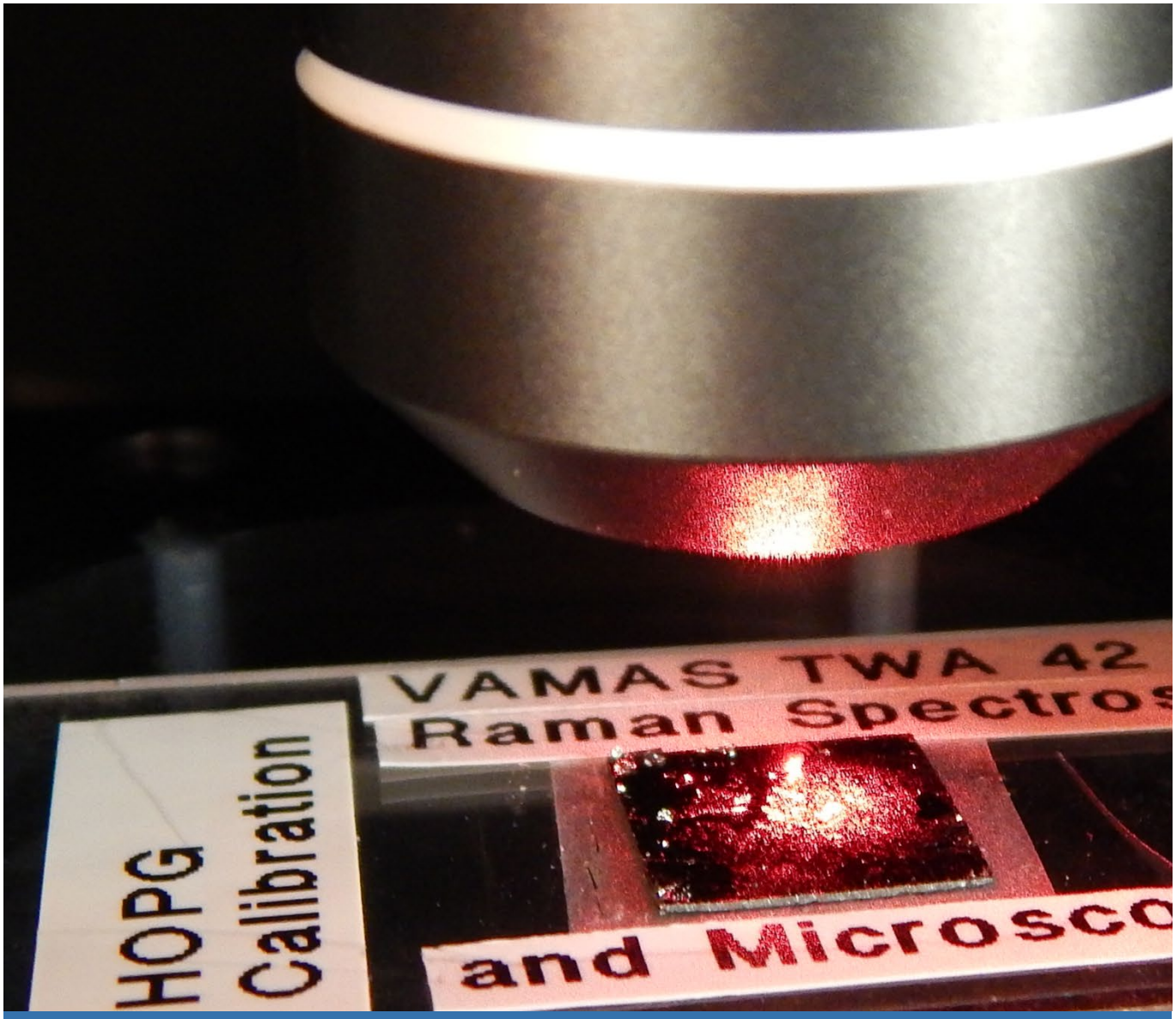
VAMAS



VAMAS TWA 42 – Project 5

Raman Spectroscopy - Consultation Survey

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The results of the consultation survey “Factors Affecting Reproducibility in Raman Spectroscopy” is summarised. This highlights the areas that the Raman spectroscopy community recognizes as weaknesses for reproducibility.

