A novel technique for Raman analysis of highly radioactive samples using any standard micro Raman spectrometer

*by: Colle, Jean-Yves; Naji, Mohamed; Sierig, Mark and Manara, Dario.*

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Dear Editor,

Hereby we would like to resubmit a revised version of the manuscript JoVE54889R2 by J-Y. Colle et al., titled "A novel technique for Raman analysis of highly radioactive samples using any standard micro Raman spectrometer", for your consideration for publication in JoVE journal.

A previous version of this manuscript was submitted to the journal and assessed by three referees. Both, first and second referee gave a positive opinion on the paper and highlights the importance/novelty of the technique for measuring Raman spectra of highly radioactive materials without the nuclearization of any part of the instrument. They also gave a positive comment on the overall quality of the Raman experiments we performed and on the validity of our conclusions; in general they judges positively the paper, though asking (seemingly out of curiosity) constructive questions that we would like to respond to it in this letter. On the contrary, the third referee casts rather ill-argumented doubts on the technical and scientific parts of the manuscript, he also accuse the authors of self-plagiarism and severe violations of the code of scientific practice. Judging from his comments, authors think that he has misinterpreted rather grossly the core of our paper and the editorial policy of the JoVE journal.

Below you will find our point-by-point reply to Referees. We hope you will find our revised manuscript suitable for publication in JoVE and look forward to hear from you.

Best Regards,

JY.Colle and M. Naji on behalf of the authors.

Reply to Editor,   
  
**Editorial comments:**  
The manuscript has been modified by the Science Editor to comply with the JoVE formatting standard. Please maintain the current formatting throughout the manuscript. The updated manuscript (54889\_R2\_080816.docx) is located in your Editorial Manager account. In the revised PDF submission, there is a hyperlink for downloading the .docx file. Please download the .docx file and use this updated version for any future revisions.

**Author reply**: We thanks the editor its comments. We replied in the text below as well as in the manuscript activating the track change option.

1. Please continue to copyedit the manuscript for grammatical errors, some of which are noted below.  
-2.7.1, 2.7.5 – “ensuring a good tightness” should be “ensuring good tightness”  
Corrected  
-2.7.5 – “the both surfaces”  
Corrected  
-4.4 – “within needed the X, Y, and Z movement of the stage”  
Corrected  
-5.3.1 – “not-encapsulated” – should be “unencapsulated”  
Corrected  
  
2. Additional detail is required: 3.2 – What sample is used here? Also, it seems as though placing the sample on the plunger is done in 3.4, not 3.2. Please make sure the order of actions is sequential and correct.  
The sequence has been modified and clarified  
  
3. Branding: 2.6.5 – Is “waves” a kind or the manufacturer? If the manufacturer, this should be deleted from the protocol section.  
Another term has been used   
  
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**Reviewers' comments:,**

(Note: Referee's comments are reported in *italic*, with our answers given below preceded by author reply.)

Editor’s Note:  We do not require in depth or novel results for publication in JoVE, only representative results that demonstrate the efficacy of the protocol. However, please ensure that all claims made throughout the manuscript are supported by either results or references to published works.  
  
**Reviewer #1:**  
*Manuscript Summary:  
This is a very useful detailed account of a safe, practical method of analysing highly radioactive materials by Raman spectroscopy.  
  
Major Concerns:  
No major concerns.  
  
Minor Concerns:  
Given the trouble of 17O labelling the Np how much of a shift in the Raman peak would be expected and is this sufficient to be able to detect and state whether the 441 peak is electronic in nature? e.g. what is the shift of the T2g peak for 17O labelled NpO2?  
  
Additional Comments to Authors:*  
*N/A*  
  
**Author reply**: We thank the Referee for the positive overall assessment of our manuscript and for his time and consideration in reviewing our manuscript. Concerning the mode at 441 cm-1, the Raman shift with the isotopic substitution would be expected for conventional one-phonon and partial substitution (∼30% 17O) to be around -2 % (downshift). Of course, this will be hardly observed in the Raman spectrum mainly because of the dispersive nature of this mode. However, we have to remind that our statement was based on the derivative of the Raman spectrum, into which any change in the asymmetry (down shift for instance) would result in a change of the position of the null-derivative of the spectrum (which was not the case here). The shift of the T2g peak is -1.7% with ∼30% 17O substitution was clearly observed in the Raman spectrum as the peak maximum down shift from 466 to 458 cm-1. Anyway, conclusions drawn concerning the origin of the asymmetry were mainly based on the temperature dependence and on the ability of the T2g mode to couple to the Gamma\_8 electronic state in NpO2. Please note that this asymmetry was also observed in recent IXS measurements of NpO2 (please see P. Maldonado et al. Phys Rev B. 93, 144301 (2016)).

