explosives especial liquid ones [10-12], and has gained extraordinary attention and approval from the whole society.

In this paper, measurement and contrasting analysis for NaNO_3 powder concealed in opaque and sub-transparent bottles have been carried out through conventional Raman configuration and SORS configuration individually. And the action mechanism how the SORS can realize the efficient detection of the media concealed in non-transparent plastic bottles has been analyzed.

2. Theory and Method

During Raman scattering, the incoming light passing through the sample will be inelastically scattered from the molecular vibration, which causes the energy (wave-

*Corresponding author.

length/ frequency) of the photons to be altered. In the conventional mode, backscattering geometry is often adopted whose focus of the collecting lens is strictly overlapped with the illuminated spot. However, the SORS is based on the collection of the Raman spectrum emanating from spatially offset regions away from the point of illumination Δs on the sample surface, see **Figure 1**, where the relative intensity ratio of Raman spectrum of the surface to the one of the subsurface varies with the different offset distance. If the spectra data of spatial offset distance $\Delta s \neq 0$ and $\Delta s = 0$ are processed, the pure Raman spectrum of the subsurface covered by the opaque/sub-transparent medium will be retrieved.

3. Experiment

3.1. Experiment Apparatus

The setup diagram of the SORS of the experiment is shown in **Figure 2**, the probe beam is generated by a temperature stabilized 532 nm constant wave laser (MGL-III-532, Changchun New Industries), the output power of which is 150mW with spectral line width is < 0.2 nm. The illuminating laser light is incident on the sample at $\sim 45^\circ$ after it is focused by lens F_1 . Here, mirror M and the sample are all placed on a 1D micro-positioning stage, keeping the point of incidence on the sample fixed with respect to the sample. In the configuration, a lens F_2 with 20mm diameter and 50mm focal length is adopted for spectra collecting and collimating, then the interaction zone of laser and the sample is imaged onto the fiber detector (a single fiber with 1mm diameter) with the ratio of 1:1 by F_3 with specifications as same as F_2 . The holographic notch filter centered at 532 nm (Kaiser Optical Systems, Inc.) between F_2 and F_3 is the crucial element, which can reduce the intensity of Rayleigh scattering by three orders of magnitude, whereas the Raman scattering light is of no attenuation. The spectra collected are measured by the miniature spectrometer (BTC112E series) produced by B&W Tek Inc.

If the mirror S in **Figure 2** is removed, then the setup will be the conventional one, where the illuminating laser is coupled into the Raman collecting system directly and normally incident on the sample as **Figure 1(a)**.

3.2. Samples and Measurements

The samples used in the experiments are chemical reagent NaNO_3 produced by Beijing Red Star Chemical Factory, white plastic bottle (opaque) with thickness of 1mm and Olay oil moisture protection cream bottle (sub-transparent hard plastic, thickness of about 6 mm), and NaNO_3 packed in the bottles aforementioned. The chemical reagent NaNO_3 is fine powder ground by a pestle and mortar, which is loosely packed in the bottles or piled on a metal plate without any mechanical tapping.

Raman spectra of powder NaNO_3 , opaque and sub-transparent plastic bottles, and bottles containing NaNO_3 are measured by the conventional setup, and the spatially offset ones with different offset distance of bottles containing powder NaNO_3 are then measured by the SORS configuration in **Figure 2**.

4. Results and Discussion

Firstly, Raman spectra of powder NaNO_3 , opaque plastic bottle with thickness of about 1mm, and the bottle containing NaNO_3 powder are individually measured by the conventional setup, and the results are shown in **Figure 3**.

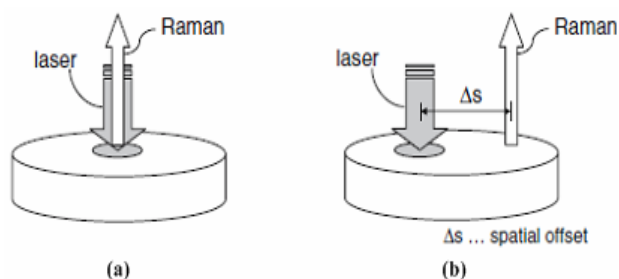


Figure 1. Schematic diagram for (a) backscattering Raman spectroscopy and (b) spatially offset Raman spectroscopy.