Versailles Project on Advanced Materials and Standards (VAMAS)
Technical Working Area (TWA) 42 - Raman Spectroscopy and Microscopy
Project 5 - Factors Affecting Reproducibility in Raman Spectroscopy: Consultation Survey

Project Leaders:
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Objective:
Consultation exercise for the community to assess the extent to which they view reproducibility as a challenge, the situations where it is a challenge, and the perceived importance of various possible technical issues.

Survey Title:
VAMAS Survey on Reproducibility in Raman Spectroscopy

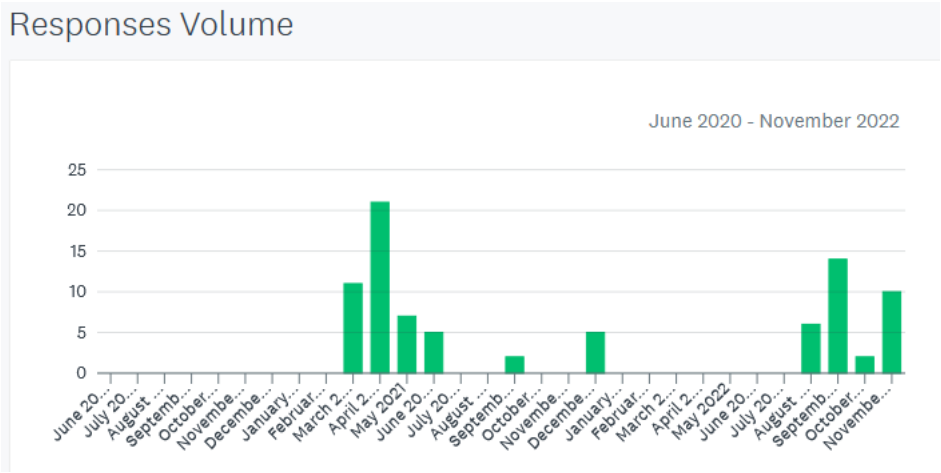
Survey Link:
https://www.surveymonkey.com/r/LQKCPGD

Dates:
Opened March 2021. Closed Dec 2022.
Note: Originally intended for Pittcon Raman Metrology Workshop (cancelled due to Covid) and ICORS Conference (postponed but eventually held Aug 2022)

Description:
17 questions. 3 demographic info. 1 email. 13 technical questions.
83 Responses were received.

Responses:
-Responses came in waves after posting link to chats at virtual conferences, posting links on websites, postering at ICORS, sending links to individuals.

Response Volume vs. Time:



Demographics of Respondents (Q1, Q2, Q17)

Academic researchers were by far the largest group of respondents (58 %, 48 responses). With the remaining responses more equally distributed between government, industrial and Raman spectroscopy components and instrumentation.
For the respondents by far the most common use was “Academic Research” (77 %, 64 respondents). Respondents reported working in many diverse fields, but the most common were advanced materials oriented:

