PERFORMANCE EVALUATION OF TWO RAMAN INSTRUMENTS FOR UNKNOWN FORENSIC SAMPLES

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ABSTRACT

The Misuse of Drugs Act 1971 classifies Class A, B and C drugs as illegal and over 30000 Class A seizures were reported in England and Wales in 2013/14.[1] The drug substance is typically formulated with an array of cutting agents, e.g. Benzocaine, Lidocaine and Phenacetin, leading to a complex mixture of organic species. Early attempts to automate identification of such materials were hampered by spectral overlap and interference. However, developments in computational deconvolution of a spectral data has led to the development of systems that potentially identify targeted components in complex mixtures.[2] In this work, a Handheld Raman instrument (Thermo-TruNarc), incorporating an implementation of such an algorithms, was tested with an array of seized samples from UK forensic investigation. These 'street' samples were unmodified from seizure and presented as powders (43 samples) and oil (1 sample). The spectral output of the Handheld system was compared with spectra from a laboratory micro-Raman instrument obtained from at least three sites in each sample. Spectra from the laboratory system were assigned and the results compared to the identification reported from the portable system. In 39/44 of cases a valid identification was obtained although, of these, 12 required a sample treatment with an ethanol extraction followed by evaporation onto a proprietary SERS substrate ('Test Stick' analysis). A detailed evaluation of spectral features was undertaken for all cases and where assignments were inconclusive after direct sampling these were mainly attributed to sample fluorescence. Hence, the TruNarc system was shown to be reliable and capable of identifying complex street sample and such identification are available to users with the minimum of spectroscopic expertise.

