

# Design proposal for a smartphone Raman spectrometer

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Term paper, CHEMENG 345 Applied spectroscopy

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March 7, 2014

## Background

**Theory of Raman spectroscopy.** Raman spectroscopy is widely used to probe molecular structures and perform substance ID. It engages roto-vibrational transitions in molecules. The frequency range is similar to IR, around  $200\text{cm}^{-1}$  to  $3500\text{cm}^{-1}$ . The mechanism and active peaks are different however. Whereas IR activity requires a change in the dipole moment in a normal mode excitation, Raman activity requires a change in the polarizability. Further, in Raman, the excitation can be of any wavelength, and the mode energy is either added to (anti-Stoke shift) or subtracted (Stoke shift, thermodynamically more probable) from the excitation photon energy. Hence what's at stake is the Raman shift from the excitation wavelength.

## Prior art of Raman instrumentation.

Traditional Raman spectrometers are expensive, bulky instruments confined to analytical laboratories. In recent years, though, several manufacturers have made handheld Raman spectrometers for doing rapid materials ID, quality control & anti-counterfeiting. For example, typical handheld Raman spectrometers offers a spectral range and resolution of  $3000\text{cm}^{-1}$  &  $20\text{cm}^{-1}$ , not as good as standalone instruments but still sufficient for many field applications. Nevertheless, handheld spectrometers can still range north of \$1000.

## Why use a smartphone? – Getting a CCD

**array, microprocessor, user interface and**

**data transfer for free.** There are now more than

2 billion smartphones around the world. This

immense market has allowed manufacturers to

leverage tremendous economies of scale to

integrate sensors and processing power at very low costs.

To do Raman spectroscopy on a smartphone, we image the grating output to a smartphone's camera, which boasts an astonishing 8MP with a 5-lens system for aberration corrections. We can write embedded software to perform image processing and estimation to extract spectroscopic data. Higher up, we can have apps that perform material identification. In doing so, we can eliminate more than half of the cost from a handheld spectrometer. All that's left is to package the optics around the smartphone. Further, the smartphone offers a user interface that's already familiar and rapid wireless data transfer to other remote systems.

**Researchers have already implemented smartphone bio-sensing and absorption spectroscopy.** The scientific potential of smartphones hasn't gone unnoticed. There are already sensors (pH, air quality etc.) that plug directly into smartphones.

In regards to spectroscopy, Cunningham et al. at UIUC has developed smartphone based platform

for doing label-free bio-sensing ([1] 2013). They made a cradle attached to a smartphone holding a white light source, collimating optics and transmission diffraction grating in line with the smartphone's camera. Then they inserted a photonic crystal (PC) sensor into the beam path. The PC sensor's spectral bandwidth changes w.r.t. adsorbents on its surface. Detection of protein monolayers and antibody binding on the PC was demonstrated.

In another *Lab on a Chip* paper, Park et al. detected Salmonella using Salmonella binding antibody complexes that clumped and produced Mie scattering when illuminated [2]. Again, the light signal was sent to the smartphone camera, which displayed bacterial detection data via a smartphone app.

Thirdly, Public Lab, a nonprofit organization, has developed an open source absorption spectrometer attachment consisting of simply a slit and plastic grating. They engaged the public to develop their own applications and share their data on line.

## **Operation and design (refer to drawings at last page)**

**In this proposal, we're designing the first (to our knowledge) a smartphone attachment for Raman spectroscopy.** We pay closer attention to optical collimation, incorporate a laser, use a commercial grating and add mirrors to adjust entrance beam angle to achieve a Raman spectrometer with spectral range and resolution. The whole package is also elegant and compact.

Our design is in principle most similar to the Public Lab absorption spectrometer. However, we added a collimating lens to greatly reduce beam divergence and mirrors so that the beam path lies neatly against the smartphone, not to mention the inclusion of an excitation laser for Raman.

**Using the diode-pumped Nd:YAG  $\lambda_0 = 532\text{nm}$  laser as Raman excitation source.**

These are the “green laser pointers” widely available. It's a diode pumped solid-state laser with consequently very narrow spectral FWHM. Other excitation wavelengths can also work as shifts in the Raman spectrum is largely

independent of excitation wavelength. However, Raman scattering scales as  $\lambda^{-4}$ , resulting in diminished signals at longer wavelengths. On the other hand, at shorter wavelengths, fluorescence can be excited, complicating the Raman spectrum. 532nm is a good compromise.

