ORIGINAL ARTICLE e-ISSN: 2349-0659 p-ISSN; 2350-0964

Detection of Carcinogenic Dye Sudan I and Rhodamine B Using Indigenous Raman Spectrometer

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Abstract

Sudan I and Rhodamine B are carcinogenic declared by European Union and California, respectively. Duo finds their uses in food and beverage products. Daily consumption can cause skin allergy and worsen to cancer. Due to its fluorescent nature it becomes erroneous to detect using Raman Spectrometer but with use of NIR diode laser it gives molecular fingerprint of dyes with associated samples. This paper presents to make an indigenous Raman Spectrometer to detect Sudan I and Rhodamine B like dyes. Raman Spectrum is taken even in water sample also through packaging.

Keywords: Dyes, Raman spectrometer, Spectrograph design

Asian Pac. J. Health Sci., (2022); DOI: 10.21276/apjhs.2022.9.4S.53

Introduction

Spectroscopic examination yields fingerprint information about the sample with light-matter interaction. Raman spectrometer is a molecular spectroscopic technique used to detect the fingerprint and gives the changes in molecular bond structure even in water solvent. It gives product information, state changes, stress, strain and crystallinity and a method to generate the vibration spectrum of molecules and polyatomic atom. Raman Spectroscopy is based on Inelastic scattering of light when irradiated by monochromatic light, a laser in most cases.[1-6] Raman spectra results molecular structure, characteristic feature, vibrational, rotational speed, polarization, rigidity, phonon interaction, arrangement of atoms, and other physical properties of molecules. It predicts about fluorescence samples such as Sudan, Rhodamine, and cyanine when irradiated with NIR lasers. Here Sudan-I and Rhodamine B samples are tested and result discussed with designed indigenous Raman Spectrometer.

Sudan ($C_{16}H_{12}N_2O$) is azo compound used as dye in Chemical, Pharmaceutical, Bio medical, and Agriculture industries to color hydrocarbon solvents, oils, shoe and floor polishes, fats, and wax. Sudan Figure 1 with chemical name 1-phenyldiazenylnaphthalen-2-ol is known as CI solvent yellow and solvent orange R, according to the EU rapid alert system Sudan-I was identified in chili powder and foods items. Sudan-I is prohibited to consume daily due to its genotoxicity and mutagenicity concerns. The European Commission banned of importing products containing spicy chili.

Rhodamine ($C_{28}H_{31}ClN_2O_3$) Figure 2, dye is used as a tracer in liquid and staining in biological analysis. Its known as 9-(2-carboxyphenyl)-6-(diethylamino) xanthen-3-ylidene]-diethylazanium; chloride. In California, it is suspected to be carcinogenic and declared warning in food and beverages items.[7]

Literature survey on Raman Spectrometer design states American society for testing and materials (ASTM) Standard Guide for Raman Shift Standards for Spectrometer Calibration states calibration standards for Raman spectrometer.[8] ASTM Standard guides to test the Resolution of a Raman Spectrometer.[9] Design techniques for analytical instruments stated by Frank and Settle.[10] Griffiths gave resolution for the Raman instrument.[11] Fountain *et al*. III established the instrument parameter for the spectrograph.[12] Intensity correction of Raman System betters the instrument accuracy for quantitative analysis presented by Choquette *et al*., Pollard *et al*., Dubesy *et al*., and Schlosser *et al*.[13-16] Raman Spectrometer's tight align and calibration produces optimum results. NIR Lamp selection for the present work is based Oriel Instruments.[17] Chao designed spatially offset Raman Spectrometer analyzes the spectra in packing wraps without intervening packet.[18] Raman probe designed and stated by S Esposito is suitable for *in vivo* analysis.[19] Allemand gave Raman Spectrometer design rules stated Raman output depends on light source, collection of light, signal to noise ratio (SNR) of spectrograph, and quantum efficiency (QE) of detector.[20] Maity *et al*. designed line confocal microscope suitable for protein analysis using surface enhance Raman spectrometry.[21] Kavitha *et al*. designed Raman spectroscopy proved to be an effective tool to study the one-dimensional systems structures.[22]

Paper presents Indigenous design and fabrication of Raman Spectrometer for dyes samples detection.

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How to cite this article: Upadhyay P, Bhaskar P, Datla R. Detection of Carcinogenic Dye Sudan I and Rhodamine B Using Indigenous Raman Spectrometer. Asian Pac. J. Health Sci., 2022;9(4S):280-283.

Source of support: Nil.

Conflicts of interest: None.

Received: 01/02/2022 **Revised:** 22/03/2022 **Accepted:** 03/04/2022

Materials and Methods

Diagram of the Raman Spectrometer

Figure 3 shows the block diagram of Raman Spectrometer. It consists of three major parts Laser, Collection and Filter Optics, and a Spectrograph.