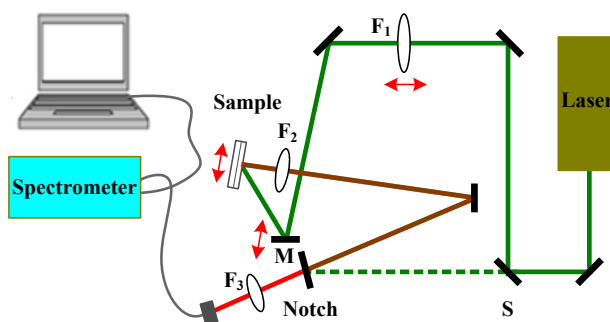


Figure 2. Setup of spatially offset Raman spectroscopy.

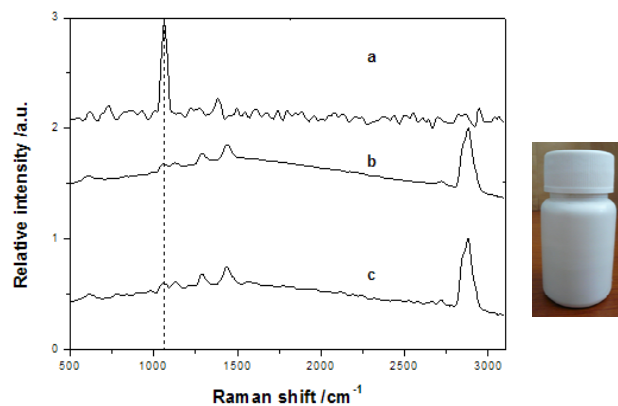


Figure 3. Conventional Raman spectroscopy of NaNO_3 powder, white plastic bottle (thickness of ~ 1 mm), and the bottle containing NaNO_3 : (a) NaNO_3 ; (b) bottle containing NaNO_3 ; (c) empty bottle.

As shown in the figure, there is a sharp Raman peak of the NO_3^- in the spectrum of NaNO_3 piled on the metal plate, however, the Raman spectrum of NaNO_3 concealed in the plastic bottle is remarkably similar to the one of the empty bottle, without obviously peak near 1062cm^{-1} at all. All these results indicate that it is very efficient for the conventional Raman spectroscopy to probe the near surface ingredient, nevertheless, this approach is hampered or fails when facing to the detection of the subsurface concealed in the opaque plastic bottle, because the illumination and collection zones are coincided, the fluorescence and Raman spectra generated from the bottle are intense enough to 'swamp' the detector, thus degrading or precluding entirely, the detection of the relatively much weaker Raman photons from the deep layer.

Spectra shown in **Figure 4** are the Raman spectra of the NaNO_3 powder in **Figure 3**, where the Raman spectrum collection zones are offset from the illumination zone with different distances, here the Raman peak intensity of the plastic bottle is normalized. Seen from above figure, the ratio of the relative Raman intensities of NO_3^- to the plastic bottle increases with the spatial offset distance, that is, SORS depresses the interference of the Raman and fluorescence coming from the surface layer. However, when the offset distance is more than 6mm, the ratio of the signal to the noise becomes worse, and the increase of the relative intensity of NO_3^- Raman spectrum becomes unobvious. Nevertheless, the penetration depth of the SORS to the opaque medium is far more than the conventional Raman spectroscopy, and the detection and identification of the subsurface in the opaque plastic bottle can be realized.

