Jain and Yadav *Egyptian Journal of Forensic Sciences* (2021) 11:15
https://doi.org/10.1186/s41935-021-00229-3

Egyptian Journal of
Forensic Sciences

REVIEW

Open Access

Vibrational spectroscopy and chemometrics in GSR: review and current trend

Bharti Jain[1*] and Poonam Yadav[2]

Abstract

Background: This review represents many significant methods of chemometrics applied as data assessment methods originated by many hyphenated analytical techniques containing their application since its origin to today.

Main body of the abstract: The study has been divided into many parts, which contain many multivariate regression methods. The main aim of this study is to investigate the chemometrics tools used in GSR (gunshot residue) or forensic ballistics.

Short conclusion: As a final point, the end of part of this review deals with the applicability of chemometric methods in forensic ballistics. We select to give an elaborate description of many significant tools established with their algorithm in admire of utilizing and accepting them by researchers not very aware with chemometrics.

Keywords: GSR, Multivariate analysis, Hyphenated analytical techniques, Chemometrics, Forensic ballistics

Background

The increase in reported gun violence is a huge problem these days, specifically given the increased proliferation of weapons and the ease at which they can be obtained (GVA 2017). GSR is an incredibly valuable form of proof for crimes related to weapons (Brozek-Mucha 2009). It is being used to identify when a suspect has fired a single shot, to connect suspects and victims to a scene of the crime, to assist discern suicide from murder, to measure the distance of the gunshot, and to identify gunshot injuries from firearm injuries, and many more. The reciprocal existence of antimony (Sb), lead (Pb), and barium (Ba) in orbicular formed particles is previously defined by GSR (Maitre et al. 2018). It consists of a mixture of by-products formed in the period of firearm release process that are charred, slightly charred, and incomplete combustion. Such elements contain ammunition, propellant, organic gunshot residue (OGSR) particles, and even some bullet, cartridge case, and inorganic GSR (Dalby et al. 2010). Nowadays, studies have shown that the extreme accumulation of heavy metals found in routine ammunition poses a danger to frequent gunmen. It culminated in the production of non-toxic ammunition, also known as lead-free ammunition (Carneiro et al. 2019). In view of this, attempts have been made by the research community to examine organic gunshot residues (OGSR) in order to evaluate GSR from non-toxic ammunition traces (Khandasammy et al. 2019). Few researches have indicated the chances of having GSR-like objects, in cases which are not linked to criminal offenses, this leads to a number of false positives. Instances of which include car brake pad particles, vehicle hybrid airbags, fireworks, and particles from the welding process (Bueno and Lednev 2014; Abrego et al. 2012; Taudte et al. 2014; Brozek-Mucha 2015).

As advances continue on the ammunition market globally, it is becoming increasingly important to estimate a discovered object to a specific ammunition company. A wide range of methods are already used throughout the period to analyze GSRs.

In forensic applications, the detection of gunshot residue (GSR) has traditionally been done using scanning electron microscopy-energy dispersive X-ray spectroscopy

---

* Correspondence: bhartijain871@gmail.com
[1]Panjab University, Chandigarh, India
Full list of author information is available at the end of the article

(SEM-EDX) but this method has certain limitations. SEM-EDX cannot be used to distinguish “green” (lead-free) ammunition due to the lack of lead which is needed for GSR identification by this technique (Brożek-Mucha 2017; Muro et al. 2015).

On the other hand, vibrational spectroscopic techniques like infrared and Raman have acquired special significance whereas they merge a variety of features (Doty et al. 2016; Mou et al. 2008). Recently, Fourier transform infrared (FTIR) spectroscopy is now being incorporated as a genuinely valuable GSR evaluation method with sufficient precision and flexibility for the detection of organic compounds in GSRs (Bueno et al. 2012; López-López et al. 2012). Raman spectroscopy is also being implemented as a viable approach for the study of gunfire traces, with an emphasis on segregation in the formation of sourcing ammunition and the caliber of ammunition (Latzel et al. 2012). It must explain the composition of a vast number of organic and inorganic components detected at the crime scene while also attempting to reconstruct its source, which must be non-destructive and very simple to utilise. In addition, the instrumental flexibility of handheld, durable, mapping and detecting methods allows for a range of valuable analytical choices (Sharma and Lahiri 2009; Zeichner 2003).