Laser

A monochromatic single longitudinal mode (SLM) lasers are suitable for the Raman spectroscopy. NIR 785 nm laser are opted for current design. NIR 785 nm laser is used to offer balance between scattering efficiency, influence of fluorescence, detector efficiency, and availability of cost efficient and compact high quality laser sources, at this wavelength fluorescence suppression observed as fluorophores does not give fluorescence in NIR region. Raman-scattering efficiency is weaker in the near-IR.

Integrated Optics Inc. Lithuania make 130 mW, Diode laser 785 NM SLM LASER (VBG DIODE; FREE-SPACE) is used in current design configuration.

Scattering collection and filter optics

Collection and filter optics consist of dichroic filter, objective lens, long pass filter, and a concave mirror.

Dichroic Mirror (Semrock) reflects the laser light toward samples through objective lens, objective (Olympus) lens focuses laser light onto sample and Collects scattering light which is directed to concave mirror through long pass filter (Semrock), filter removes anti-stokes, and Rayleigh scattering. Concave mirror (Thorlabs) focuses stokes scattering onto spectrograph.

Spectrograph

Spectrograph plays a key role in spectrometer design. It distinguishes the input light into its component wavelengths. Spectrographs implies in both qualitative and quantitative analysis. Fabrication of spectrograph consists of three key components-Slit, Grating and Array Detector which decide the resolution, precision, repeatability, QE, SNR, and other factors.

Figure 4 shows the 3D picture of designed Raman Spectrometer.

Slit determines the resolution of the spectrometer but compromise the intensity of light. When slit size is more, less intensity of light observed and resolution gets increased, vice versa. A slit of 15 micron from thorlabs is used in Raman spectrograph design.

Grating separates the input light into its components wavelengths. Gratings are selected by groove lines per millimeter which decides the resolution of spectrograph. Greater groove lines yields better resolution. A grating of 719 grooves/mm of NIR range 700–1100 nm is used in current design.

Charge-coupled device (CCD) is an array detector that provides high sensitivity, low noise better image quality. Hamamatsu Japan, make thermo-electric cooler based CCD is used in current spectrometer design.

Figure 5 shows the optical layout arrangement of the indigenously designed Raman Spectrometer. In Figure 5, a diode laser impinges sample through dichroic mirror and objective lens and scattered light is collected back by objective lens further directed towards spectrograph through Edge filter and focusing mirror (OAP). Spectrograph detects the Raman signal and shows the result.

Calibration and Resolution

Spectrograph calibration is the process of comparing and correcting the output of an instrument against the established standard.

Raman Spectrometer is calibrated using standard light source Argon, Xenon pen lamps from New Port and Silicon

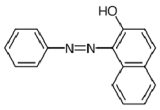

Figure 1: Sudan I molecular structure

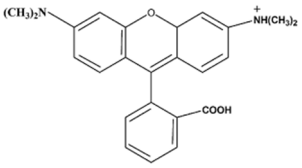

Figure 2: Rhodamine B molecular structure

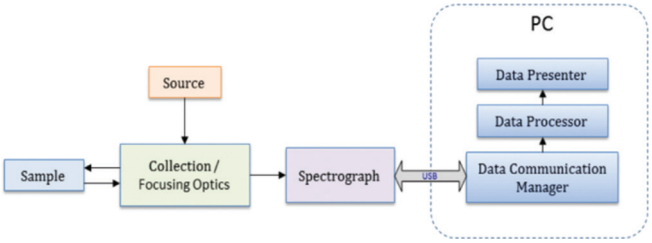

Figure 3: Raman spectrometers block diagram

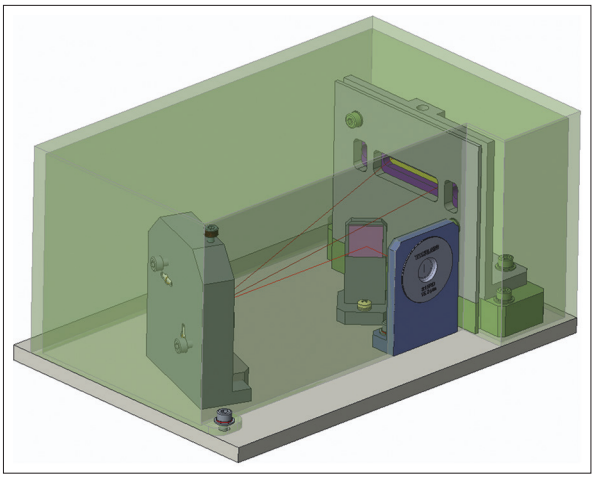

Figure 4: Designed and fabricated Raman spectrograph 3D

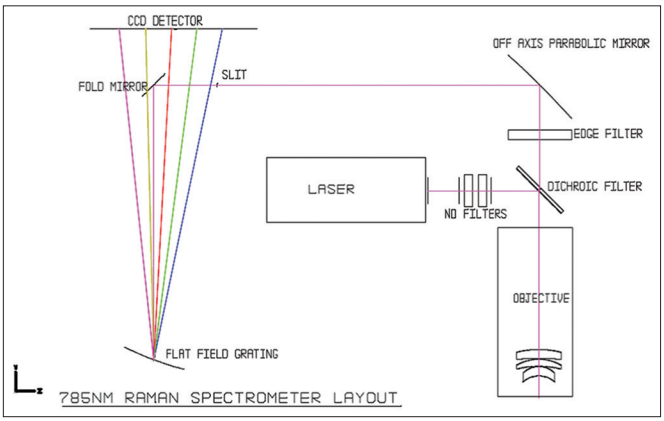

Figure 5: Optical layout of Raman spectrometer (zemax)