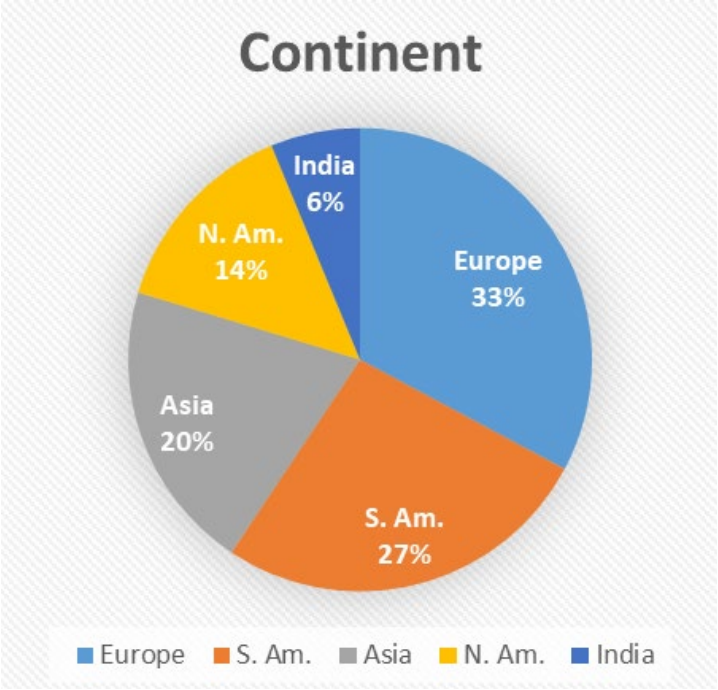
48 % carbon materials, 40 responses,
31 % other materials, 31 responses
25 % semiconductors, 25 responses

Regions:

(Only 64 all respondents provided a country name)
By continent
Responses were **diverse across the world**, except Africa. Europe had the largest number of responses.

By country

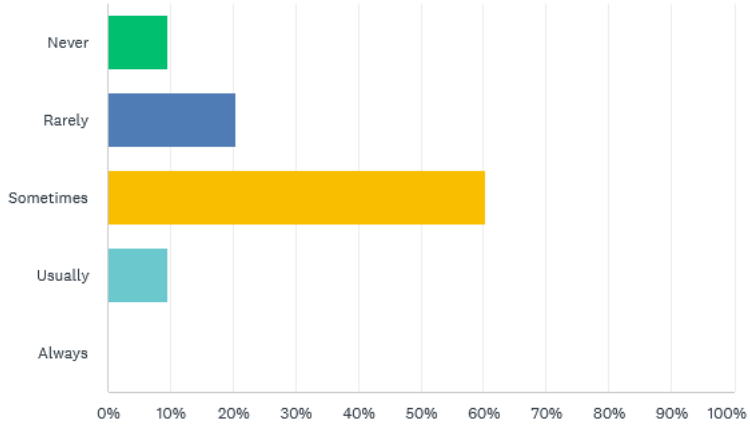
Responses came from many countries, but Brazil and the UK were very strongly represented.



Country	Responses
Brazil	13
UK	10
Japan	6
USA	5
Canada	4
Germany	4
India	4
Singapore	3
Taiwan	3
Argentina	2
France	2
Poland	2
Switzerland	2
Belgium	1
Chile	1
China	1
Colombia	1

Q3. How often do you have difficulties reproducing results?

About **2/3 report difficulties with reproducibility**. This seems large!
60 % sometimes. (71 % sometimes or usually.)
Less than 1/3 indicate that they rarely or never have difficulties.