This review offers a valuable overview of present scientific studies which used vibrational spectroscopy techniques combined with chemometrics in forensic ballistics scenarios; in fact, an evaluation one of most major aspects of forensic evidence like explosive traces, body fluids, and gunshot residue (Fig. 1).

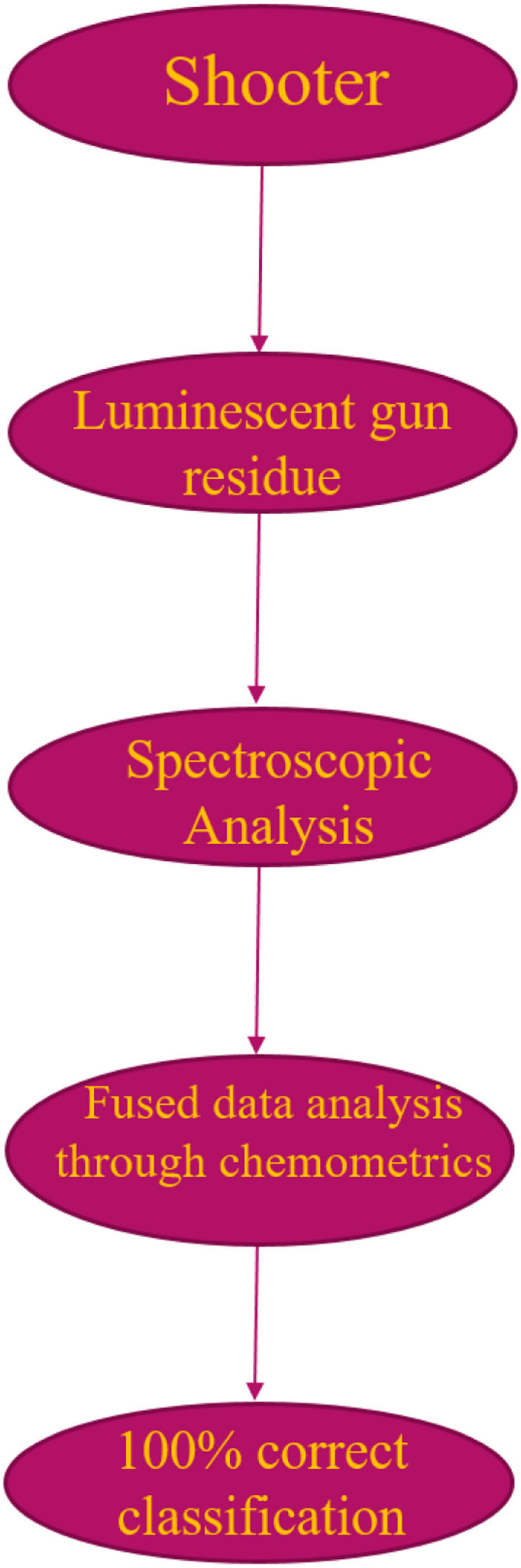

Fig. 1 Graphical representation of identification of GSR

Chemometrics

Chemometrics tends to be the inevitable outcome of the qualitative and quantitative separation of the useful details from spectroscopic data. In certain cases, chemometrics offers a statistical context and a degree of trust for the accurate detection of substances of interest, thus assisting researchers in the decision-making process and in collecting appropriate proof for additional study. Based on the situation at hand or even what data is required, a variety of chemometric methods may be used in forensic testing.

In forensic investigations, pattern recognition is especially impressive because it detects reliability in the set of data and that can distinguish unknown samples into various groups (Bishop 2006).

There have been various pattern recognition methods that can only be loosely categorized into methods of the following:

- Supervised
- Unsupervised
- Classification
- Regression

In order to eliminate unnecessary data which can be produced by instrumental variance, scattering, false interference, and sometimes unnecessary irregularities in the specimens, this becomes highly essential to formulate pre-processing steps before any statistical analysis. A few revision is typically needed for data from spectroscopic methods like FTIR and Raman.

The unsupervised method which does not have user-defined tags because the information gathered has been used to create the frameworks. There are two types of unsupervised method:

- PCA (principle component analysis)
- HCA (hierarchical cluster analysis)

In order to process the data gathered to provide effective segregation and identification abilities, supervised method contains the procedure of user-defined data tag (Tuncer et al. 2008). There are few types of these methods:

- Linear discriminant analysis (LDA)
- Partial least squares discriminant analysis (PLSDA)
- Support vector machines discriminant analysis (SVMDA)
- Artificial neural networks (ANN)

The introduction of the methodology of variable selection, like the genetic algorithm (GA), will indeed help with the skills of categorization (Varmuza and Filzmoser 2016; Fikiet et al. 2018).