To the detection of the subsurface concealed in the sub-transparent medium, Raman spectra of powder NaNO_3 , OLAY® moisture protection cream bottle (thickness of about 6mm, sub-transparent) containing NaNO_3 and the empty bottle measured by the conventional Raman spectrum configuration are shown in **Figure 5**. As same as the spectra in **Figure 3**, the Raman spectrum of the bottled NaNO_3 is extremely similar with the one of the empty bottle, without obvious NO_3^- Raman peak near 1062cm^{-1} at all. And compared with spectrum of the empty bottle, there is only a little difference near 1062cm^{-1} . Therefore, it is difficult to authenticate the ingredient in the subtransparent bottle according to the spectral data in **Figure 5**.

The SORS of NaNO_3 contained in the sub-transparent plastic bottle with different spatially offset distance are shown in **Figure 6**, where Raman peak intensity of the bottle is normalized. Compared with the conventional one, the relative intensity of NO_3^- near 1062cm^{-1} in the SORS increased with the spatial offset distance, and the clear Raman peak is already present at $\Delta s=3\text{mm}$, that is, the interference of the Raman and fluorescence signals from the surface has been depressed to a great extent.

Seen from above experimental study, the conventional Raman spectrum emphasizes the signals emitted from the container wall (although a contribution from the concealed substances may also be apparent). The SORS is also taken at the surface of the container, but at a position spatially offset from the illumination zone, and this measurement is effective at capturing subsurface photons, owing to the ability to achieve significant suppression of the surface Raman and fluorescence signals, thereby the efficient detection of the substance concealed in non-transparent diffusely scattering bottles can be carried out. The action principle of the latter is as follows (**Figure 7**): When the illuminating laser incident on the sample penetrates (with exponentially intensity) into the diffusely scattering sample, the original straight trajectory of the photons is rapidly converted to a range of sideways scatters, which eventually completely randomize the path of the photons after being scattered several times. Provided the bottle wall is not too thick, some of the photons will

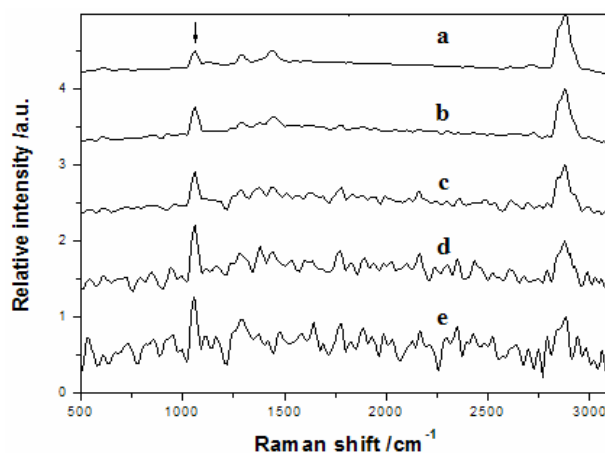


Figure 4. SORS with different spatial offset of NaNO_3 contained in white plastic bottle (Raman peak intensity of the bottle is normalized): (a) 1.5 mm offset; (b) 3.0 mm offset; (c) 4.5 mm offset; (d) 6.0mm offset; (e) 7.5 mm offset.

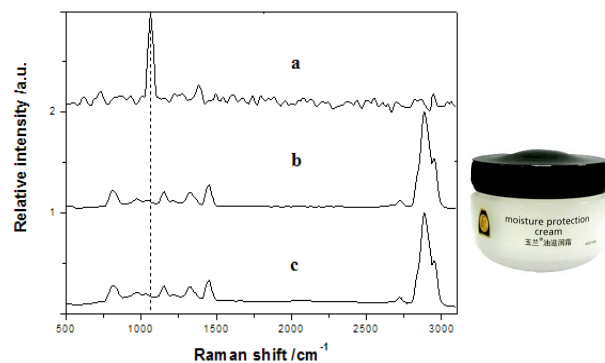


Figure 5. Conventional Raman spectroscopy of NaNO_3 , OLAY® moisture protection cream bottle containing NaNO_3 and the empty bottle: (a) NaNO_3 ; (b) bottle(thickness of 6mm) containing NaNO_3 ; (c) empty bottle.