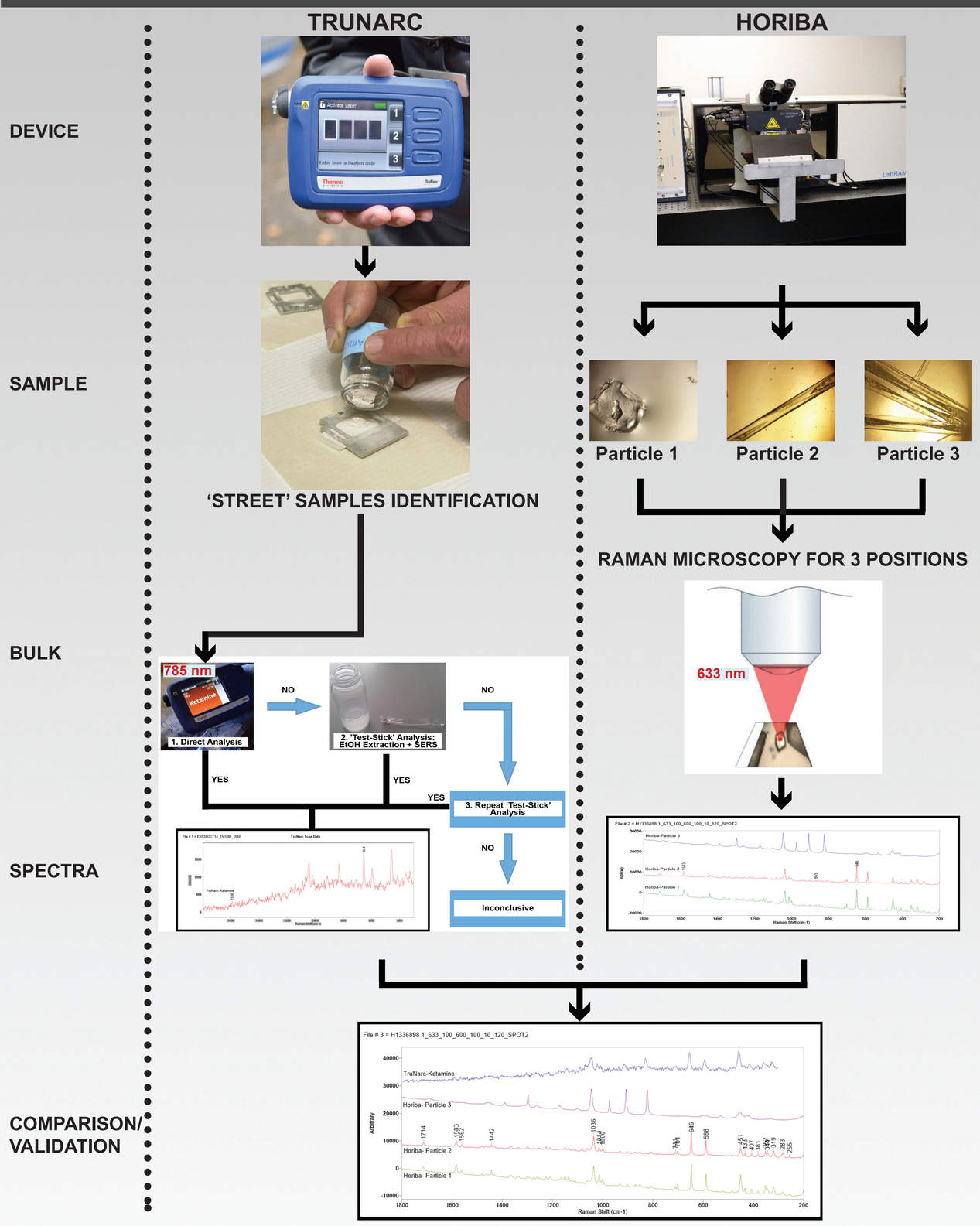
INTRODUCTION

There a lot of Raman scattering technique has been produced including Raman microscopy, surface-enhanced Raman scattering (SERS) and a compact Raman instrument after 87 years.[3] A compact Raman is a user friendly and green vibrational analytical method for the detection of the substance. It has used been used in geology [4], archeology [5], meat industry [6], food [7], pharmacy [8] and forensic [9] to suit its purpose.

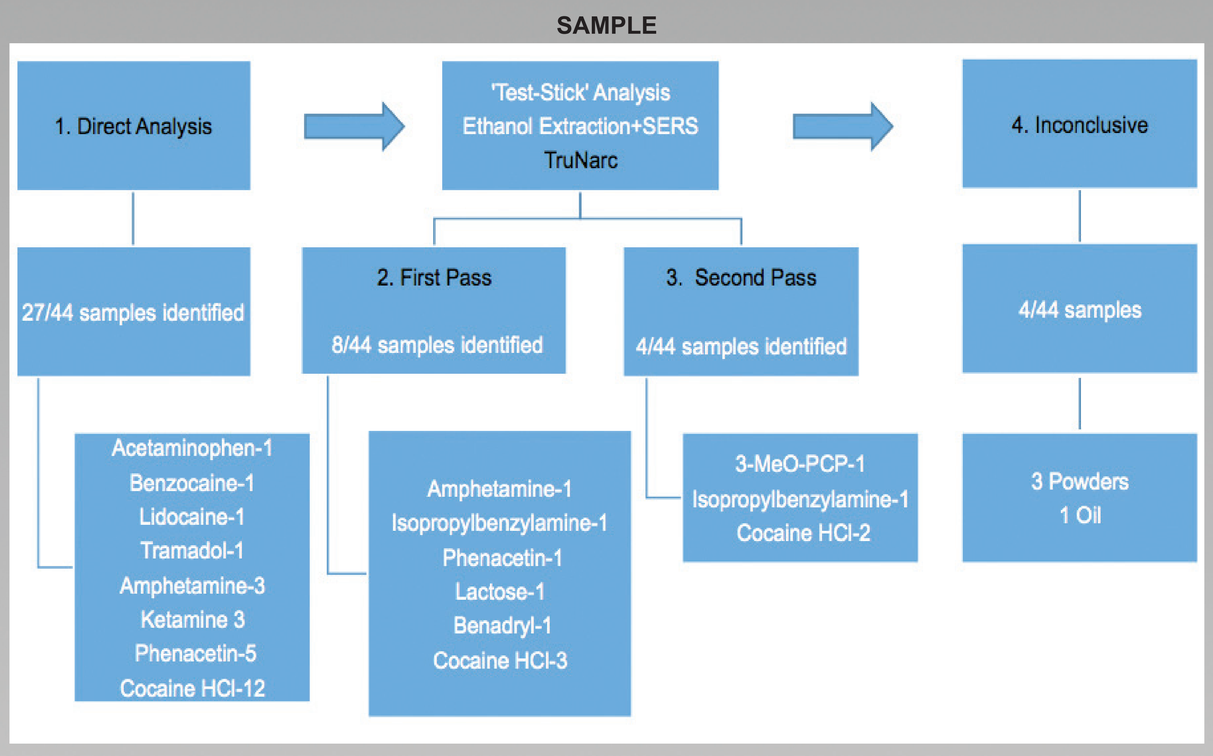
In the latter field, there is less number of the portable Raman used for the detection of drug of abuse. Although a 21 kg Raman instrument is considered heavy and not a mini instrument, it still produced rapid screen of liquids and powders for the detection and identification of a number of controlled substances.[10] In earlier method [11], a portable Raman equipped with a fiber-optic Raman probe showed a rapid identification of a Class A drug and selected adulterants. Two portable Raman (Renishaw and Delta Nu) from different manufacture were proven for the detection of three controlled drugs based on the analysis conducted at UK airport.[12] A portable Raman was used to analyze simulated street drug mixtures. Chemometric method was proven to resolve the spectral differences between benzocaine, lidocaine, isoxsuprine, and norephedrine. Limited number of the reference spectra in the database might reduce the detection performance.