Raman spectroscopy

Since becoming found nearly 90 years previously, it clearly shows widespread fame as a valuable analytical method for several various purposes. Forensic science, and especially for safety reasons, is among the most popular field of expertise in the use of Raman spectroscopy.

If a monochromatic laser light hits material, it is dependent on the inelastic light scattering. The dispersed beam seems to have a distinct intensity from the laser frequency and is induced by vibrations which have altered the polarization of the particle's electronic configuration. Therefore, molecular vibrations and the chemical composition describe the relative intensity (Eliasson et al. 2007).

Free from its chemical status and no need for specimen preparation, this can analyze a broad variety of materials. Because of the low-intensity laser properties applied, this technique is non-destructive and sufficient to preserve residue credibility. Especially in comparison to other analytical tools, the performance variables are few and the method needs just a few seconds to acquire spectral information with an adequate signal-to-noise ratio, making this one a quite easy and fast method. The spectra are extremely informative, spanning the area from 4000 to 50 cm^{-1} in a single analysis, which may have several intense peaks (Olds et al. 2012).

As far as instrumentation is concerned, it is really robust. The precisely oriented laser light enables examination of tiny places. When the device is connected with a solid microscope, dimensional ranges of 1 μm or less are feasible. Numerous advanced technologies include automated sampling levels for two or three-dimensional spectroscopic modeling and imaging purposes. It is especially valuable when retrieving quantitative data from heterogeneous specimens. There have been a number of lasers present that are beneficial for compatible blend evaluation and even for greater classification accuracy. Fluorescence, from contaminants or the specimen as a whole, that further occur as long, curved, and extreme signals which cover the usually lower Raman peaks, are a few drawbacks for such process. In addition, including a narrow area of interest, the laser light may be too strong and induce specimen burning and heating.

Nevertheless, surface-enhanced Raman spectroscopy (SERS) involving near interaction of the specimen with metallic nanosubstrates has to be the most successful technique. The nanosubstrate analyte's surface plasmon is reported to amplify the strength of the Raman signal up to 10^3 to 10^6 levels of amplitude and extinguish fluorescence at the same time (Qiu et al. 2015).

Upcoming SERS implementations in forensics were already studied; furthermore, the use of chemometrics in conjunction with SERS implementation still seems to be uncommon.

This technique has benefits and disadvantages as compared to infrared spectroscopy. The key benefits included that water has quite a minimal to no spectral signal, allowing the study, without significant intervention of aqueous medium and specimens with a higher moisture content. However, IR is well-known technique in forensic laboratory as compared to Raman spectroscopy, based on the fact that this technique is not widely known to forensic scientists because it is very expensive technique and not reachable like IR (Chew and Sharratt 2010).

Infrared spectroscopy

The molecular absorption of energy induces vibrational and rotational motions in IR spectroscopy. The spectrum zones between 12,800 and 10 cm^{-1} are characterized of IR, whereas three distinct areas has been described:

- Near infrared from 12800 to 4000 cm^{-1}
- Middle infrared from 4000 to 200 cm^{-1}
- Far infrared from 200 to 10 cm^{-1}

Near infrared and middle infrared produce facts about overtones and combination bands, due to this technique have been extensively used in forensic approach. This technique is used in forensic field because of extraordinary adaptability and analyze the sample in form of liquid, gaseous, or solid with least or no sample preparation in a non-invasive mode. In this technique, NIR area gives the information about chemical data with the use of statistical technique whereas MIR area gives the data related to functional groups. Infrared is inexpensive, robust, and easy to access technique. This is also well-known as hyperspectral images (HSI) because it allows image acquisitions very fast.

There is unlimited benefit of this technique over Raman due to the uncomplicatedness and quickness of spectral acquisition of IR (Chew and Sharratt 2010; Pasquini 2018; Pasquini 2003; Salzer and Siesler 2009).

Advantages

Despite the fact that Raman and IR spectroscopy have been used to analyze a wide range of samples for nearly a century, it has only recently been recognized as a valuable method in forensic science. The invention of portable and hand-held spectrometers that enable for data collection and material detection immediately in the field like at a crime scene or at points of entry/exit of an airport or a country's border is becoming one of the big trends that have emerged. One concern is that portable or hand held instruments have poorer sensitivity that benchtop instruments. Often, in the case of forensics, the established technique must be critically checked which takes a long time and follows very strict guidelines, particularly if a forensic lab is certified (Smith et al. 2017).