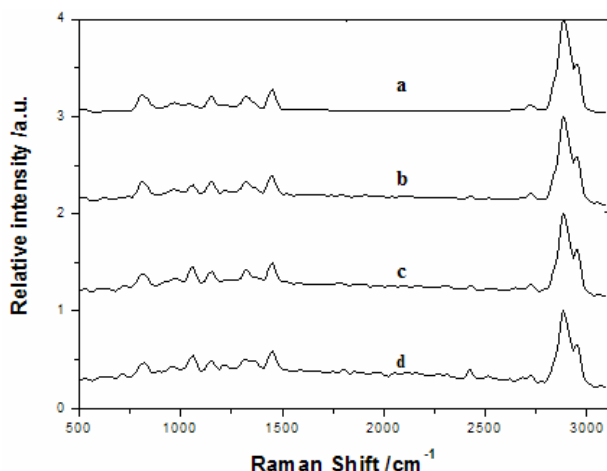


Figure 6. Contrast between SORS with different spatially offset and conventional Raman spectrum of OLAY® moisture protection cream bottle containing NaNO_3 (Raman peak intensity of the bottle is normalized): (a) conventional Raman spectrum; (b) 1 mm offset; (c) 3 mm offset; (d) 5 mm offset.

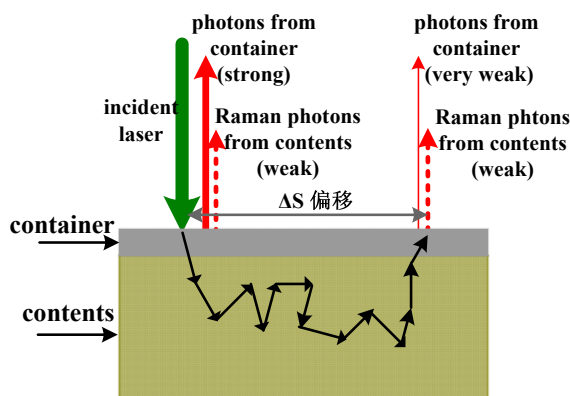


Figure 7. Diagram of the SORS action principle.

reach the NaNO_3 in the bottle, whereafter they will be randomized by NaNO_3 powder. And those photons that are randomly scattered back toward the bottle wall will reemerge. On average, the deeper the photon has travelled into the bottle, the further away from the original point of entry that it reemerges from the bottle surface[2]. Most of the photons collected from the point offset from the entry point Δs are Rayleigh scattered ones. Nevertheless, some of them will involve Raman scattering ones taking information of the sample. Collecting these photons originating at an appropriate offset will thereby bias the collection towards the Raman signals of the underlying NaNO_3 . In comparison, the Raman photons originating from the plastic bottle decay very rapidly with increasing offset from the illuminating point, since they have had much less opportunity to travel sideways by scattering, than those emerging from the underlying layers[2]. Consequently, SORS technique has the ability to

depress the Raman and fluorescence signals emanating from the surface (bottle wall) significantly, breaking through the neck of the Raman spectroscopy detection and realizing the probing of the substance concealed in the diffusely medium (opaque or sub-transparent plastic bottle). Therefore, SORS has advantages that the conventional Raman spectroscopy can't provide at the detection of the underlying substance below diffusely scattering nontransparent medium.

5. Conclusions

Raman spectra of NaNO_3 powder concealed in nontransparent media (opaque and semi-transparent plastic bottles) are studied using conventional Raman spectroscopy and the SORS individually. The comparison between the two kinds of technique for detection shows that the conventional one only adapts to the probe of near surface ingredient of the nontransparent media, whereas SORS has further penetration depth than the former, and it can depress the fluorescence and Raman spectrum of the surface (plastic bottles) to a great extent, by which the probe for the subsurface concealed in the nontransparent medium (opaque and sub-transparent plastic bottles) can be realized. The further work is in progress.

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