In United Kingdom (UK), TruNarc is already approved as a presumptive drug analyzer for Ketamine and Mephedrone based on the Home Office guidance in 2014.[13] Further performance evaluation of TruNarc spectrometer compared with the benchtop one is still required. To the best of our knowledge, this work is the first study of TruNarc for bulk sample and the result obtained was validated with a benchtop Raman spectrometer.

METHOD



RESULT



COMPARISON / VALIDATION

Comparison of the experimental peak positions in cm^{-1} of Particle 1, 2, 3 along its TruNarc data and the estimated vibration assignment of Ketamine

Experimental								This Work
Horiba-Particle 1	Relative Intensity	Horiba-Particle 2	Relative Intensity	Horiba-Particle 3	Relative Intensity	TruNarc-Ketamine	Relative Intensity	Probable Assignment (Ketamine)
		220.60	vvw					
		224.15	vvw					
255.88	vvw	255.45	vvw					C-N torsional
283.69	vw	283.67	vw					CH_3 rocking, C-Cl out of plane bending
319.47	w	318.64	w			327.10	w	C-Cl in plane bending
344.00	w	342.91	vw	330.31	vvw			
352.06	w	352.02	vw			360.27	w	N-H out of plane bending
381.42	vw	381.88	vvw			381.12	w	
407.21	vw	407.34	vw	415.83	vw	413.71	w	
433.49	vw	433.74	vw	427.11	vw	442.17	w	Out of plane ring deformation
451.00	m	451.10	w	453.73	w	458.17	vs	CCC bending of cyclohexanone ring
		467.09	vvw					
470.63	vvw	470.03	vvw					
484.85	vvw	485.27	vvw					
519.05	vvw	519.42	vvw					CH_3C-N stretching
				530.78	vw			
571.06	vvw	571.49	vvw					
588.53	m	588.75	m	592.28	vvw	594.56	m	In plane ring deformation
				603.99	vvw			
						615.28	w	
646.46	vs	647.40	vs			654.53	s	C-Cl stretching
701.46	w	701.66	vw			707.54	w	
711.01	vw	711.28	vvw					

Abbreviations: vvs, very very strong; vs, very strong; m, medium; w, weak; vw, very weak; vvw, very very weak

CONCLUSION

44 'street' samples donated from UK Police have been analyzed using TruNarc and successfully identified organic substances including Class A, B, C drugs, active pharmaceutical substance, cutting agents (adulterants and diluents) and excipients at gram level without destroying the powder. Valid identification was obtained after Direct Analysis and Test Stick Analysis. TruNarc user only requires minimum training to use the instrument and obtain those prompt results. TruNarc method does not require a high budget, easily deployable, no sample preparation (Direct Analysis), small quantity of sample and minimum spectroscopic skills compared with Horiba. Test Stick Analysis requires organic solvent for sample extraction and SERS substrate. Spectral validation with Horiba showed peaks consistency, better quality of Raman spectra and wider spectral range. The equipped microscope allowed particle size, transparency and morphological surface observation. It also captured a good quality of image of each particles. Raman peaks were assigned with the help of literatures and good agreement was observed. The assignment work was challenging and the several Raman spectra were left unassigned because they are not always be identified.

FUTURE WORK

1. Peak shifting has been observed in the spectra. In future effort, this work aims to perform x-axis correction (offset) in all Horiba spectra. This correction should be applied to get a corrected spectra which are similar to the literature. It can be done by using "X-Axis Shifting" mode in GRAMS/AI. These new spectra should bring improvement for the comparison of the stacked spectra.

2. Computational chemistry allows us to calculate the theoretical Raman peak and the spectrum in gas, liquid and solid phase. Molecules can be build using Gaussview 5.00 and the calculation will be done using Gaussian 09W. The steps are; build the molecule in Gaussview, optimize the geometries to find the most stable conformer and obtain the vibrational peak position using DFT calculation for the most stable conformer. Softwares and a dual processor computer (128 GB RAM) are available to speed up this future work. Raman acitivity, Animation and the theoretical spectrum will be displayed by Gaussian.

3. This work has produced 12 reference spectra and they can be used to identify the chemical composition of the remaining 'street' samples. This can be done comparing the reference spectra with the Horiba spectrum by either visual inspection or chemometric study.

4. After second 'Test Stick' finished, several samples still not subjected to ethanol extraction and SERS. The next task is to use these samples and collect their Raman spectra using SENTERRA Raman Microscope.

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