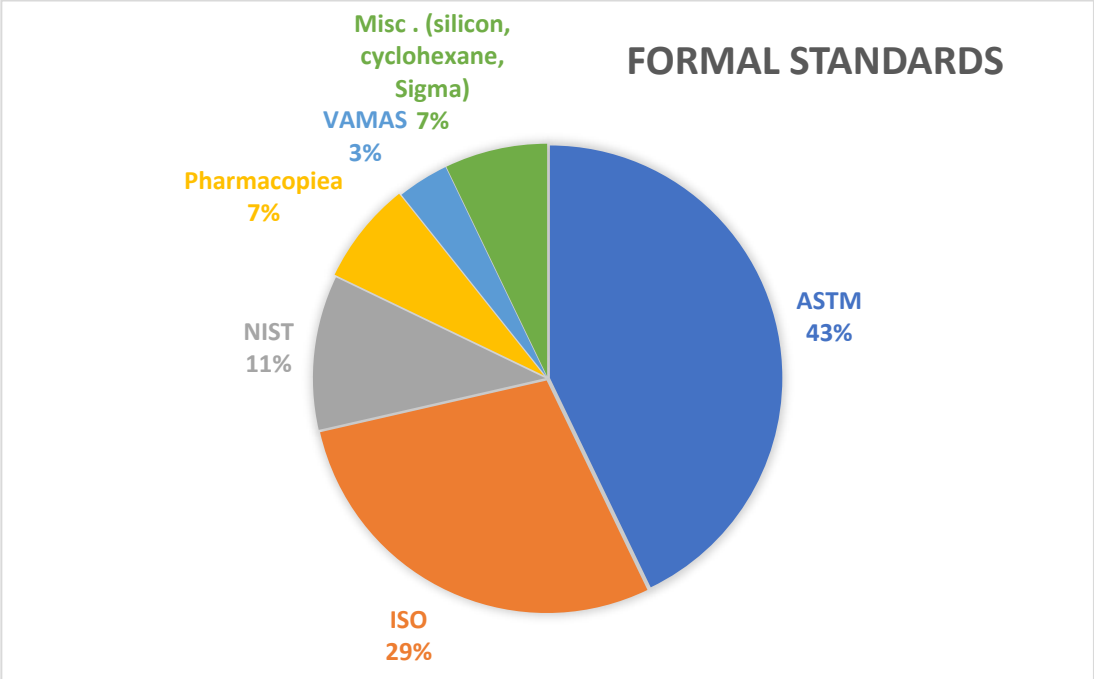


Q4. I have difficulties reproducing results from

The number of people reporting **difficulties with reproducibility from the same instrument on different days is high,** which might be surprising. The number of people with difficulties reproducing published work is also high, but maybe more understandable.
43 % externally published reports and/or scientific papers
4 1% the same instrument on different days
~30 % different instruments, or different facilities
* Many wrote in **that samples themselves were a problem for reproducibility**, either due to the instability of the sample, or variability in the material itself. (5 respondents!)
Q5. Use of procedures/standards/reference materials
*** Adoption of standards developed by a formal standards organization is low!**
(19 %, 16 respondents).
Most use standards developed in the own laboratory (65 %, 54 responses)
Many use published standards (45 %, 37 responses) standards provided by vendors (35 %, 29 responses)

For Raman spectroscopy, I use procedures/standards/reference materials (check all that apply)		
Answer Choices	Responses	
	%	#
None of the above	0	0
developed in our own laboratory	65.06	54
provided by vendors	34.94	29
developed by collaborators	18.07	15
published in scientific/technical literature	44.58	37
developed by a formal standards organization	19.28	16
I use procedures/standards/reference materials from other sources not reflected in this list (please specify):		6
	Answered	**83**

Respondents indicated they used silicon wafers (2), lamps (1), or pharmacopeia. One wrote in about the EU CHARISMA project in this area.



Q6. Indicate which standards developed by formal standards organizations that you use

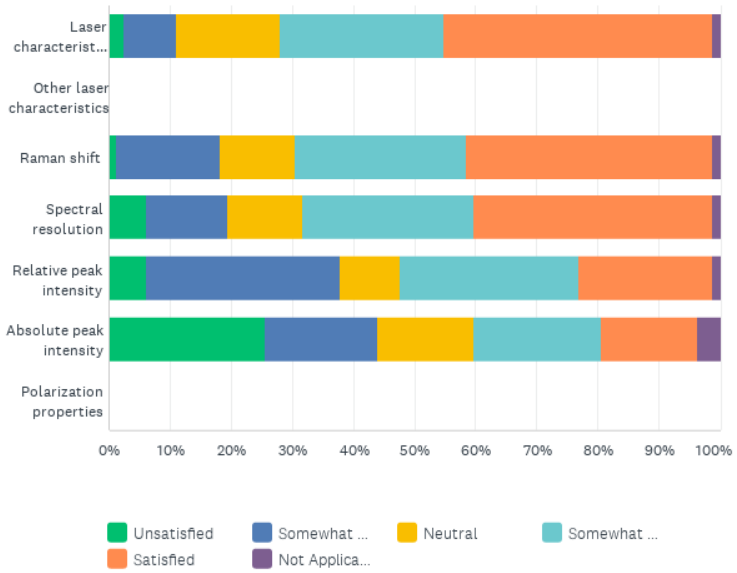
Of the only 1/5 who reported using formal standards, respondents reported **ASTM and ISO were the most used** formal standards (ASTM 4 3%, 12 counts, ISO 29 % 8 counts)