Raman spectroscopy in gunshot residue analysis

This is a valuable technique for illustrating the organic component in lead-free ammunition and identifying various metal anions in GSR like lead, blend of carbonates, and barium. Though, some researches have published the use of Raman spectroscopy combined with chemometrics for GSR analysis.

Lednev et al. worked on three studies of GSR for discrimination of firearm caliber with the help of confocal Raman technique (laser excitation 785 nm).

In his first study, he examined close range firing (30 cm) by a 0.38 mm revolver and a 9 mm firearm and its GSR particle extracted from a cloth. These particles revealed great fluorescence and were rejected; the rest of residue divided into two categories based on their color. When band procedure was done of organic and inorganic of GSR then GSLW, pre-processing was used for reducing the disperse features of every caliber and separating of residues based on caliber by PCA tool. He also used PLS-DA, SVM-DA, and k-NN tools for classification (Lednev and I. K. 2015). In this, k-NN and SVM-DA had been given inaccurate classification of one spectrum but PLS-DA provided accurate classification. In second study, there were used Raman and ATR-FTIR both for distinction of caliber. When Raman coupled with PLS-DA method, so it revealed Sn and Sp equal to 98% and in ATR-FTIR, 94 and 97% respectively. This combination gave accurate classification.

In his third study, he used double-sided adhesive tape for collection of GSR from cotton cloth. This instrument covered 2 mm^2 area of the sample for analysis. The GSR specimens were categorized into four parts by using PLS-DA:

- Organic gunshot residue
- Inorganic gunshot residue
- Tape
- Unassigned category

At the time of experimental problems, he stated that particles should need to be larger than 3.4 μm for accurate determination.

Lopez-Lopez et al. evaluated four types of ammunition from GSR particles (one non-toxic and three conventional of different caliber) by using Raman imaging (laser excitation 455 nm). Specimens collected with an adhesive tape from cloth. He used MCR-ALS to distinguish between substrate and GSR in the place of classification. He also used blood in few samples to identify the potential of this method (López-López et al. 2013).

Infrared spectroscopy in gunshot residue analysis

This instrument is valuable for identification of organic gunshot residue like Raman. The spectra of this instrument are extremely discriminating and evaluation is non-destructive. There have been published some researches on IR for GSR analysis by using chemometrics.

Weber and his co-workers researched on metal organic frameworks (MOFs) and based on this they differentiate luminescent markers in ammunition for identification of GSR from non-toxic ammunition. Moreover, they stated that new outlooks for ammunition encoding are possible due to chemical composition of luminescent markers (Weber et al. 2011; Lucena et al. 2013).

Bueno et al. used ATR-FTIR for analysis of GSR from three different ammunitions (0.38, 0.40, and 9 mm calibers) which was collected from cloth at close distance (30 cm). There were GSRs divided into two categories for PLS-DA which was collected from additional discharge: first set contained 160 GSR spectra and second set contained 30 GSR spectra. Unidentified samples were allocated accurate group of caliber in the validation and 93.3% samples were accurately categorized in the prediction (Bueno et al. 2013).

Ortega-Ojeda et al. used GSR samples from traditional and non-toxic ammunition (9 mm caliber) which was collected from white, white stamped, and black cotton fabrics and also used CLS for samples analysis. They analyzed two calibration data sets: first contained uncontaminated standard of compound which was presented in ammunition and second contained both types of ammunition which spectra related to isolated propellants. In second, data set GSR arrangements showed larger as compared to target shots with non-toxic ammunition by using CLS maps. However, the analysts indicated apprehension with the use of this approach, as not all forensic laboratories have appropriate portion of sample libraries with suitable varieties of ammunition propellants that were used as criteria. The strongest indications contained across many parameters were nitrocellulose using the second calibration set; numerous different elements were identified as well like DNT, nitro guanidine, and 4-nitro-ethyl-centralite. The analysts stated that because the specifications for various ammunition elements become available on the market, this calibration collection is somewhat more flexible. They suggested that nitrocellulose should be used as usual. As a result, using the prescribed calibration range for black and white cotton, the lack of fit responses for traditional and non-toxic ammunition was 31.3% (conventional on black cotton), 21.3% (non-toxic on black cotton), 39.3% (non-toxic on white cotton), and 39.8% (conventional on white cotton). For both forms of ammunition, the R2 values were nearly 0.84 for white-cotton cloth and more than 0.90 for black cotton; however, the correlation coefficients showed values about 0.94 (Ortega-Ojeda et al. 2017).