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**Reviewer #2:**   
*Manuscript Summary:*  
This paper describes a technique that allows handling a radioactive material outside of a glove box for performing Raman experiment.  
The confinement is obtained in a especially designed capsule, with different possible configurations.  
A special procedure is used to take the capsule out of the glove box safely.  
Examples of Raman data obtained using this capsule are presented.  
  
*Major Concerns:*  
N/A  
  
*Minor Concerns:*  
The authors should explain how they cope with a possible Raman signal due to the double sided adhesive tab.  
  
*Additional Comments to Authors:*  
N/A  
**Author reply:**   
We thank the referee for his time in reviewing our manuscript and for raising an important possible issues with the double sided adhesive. We replied by adding a sentence in the protocol §5.3.1 as well as in the discussion.

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**Reviewer #3:**  
**Author reply:**

The authors do not want to comment on the reviewer three's report. Authors think that there is no plagiarism, since our self-work are cited and the presented results are in perfect agreement with JoVE editorial policy.

*Manuscript Summary:*  
The paper by J-Y. Colle et al. describes an experimental technique to shield and confine highly radioactive solid samples in a custom made capsule body. The capsule is equipped with an optical window and therefore allows the analysis of the samples using confocal Raman spectroscopy without the risk of contaminating and radiation-damaging the optical instruments. In addition to the standard capsule a modified capsule model is presented which is capable to store the sample in vacuum or in a inert atmosphere of up to 20 bar. A detailed description is given how to mount the capsule and insert the highly radioactive samples and perform the Raman measurements. Raman spectroscopic analyses of AmO2, NpO2 and Chernobyl lava samples are presented as examples to demonstrate the functioning of the capsules.

*Major Concerns:*  
A brief literature review shows that most of the content has been already published recently by the authors in the following two publications:  
Paper 1:  
An original approach for Raman spectroscopy analysis of radioactive materials and its application to americium-containing samples  
Mohamed Naji, Jean-Yves Colle, Ondrej Beneš, Mark Sierig, Jouni Rautio, Patrick Lajarge, Dario Manara  
J. Raman Spectrosc., 2015, 46, 750-756.  
DOI: 10.1002/jrs.4716  
Paper 2:  
Raman Scattering from Decoupled Phonon and Electron States in NpO2  
M. Naji\*, N. Magnani, J.-Y. Colle, O. Beneš, S. Stohr, R. Caciuffo, R. J. M. Konings, and D. Manara  
J. Phys. Chem. C, 2016, 120 (9), pp 4799-4805  
DOI: 10.1021/acs.jpcc.5b12068  
  
Also the figures 1, 3, 5, and 6 were taken directly from these publications without any changes (or only with trivial design changes) and in particular without referencing the original publication.  
  
I do not list all subjects/topics/results of the present paper that were published in the two papers listed before since this would be a very lengthy list. Instead, I list only those findings/results that I did not find easily during my brief literature search in already existing publications:  
- Technical description of the high-pressure proof sample capsule (lines 140 - 156, figure 2 and parts list.)  
- Detailed technical description of the protocol for capsule mounting, sample insertion, and Raman measurement (lines 187-395. Keep in mind that nearly every second line is blank!)  
- Raman analysis of Chernobyl lava (lines 456-474 and figure 8)  
- Some paragraphs from the section "DISCUSSION" that deal with technical details and the limitations of the sample capsule.

*Minor Concerns:*  
This review will not further discuss details of the manuscript (missing or unclear information and issues related to spelling or wording) due to the severe violations of the code of best scientific practice that were found before.   
*Additional Comments to Authors:*  
The central claim of the authors in this paper is to present a novel enclosure for radiation-safe Raman analysis of samples. This claim is incorrect as this device was already presented in detail in another publication (paper 1). Two of the three exemplary Raman analyses presented here were already published by the authors before, to some extend also using identical plots. Also the statement that the 431 cm^-1 mode of NpO2 is presented in the present paper for the first time (line 449) is incorrect as this feature is shown and discussed in one of the foregoing publications (paper 2). The remaining, not yet published, content of the paper is mostly of technical nature and does not contain significant scientific content.  
The lack of significant new scientific findings would alone raise the question whether this manuscript should be published in the current form. The violation of the code of best scientific practice by plagiarizing own existing publications is unapologetic. The reviewer therefore strongly recommends to reject the paper and refuse its publication.