Standard	**#**
ASTM	12
ISO	8
NIST	3
Pharmacopeia	2
VAMAS	1
Misc . (Silicon, cyclohexane, Sigma)	2

Q7. Satisfaction reproducing spectroscopic parameters

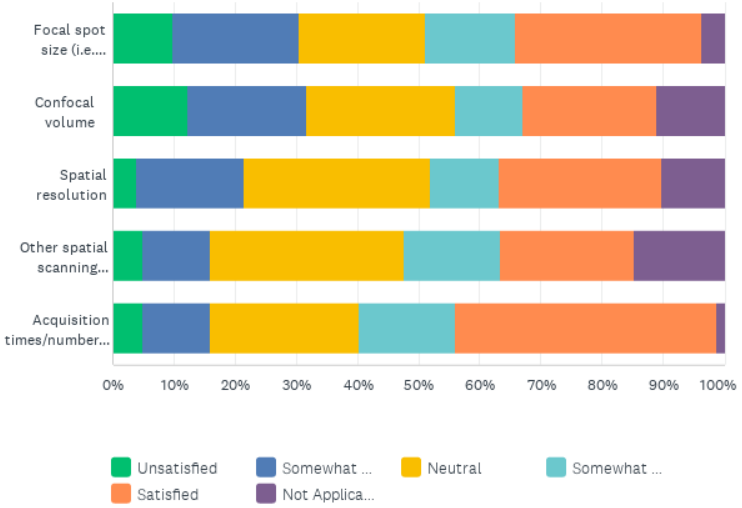
Respondents were mostly satisfied with reproducing laser characteristics, Raman shift and spectral resolution, although 18 % (15 respondents) were still unsatisfied or somewhat unsatisfied with Raman shift reproducibility.
There was **significant dissatisfaction about peak intensity reproducibility**, with 48 % (39 responses) neutral to unsatisfied about the reproducibility of relative peak intensities, and 60% (49 responses) neutral to unsatisfied about the reproducibility of absolute peak intensities. For absolute peak intensity in particular there were many responses of unsatisfied. (26 %, 21 responses)

Polarization properties may be being ignored since there were no answers for that category.



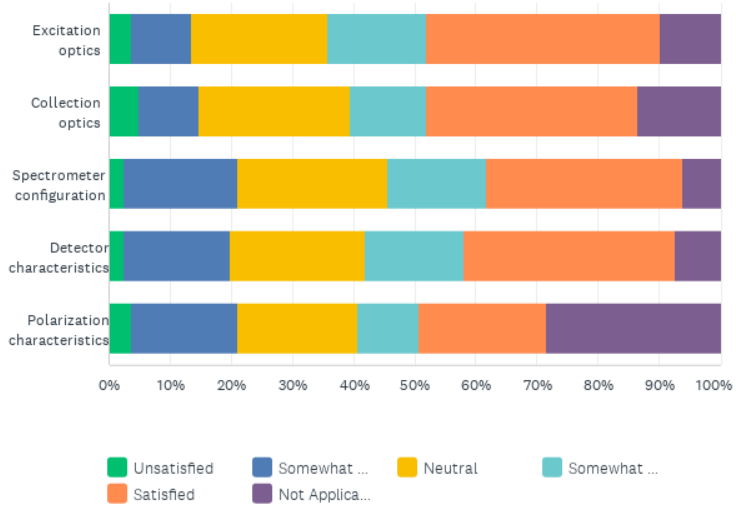
Q8. Satisfaction reproducing sampling parameters

Many respondents were neutral about sampling parameters. The **least satisfactory sampling parameters** were **confocal volume** (56 %, unsatisfied to neutral, 46 responses), and focal spot size (52 % unsatisfied to neutral, 42 responses). However, the number of unsatisfied was low.