In order to promote the identification and quantification of GSR from non-toxic ammunition, Weber et al. suggested integrating luminescent indicators in ammunition focused on metal organic frameworks (MOFs). In addition, he concluded that changing the chemical structure of luminescent indicators created some great possibilities for interpreting ammunition. MCR-ALS and NIR imaging used for identification between GSR particles possessing three separate indicators focused on MOFs ([Eu] (DPA)) functionalities were demonstrated by Carvalho et al. They analyzed GSR particles precisely on adhesive medium or clothing by using HIS-NIR and ATR-FTIR. Instead of this, different chemometric methods were used such as CLS, PLS-DA, and MCR-ALS for calibration, classification, and resolution respectively (Albino de Carvalho et al. 2018).

Conclusion

The ability and developments produced after integrating the methods of vibrational spectroscopy with chemometric methods are inevitable during comprehensive literature studies. The approaches mentioned herein must be considered to provide a significant effect on forensic practices when explaining their potential because most forensic laboratories become connected with either a Raman, an infrared, or spectrometer and both in certain ways.

Depending on the gunpowder residue and even the methodology that utilized to tackle the issue, the chemometric methods employed can often differ.

As regards unsupervised methods, PCA is prevalent in the entirety of forensic analysis that included chemometrics. In addition to monitoring examination, its potential to emphasize discrepancies and resemblances is quite known and discussed for prediction.

As regards classification tools, currently the most popular techniques that are used in supervised manner are PLS-DA, LDA, and SVM-DA. This becomes particularly essential to understand its need for scientific work which could incorporate forensic concerns including various methods of class modeling.

The substrate effect is a big concern found particularly in GSR recognition and so many other applications. This approach to minimize these issue relies on the analytical methodology used. Some chemometric strategies have shown fascinating in MCR-ALS, pre-processing technique, and weighted least square. It seems to have a privilege because of its versatility throughout model development and if not all sections introduce seem to be well, this can be extended to a number of forensic challenges.

The future scenario for forensic examination is indeed developing attention and enhancing when vibrational spectroscopy combined with chemometric tools. It is even now troublesome to require durable, efficient, and reliable models.

Abbreviations

GSR: Gunshot residue; OGSR: Organic gunshot residue; FTIR: Fourier transform infrared spectroscopy; PCA: Principle component analysis; HCA: Hierarchical cluster analysis; LDA: Linear discriminant analysis; PLS-DA: Partial least squares discriminant analysis; SVM-DA: Support vector machines discriminant analysis; ANN: Artificial neural networks; SERS: Surface-enhanced Raman spectroscopy; HSI: Hyper spectral images; GLSW: Generalized least squares weighting; k-NN: k-Nearest neighbor; ATR-FTIR: Attenuated total reflectance-Fourier transform infrared spectroscopy; MCR-ALS: Multivariate curve resolution alternating least square; MOFs: Metal-organic frameworks; CLS: Classical least squares; DNT: 2,4-Dinitrotoluene; NIR: Near-infrared spectroscopy; HSI-NIR: Hyper spectral images near-infrared spectroscopy

Acknowledgements

Not applicable

Authors' contributions

BJ wrote the article and PY gave the structure of the article. The authors read and approved the final manuscript.

Funding

Not applicable

Availability of data and materials

Not applicable

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Competing interests

The authors declare that they have no competing interests.

Author details

[1]Panjab University, Chandigarh, India. [2]Shri Vaishnav Institute of Forensic Science, Indore, Madhya Pradesh, India.