Wafer (520 cm^{-1}) from Sigma-Aldrich for the range of 100 cm^{-1} to 3700 cm^{-1}[8] and resolution is tested 10.67 cm^{-1}.[9] Standard samples paracetamol, naphthalene, cyclohexane, sulfur, and calcite is tested with designed Raman Spectrometer.[23]

Results and Discussion

Dye Test and Interpretation

Dye 1 Sudan-I

Sudan (10% w/v) mixed with water solvent Raman Spectra is taken by fabricated Raman spectrometer and graph is displayed below:

Figure 6 shows Sudan I Raman Spectra, Characteristic peaks of Sudan dye at 1222.6 cm^{-1} represents C-O stretching vibration and CCH scissoring bending of the naphthalene ring, peak 1387.6 cm^{-1} is for C=N stretching vibration and C-H in-plane bending, Raman peak at 1494.9 cm^{-1} displays C=N, N-N stretching vibration, and N-H in-plane bending vibration, and peak at 1594.4 cm^{-1} shows C-C scissoring.

Dye 2 Rhodamine B

Rhodamine B (10% w/v) also mixed with water solvent and Raman Spectra is taken by fabricated Raman spectrometer and graph is displayed below:

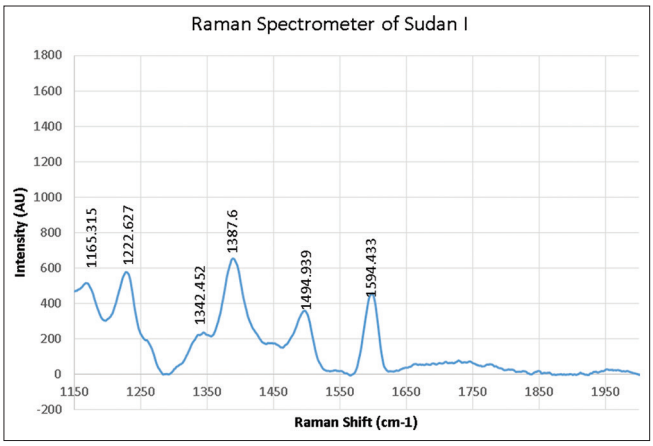

Figure 6: Raman spectra of Sudan I

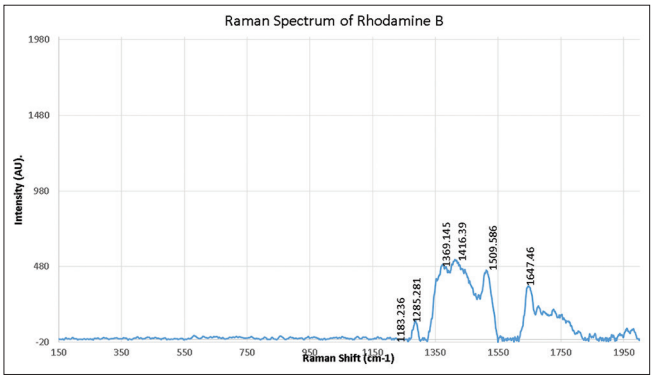

Figure 7: Raman spectra of Rhodamine B

Figure 7 displays Raman Spectra of Rhodamine B produces characteristic peaks located at 1183.2 cm^{-1} (CH bending), 1285.2 cm^{-1} (methyl wagging), 1369.3 cm^{-1} (XR stretching), 1509.5 cm^{-1} (XR stretching),), and 1647.46 cm^{-1} (XR stretching).

Conclusion

We developed indigenous designed and fabricated spectrometer and tested the azo dye Sudan I and Dye Rhodamine B, samples results are displayed in Figures 6 and 7, respectively. Raman spectra peaks found at standard modes of vibration. Further it can be incorporated with Chemometrics Analysis to give still better SNR. It is useful to detect food and beverage adulteration to find Carcinogenic Sudan and Rhodamine. Food analysis use NIR laser, Raman Spectrometer designed also uses NIR diode Laser to food analysis and suppression of fluorescence in dye samples. Using the fabricated Raman Spectrometer banned Sudan and Rhodamine can be counter checked for food samples.

Acknowledgment

The authors are grateful to M/s ELICO Limited Hyderabad to provide Fund, Infrastructure and Technical Support to carry out the project.

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