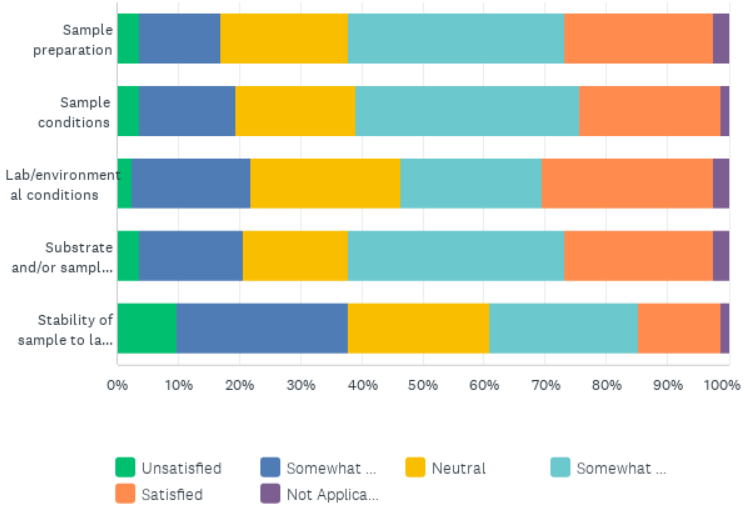
Q9. Satisfaction reproducing instrumental characteristics

Respondents seemed fairly **satisfied with reproducing instrumental characteristics**, with all categories having greater than 75 % neutral to satisfied, and less than 5 % unsatisfied.



Q10. Reproducibility of sample-related characteristics

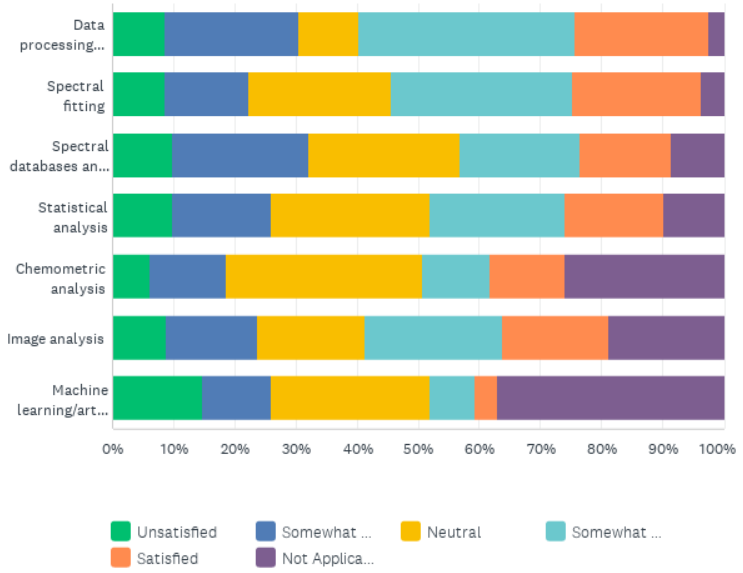
Only a small fraction of respondents (<4 %, 3 responses or less) were unsatisfied with sample conditions, with one exception. 80% were neutral to satisfied with sample preparation, conditions and sample holders, and only slightly less then that 78% were satisfied with the reproducibility of lab conditions. So overall, respondents were comfortable with reproducibility of sample related characteristics. The exception was that there was some dissatisfaction with reproducibility and stability of samples to laser exposure, with 10% unsatisfied (8 responses) and 28% somewhat unsatisfied (23 responses). So, to that extent, **stability of the sample to laser exposure is seen an issue** for reproducibility.