Another popular Raman wavelength is 785nm (near IR). However, some smartphone cameras incorporate anti-IR filters which might block out signal.

**Sample loading.** We load a solid substrate surface or liquid containing cuvette at the bottom of the instrument. In cases of a solid surface, the excitation beam deflects off at a high incidence angle, allowing it to interact more with the sample. Alternatively, the sample can be dispersed on a metallic Raman substrate with a roughened surface for enhanced interaction. In cases of liquid containing cuvettes, the light passes through the liquid and scatters off Raman photons.

**A slit-collimator-grating system accomplishes wavelength separation.** Right-angle scattered first enters a slit and is then collimated by a

cylindrical lens ( $f = 10\text{cm}$ ). The collimated beam then hits a transmission grating ( $N = 1200$  lines/mm). The grating disperses different wavelengths at a different angle which is then imaged to a line on the CCD of the smartphone camera.

**Mechanical enclosure.** A plastic enclosure housing the system can be prototyped via 3D prototyping. There need to be a few angle adjustment mechanisms on the mirrors to tune alignment and laser beam position.

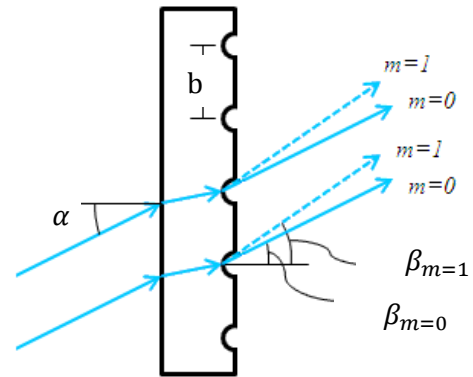
**Electrical control system.** We can use the mini-USB output of the smartphone to control the current driver to regulate laser output levels. The laser will have its own battery. The control and readout interface will be an app on the smartphone.

**Operation as an absorption spectrometer.** In this mode, may turn off the laser and instead use the smartphone flash as a broadband source. We may first collimate the flash with lens and redirect with 2 mirrors to illuminate the sample, liquid or solid (components not shown in drawing). The flash is designed by the

smartphone manufacturers to mimic the visible portions of sunlight, e.g. ranging from 400nm to 800nm with a peak around 500nm. We will show that our spectrometer can sense the entire visible spectrum.

## Theoretical performance

**Theoretical spectral bandwidth.** To a first approximation of constructive interference, we have



$$b(\sin \alpha - \sin \beta) = m\lambda \quad (1)$$

$$b = \frac{1\text{mm}}{N} = 833\text{nm} \text{ (grating separation)}$$

$$\alpha = 45^\circ \text{ (incoming incidence angle)}$$

$$\beta \text{ (Raman shifted wavelength)}$$

$$m = 1 \text{ (diffraction order)}$$

Fig. from ThorLabs

Thus, the path length difference between two rays has to be equal to an integral number of

wavelengths. A typical Raman shift spectrum goes from  $100\text{cm}^{-1}$  to  $4000\text{cm}^{-1}$  in wavenumbers, which for Stokes shifts translate to

$$\lambda_{Raman} = \frac{1}{\frac{1}{\lambda_0} - \tilde{\nu}} \in [534.8\text{nm}, 675.8\text{nm}]$$

The range of wavelengths that deflect at an angle  $\beta$  within the half-angle FOV of the camera ( $20^\circ$  conservatively for iPhone 5) is found by eqn. (1) as

$$\lambda_{acceptable} \in [263\text{nm}, 887\text{nm}]$$

Which is wider than the Raman bandwidth. We thus see that the specified Raman shifted beam always falls on the detector. In fact our wide acceptance bandwidth allows the instrument to be used just as an absorption spectrometer.

**Theoretical spectral resolution.** There are several resolution limiting elements. First, the best possible resolution of the grating near  $\lambda_0$  is

$$\Delta\lambda' = \frac{\lambda_0}{n} = 0.15\text{nm}$$

Where  $n = NL = 3600$  is the number grating periods under illumination. Second, the pixel size on the CCD determines a smallest

resolvable wavelength resolution (in a small angle approximation from eqn. (1)) as

$$\Delta\lambda'' = b \cos \beta \Delta\beta < b\Delta\beta = 0.28\text{nm}$$

Where

$$\Delta\beta = \frac{\text{FOV}}{N_{pixels}} = \frac{\text{FOV}}{\frac{s}{d_{pixel}}} = \frac{40^\circ}{\frac{3.44\text{mm}}{1.5\mu}} = 0.34\text{mrad}$$

Where  $N_{pixels}$  is the number of pixels along one side of the CCD.