Received: 13 January 2021 Accepted: 28 June 2021

References

Abrego Z, Ugarte A, Unceta N, Fernández-Isla A, Goicolea MA, Barrio RJ (2012) Unambiguous characterization of gunshot residue particles using scanning laser ablation and inductively coupled plasma-mass spectrometry. Anal Chem 84(5):2402–2409. https://doi.org/10.1021/ac203155r

Albino de Carvalho M, Talhavini M, Pimentel MF, Amigo JM, Pasquini C, Junior SA, Weber IT (2018) NIR hyperspectral images for identification of gunshot residue from tagged ammunition. Anal Methods 10(38):4711–4717. https://doi.org/10.1039/c8ay01341a

Bishop CM (2006) Pattern recognition and machine learning. Springer, New York, USA

Brozek-Mucha Z (2009) Forensic Sci Int 183(1−3):33–44

Brozek-Mucha Z (2015) Chemical and physical characterisation of welding fume particles for distinguishing from gunshot residue. Forensic Sci Int 254:51–58. https://doi.org/10.1016/j.forsciint.2015.06.033

Brożek-Mucha Z (2017) Trends in analysis of gunshot residue for forensic purposes. Anal Bioanal Chem 409(25):5803–5811. https://doi.org/10.1007/s00216-017-0460-1

Bueno J, Lednev IK (2014) Raman microspectroscopic chemical mapping and chemometric classification for the identification of gunshot residue on adhesive tape. Anal Bioanal Chem 406(19):4595–4599. https://doi.org/10.1007/s00216-014-7874-9

Bueno J, Sikirzhytski V, Lednev IK (2012) Raman spectroscopic analysis of gunshot residue offering great potential for caliber differentiation. Anal Chem 84(10):4334–4339. https://doi.org/10.1021/ac203429x

Bueno J, Sikirzhytski V, Lednev IK (2013) Attenuated total reflectance-FT-IR spectroscopy for gunshot residue analysis: potential for ammunition determination. Anal Chem 85(15):7287–7294. https://doi.org/10.1021/ac4011843

Carneiro CR, Silva CS, De Carvalho MA, Pimentel MF, Talhavini M, Weber IT (2019) Identification of luminescent markers for gunshot residues: fluorescence, Raman spectroscopy, and chemometrics. Anal Chem 91(19):12444–12452. https://doi.org/10.1021/acs.analchem.9b03079

Chew W, Sharratt P (2010) Trends in process analytical technology. Anal Methods 2(10):1412–1438. https://doi.org/10.1039/c0ay00257g

Dalby O, Butler D, Birkett JW (2010) Analysis of gunshot residue and associated materials - a review. J Forensic Sci 55(4):924–943. https://doi.org/10.1111/j.1556-4029.2010.01370.x

Doty KC, Muro CK, Bueno J, Halámková L, Lednev IK (2016) What can Raman spectroscopy do for criminalistics? J Raman Spectrosc 47:39–50

Eliasson C, Macleod NA, Matousek P (2007) Noninvasive detection of concealed liquid explosives using Raman spectroscopy. Anal Chem 79(21):8185–8189. https://doi.org/10.1021/ac071383n

Fikiet MA, Khandasammy SR, Mistek E, Ahmed Y, Halámková L, Bueno J, Lednev IK (2018) Surface enhanced Raman spectroscopy: a review of recent applications in forensic science. Spectrochim Acta A Mol Biomol Spectrosc 197(2017):255–260. https://doi.org/10.1016/j.saa.2018.02.046

GVA (2017) Gun violence archive. Gun Violence Archive (GVA), Washington, DC

Khandasammy SR, Rzhevskii A, Lednev IK (2019) A novel two-step method for the detection of organic gunshot residue for forensic purposes: fast fluorescence imaging followed by Raman microspectroscopic identification. Anal Chem 91(18):11731–11737. https://doi.org/10.1021/acs.analchem.9b02306

Latzel S, Neimke D, Schumacher R, Barth M, Niewöhner L (2012) Shooting distance determination by m-XRF-Examples on spectra interpretation and range estimation. Forensic Sci Int 223(1–3):273–278. https://doi.org/10.1016/j.forsciint.2012.10.001

Lednev JB, I. K. (2015) Multi-phase semicrystalline microstructures drive exciton dissociation in neat plastic semiconductors. J Mater Chem C 3(207890): 10715–10722. https://doi.org/10.1039/b000000x

López-López M, Delgado JJ, García-Ruiz C (2012) Ammunition identification by means of the organic analysis of gunshot residues using Raman spectroscopy. Anal Chem 84(8):3581–3585. https://doi.org/10.1021/ac203237w

López-López M, Ferrando JL, García-Ruiz C (2013) Dynamite analysis by Raman spectroscopy as a unique analytical tool. Anal Chem 85(5):2595–2600. https://doi.org/10.1021/ac302774w