Q11 Reproducibility of data processing

Respondents were mostly neutral to satisfied about the reproducibility of data processing steps. No one category stands out. However, it is notable that as the analysis becomes more involved, more and more responded “not applicable/don’t know” For example 10 % (8 responses) had this response for statistical analysis, 19% had this response for image analysis (15 responses), 26 % (21 responses) had this response for chemometric analysis and 37 % (30 responses) had this response for machine learning/AI. That could mean that these techniques are not used by a significant fraction of respondents, or that they do not know how reproducible these kinds of analyses are.

If we consider only the respondents who did not chose “not applicable/don’t know”, things look much more problematic. It is evident that there is a **significant dissatisfaction with machine learning/AI reproducibility** in particular 81 % unsatisfied to neutral (52 responses), and **chemometrics** 67 % unsatisfied to neutral (41 responses). Spectral databases/database matching and statistical analysis are both more than 50 % unsatisfied to neutral. Thus, despite the large number of “n.a./don’t know” responses this is likely an area that needs work.



Q12. Presentation in papers

Respondents were overall **satisfied with the presentation of results in papers.**

Response	**%**	**#**
Unsatisfied	1	1
Somewhat unsatisfied	16	13
Neutral	2	17
Somewhat satisfied	38	31
Satisfied	23	19
Not Applicable/Don't know	1	1

Q13. Access to data

There was no strong tendency with respect to access to data, with 26 % unsatisfied, and 38 % satisfied, and many neutral.

Response	%	#
Unsatisfied	11	9
Somewhat unsatisfied	15	12
Neutral	27	22
Somewhat satisfied	9	7
Satisfied	17	14
Not Applicable/Don't know	21	17

Q14. Other reproducibility issues

-I don't know how to subtract the background in a reproducible way."
-Temperature dependent measurements.
-Users are often not aware how to use devices/corrections/standards (e.g., intensity correction) available to them."
-Reproducibility and sensitivity of SERS experiments.
-Relative Raman intensities vary significantly between instruments
-Accuracy of power meter.
-Reproducibility of laser power meters.
-Published data is heavily corrected but processing is not disclosed
-Need a good "standard surface" and "standard molecule" for SERS
-Crystalline/amorphous graphite, proteins in milk, substances in urine

Q15. Comments

"Most of my unsatisfaction [sic] answered above is due to lack of information on most papers and articles that use Raman spectroscopy as a characterization method. Commonly, when doing research on my material of interest, the majority of papers **only provide information** of laser wavelength, sometimes the equipment specification and the lens used. It is also common to find **figures with low quality** and/or with peaks with low intensity that are hardly distinguished."
"The conference should have also included the **experimental basics of data acquisition and analysis** for standard publication with simple steps."
"An **open-source** Raman library will be useful."
"What is missing from my point of view is a **sample for intensity calibration**. A luminescent sample would be good here, but it would have to be a volume sample (*i.e.,* a liquid), where chromatic errors as a function of focus can be excluded.
"We perceive a problem in the recent years, where customers present us information from marketing as real features of devices, e.g., some American **companies presenting their units as calibration free**, or customer **using materials that are not adequate for the expected correction,**

e.g., NIST 2241 or 2241 for calibrating intensity in areas not covered by the standard (50-200cm^{-1} or 3000-4000cm^{-1})"

"We are working to introduce some basic normalisation protocols at **CHARISMA,** and we target few basic things, first, if data is corrected for **y-axis**, we should now by using arbitrary units corrected (a.u.c.) instead that A.U.; we are working to create an outliner that correct dispersive systems, very often cause of error, we are working to **normalise** signal from confocal and fibre based system, etc."

"We are actually working with VAMAS in TiO_2 samples, via our colleague from ICV-CSIC-Spain"

"Most of the Raman systems we have developed in my laboratory that include micro-Raman, standoff time-resolved Raman, and combined Raman-LIBS system, and more recently monolith spatial Heterodyne Spectrometer. We do have Renishaw and Kaiser Micro-Raman system for mapping and analyzing biological and minerals in meteorites."

"Is a work about **database** for gold, silver, copper nanomaterials?"