Thirdly, the lens collimated beam of the light passing through the slit has a beam divergence of

$$\frac{d_{slit}}{f} = \frac{100\mu}{10\text{cm}} = 1\text{mrad}$$

$$\Delta\lambda''' = b \cos \alpha \Delta\alpha < b\Delta\alpha = 0.83\text{nm}$$

The total wavelength resolution is very roughly estimated as

$$\Delta\lambda = \sqrt{\sum_i \Delta\lambda_i^2} = 0.9\text{nm}$$

Now, near 532nm, our 0.9nm difference corresponds to  $32\text{cm}^{-1}$ , which is comparable to a commercial handheld instrument.

## Post processing

**Data extraction.** The camera output looks like the next fig. produced by a Public Lab spectrometer. We need to translate it into a graph of intensity vs. Raman shift using image processing algorithms.

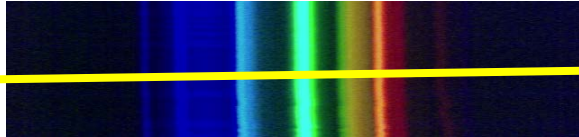


Fig. Spectrometer output from Public Lab

First, we determine the central axis of grating lines and extract intensity vs. pixel on the axis (shown in yellow in previous fig). We can use calibration data (described later) to map pixel positions to wavelengths and hence Raman wavenumber shifts.

**Signal estimation enhancements.** Each CCD unit has 3 detectors for 3 color bands (e.g. RGB), each with a different sensitivity for any wavelength. Thus, we actually get 3 different intensity estimates for each wavelength, on which we can do a weighted average (giving greatest weight to color detector with highest sensitivity). This is an example of leveraging the color CCD to enhance signal estimation.

## Experimental calibration

**Wavelength-pixel calibration.** We place a Xe lamp besides the slit. The lamp emits lines corresponding to the atomic transitions between energy levels of Xe. A high voltage discharge creates electronically excited species which then relax, emitting photons. Xe (or other noble gas) discharge lamps is often used as a spectrometer calibration source because it emits bright lines in the visible range of 400nm to 700nm.



Fig. Lines of a Xe discharge lamp

We can then map documented emission wavelengths of Xe to the lines we see on our spectrometer. We can then use regression to fit polynomial splines relating pixel position to wavelength.

**Resolution.** Linewidths of the Xe lamp (natural linewidth broadened by Doppler and pressure) are many orders of magnitudes smaller than any spectrometer resolution. Therefore, we may obtain the FWHM of each line on our image

cross section to derive a wavelength dependent resolution.

**Sensitivity and noise.** Raman scattering is low likelihood event. Estimates are 1 in 1000 photons undergo scattering near right-angle, and of those, 1 in 1000 undergoes Raman. Therefore, we get a ~60dB attenuation in our signal from the original source. Detector sensitivity is thus an issue, though the “over-engineered” iPhone camera CCD is comparable in sensitivity to (if not better than) CCD used in existing handheld Raman scanners.

To experimentally determine sensitivity, we collimate light from a Xe lamp and direct it toward the slit. We also place a beam splitter whose power splitting ratio we calibrate beforehand. We put a thermal power detector behind one arm of the beam splitter to monitor power of the collimated beam. Using datasheet from the lamp manufacturer at typical operating conditions, we know percentage and therefore the power of each spectral line in or beam.

We now place a variable wheel optical attenuator right after the beam source and slowly

ramp up the power. At extremely low light levels, we expect the CCD output to be speckled. There’s photon shot noise (due to Poisson process of discrete photon arrival) as well as stray light and a menagerie of electronic noise. We can thus characterize signal to noise ratio (SNR) as a function of both power and wavelength. We expect SNR to increase at higher powers (higher signal) and lower wavelengths (higher energy photons). A wavelength dependent signal threshold can be computed.