Lucena MAM, De Sá GF, Rodrigues MO, Alves S, Talhavini M, Weber IT (2013) ZnAl2O4-based luminescent marker for gunshot residue identification and ammunition traceability. Anal Methods 5(3):705–709. https://doi.org/10.1039/c2ay25535a

Maitre M, Kirkbride KP, Horder M, Roux C, Beavis A (2018) Thinking beyond the lab: organic gunshot residues in an investigative perspective. Aust J Forensic Sci 50(6):659–665. https://doi.org/10.1080/00450618.2018.1457718

Mou Y, Lakadwar J, Rabalais JW (2008) Evaluation of shooting distance by AFM and FTIR/ATR analysis of GSR. J Forensic Sci 53(6):1381–1386. https://doi.org/10.1111/j.1556-4029.2008.00854.x

Muro CK, Doty KC, Bueno J, Halámková L, Lednev IK (2015) Vibrational spectroscopy: recent developments to revolutionize forensic science. Anal Chem 87(1):306–327. https://doi.org/10.1021/ac504068a

Olds WJ, Sundarajoo S, Selby M, Cletus B, Fredericks PM, Izake EL (2012) Noninvasive, quantitative analysis of drug mixtures in containers using spatially offset raman spectroscopy (SORS) and multivariate statistical analysis. Appl Spectrosc 66(5):530–537. https://doi.org/10.1366/11-06554

Ortega-Ojeda FE, Torre-Roldán M, García-Ruiz C (2017) Short wave infrared chemical imaging as future tool for analysing gunshot residues patterns in targets. Talanta 167:227–235. https://doi.org/10.1016/j.talanta.2017.02.020

Pasquini C (2003) Near infrared spectroscopy: fundamentals, practical aspects and analytical applications. J Braz Chem Soc 14(2):198–219. https://doi.org/10.1590/S0103-50532003000200006

Pasquini C (2018) Near infrared spectroscopy: a mature analytical technique with new perspectives – a review. Anal Chim Acta 1026:8–36. https://doi.org/10.1016/j.aca.2018.04.004

Qiu Y, Yang C, Hinkle P, Vlassiouk IV, Siwy ZS (2015) Anomalous mobility of highly charged particles in pores. Anal Chem 87(16):8517–8523. https://doi.org/10.1021/acs.analchem.5b02060

R. Salzer and H. Siesler eds (2009) Mid-infrared, near-infrared and Raman instrumentation for mapping and imaging. P.R. Griffiths in Infrared and Raman Spectroscopic Imaging Wiley-VCH, Weinheim, Germany ISBN: 978-3-527-31993-0

Sharma SP, Lahiri SC (2009) A preliminary investigation into the use of FTIR microscopy as a probe for the identification of bullet entrance holes and the distance of firing. Sci Justice 49(3):197–204. https://doi.org/10.1016/j.scijus.2008.07.002

Smith JP, Smith FC, Ottaway J, Krull-Davatzes AE, Simonson BM, Glass BP, Booksh KS (2017) Raman microspectroscopic mapping with multivariate curve resolution–alternating least squares (MCR-ALS) applied to the high-pressure polymorph of titanium dioxide, TiO2-II. Appl Spectrosc 71(8):1816–1833. https://doi.org/10.1177/0003702816687573

Taudte RV, Beavis A, Blanes L, Cole N, Doble P, Roux C (2014) Detection of gunshot residues using mass spectrometry. Biomed Res Int 2014:1–16. https://doi.org/10.1155/2014/965403

Tuncer Y, Tanik MM, Allison DB (2008) An overview of statistical decomposition techniques applied to complex systems. Comput Stat Data Anal 52(5):2292–2310. https://doi.org/10.1016/j.csda.2007.09.012

Varmuza K, Filzmoser P (2016) Introduction to multivariate statistical analysis in chemometrics. CRC Press. https://doi.org/10.1201/9781420059496

Weber IT, De Melo AJG, Lucena MADM, Rodrigues MO, Alves Junior S (2011) High photoluminescent metal - organic frameworks as optical markers for the identification of gunshot residues. Anal Chem 83(12):4720–4723. https://doi.org/10.1021/ac200680a

Zeichner A (2003) Recent developments in methods of chemical analysis in investigations of firearm-related events. Anal Bioanal Chem 376(8):1178–1191. https://doi.org/10.1007/s00216-003-1994-y

Publisher's Note