**Automatic field calibration.** The aforementioned discharge lamp calibration can be performed in the research phase but is impractical for the end user. However, opto-mechanical alignment variations do affect different production units. To correct this, we may provide the user with a “calibration substrate” (e.g. a piece of polymer with distinct Raman peaks at known wavelengths). The user can first scan the “calibration substrate,” whose peaks’ wavelengths as determined by the spectrometer may be slightly off. We use this to make another fine calibration.

## A potential application of smartphone Raman spectroscopy

### Low-cost detection of antimalarial

**counterfeits.** Artesunate is a small-molecule antimalarial agent. Counterfeits are prevalent in Africa and Asia. Veij et al. demonstrated using Raman spectroscopy to distinguish genuine and counterfeit versions ([3]). The  $200\text{cm}^{-1}$  to  $1600\text{cm}^{-1}$  regions are often termed the “fingerprint” of an organic molecule because they’re highly distinct, corresponding to normal modes of lower-energy bending and twisting on the carbon backbone.

To identify a substance from its Raman spectrum, we may normalize a spectrum according to total intensity and treat it as a N-dim vector where N is number of wavenumbers sampled. We may compute a correlation measure (0 to 1) between 2 spectrums as a dot product of their normalized vector representations. We can then see if the substance spectrum matches a spectrum within our library based on the correlation measures. More

sophisticated techniques like principal component analysis (PCA) can also be used.

The aforementioned algorithms are straightforward to implement on a smartphone and can be integrated on a “Raman app.” Our smartphone Raman scanner are very low-cost (~\$140, next fig) and portable. We may extend use of Raman spectroscopy to important applications like drug anti-counterfeiting in field and resource-limited settings.

Grating	\$80
Diode-pumped Nd:YAG or direct diode laser	\$20
Lens, slits, mirrors	\$20
3D printed or injection molded case	\$20
Total	<b>\$140</b>

Fig. Projected cost of smartphone Raman

## Summary

We proposed a design for a smartphone integrated Raman & visible absorption spectrometer. We use a compact Nd:YAG 532nm source to excite a liquid cuvette or solid



sample. The scattered light at right angle is collimated by a slit/lens system and projected onto a transmission grating that performs wavelength separation. Finally, the color band is imaged by the camera on a smartphone, which also provides image processing and user interface. Alternately, the device can be used as an absorption spectrometer by instead direct the smartphone broadband flash onto the sample. In Raman mode, we calculate a theoretical range of  $> 4000\text{cm}^{-1}$  and a resolution of  $\sim 35\text{cm}^{-1}$  ( $\sim 1\text{nm}$  at  $532\text{nm}$ ), comparable to existing handheld models but at a fraction of the cost at \$140. Spectral accuracy, resolution and sensitivity can be measured using a Xe discharge lamp.

The bulk of our design effort is on the detector side. Our model can really accommodate a wide range of excitation sources, which may extend the instrument's use to fluorescence and absorption spectroscopy. Different gratings (perhaps in an easily adjustable mount) can offer different spectral ranges and resolutions. There's also the possibility of modifying the instrument

to do Raman microscopy by adding a microscope objective.

Affordable smartphone based instruments can bring scientific tools to a much wider audience, for commercial, health or educational purposes.

## References

1. Dustin Gallegos, Kenneth D. Long, Hojeong Yu, Peter P. Clark, Yixiao Lin, Sherine George, Pabitra Natha and Brian T. Cunningham. "Label-free biodetection using a smartphone." *Lab on a chip*. 2013, 13, 2124.
2. Tu San Park, Wenye Li, Katherine E. McCracken and Jeong-Yeol Yoon. "Smartphone quantifies Salmonella from paper microfluidics." *Lab on a Chip*. 2013, 13, 4832.
3. Veij, Marleen et al. "Fast detection and identification of counterfeit antimalarial tablets by Raman spectroscopy." *Journal of Raman Spectroscopy*. 2007, 38.

## Drawings

1. Grating (in front of camera), horizontal rulings, 1200 lines/mm
2. Mirror
3. Collimating cylindrical lens,  $f=10\text{cm}$  (curvature not drawn to scale)
4. Pupil
5. Collimating slits,  $d=0.10\text{mm}$
6. Substrate (solid or liquid containing cuvette)
7. Nd:YAG laser,  $\lambda=532\text{nm}$
8. Smartphone lens (not shown)
9. Smartphone CCD array
10. Mirror
11. Smartphone

