January 01, 2006

Denoising of Raman Spectroscopy Signals

Luis A. Quintero
University of Puerto Rico - Mayaguez

Shawn D. Hunt
University of Puerto Rico - Mayaguez

Max Diem
Northeastern University

Denoising of Raman Spectroscopy Signals

LUIS A. QUINTERO[1], SHAWN HUNT[2] and MAX DIEM[3]

1 luis.quintero@ece.uprm.edu, Electrical and Computer Engineering, University of Puerto Rico, Mayagüez, PR
2 shawn@ece.uprm.edu, Electrical and Computer Engineering, University of Puerto Rico, Mayagüez, PR
3 m.diem@neu.edu, Department of Chemistry & Chemical Biology, Northeastern University, MA

ABSTRACT

Raman spectroscopy measurements are affected by various types of spurious signals or noise. These spurious signals in the detection system are mainly produced by cosmic rays, read-out noise and thermal noise. Because of the very different nature of the various noise signals, the procedure to estimate a desired materials spectral response from the measured signal is generally divided into two sequential stages. The first stage removes the impulsive noise caused by cosmic rays, and the second attempts to remove the rest of the noise. In this work, the algorithm for removing the impulsive noise is based on a system which uses both a median filter and classic pattern recognition techniques. The algorithm not only removes the impulse, but replaces the missing values with the best estimates including system noise. In addition, spectrum denoising to minimize the loss of information is studied. The implemented algorithms are tested with synthetic and real spectrums; real spectrums are from Raman Imaging of biological materials which were provided by the research group led by professor Max Diem at Northeastern University. The algorithms are useful for all software tools that analyze Raman spectroscopy data.

STATE OF THE ART

The Raman micro-spectroscopy is a powerful tool used in the estimation of chemical and physical properties of the materials, particularly is used in the analysis of biological materials (BoiBED) by the professor Max Diem in his laboratory. Commonly is used CCD sensors to detect the Raman Scattering, it instrumentation system is affected of multiple noise sources.

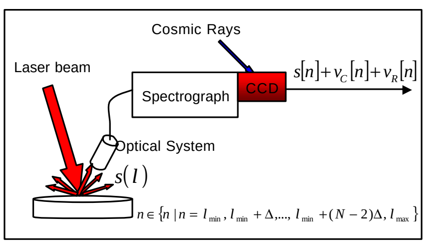


Figure 1. Raman Micro-Spectroscopy – Basic Model

A common Raman spectrum is composed of peaks, representative of the molecular vibrations in the material under study. In several cases, noise is present in the measurement system and is caused mainly by: read out noise, thermal noise and impulsive noise. Figure 2 shows the signal model used, where s[n] is the discrete estimate of s(?), the Raman Scattering signal. The read-out noise and thermal noise are represented by $v_R[n]$ and the impulsive noise by $v_C[n]$.

Several methods have been used to denoise the Raman spectrums, in general, first remove the impulsive noise and second smooth the signal with a Savitzky-Golay filter[2]. Some advanced methods have been implemented to detect and remove the impulsive noise, for example, the use of Wavelet transform[3].

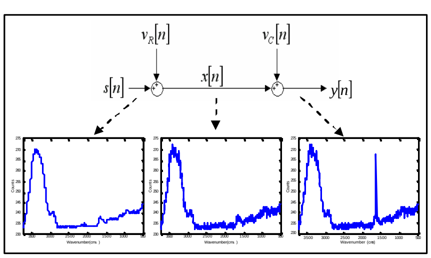


Figure 2. Signal model with examples

SIGNAL PROCESSING SYSTEM

A signal processing system to estimate the signal s[n] based on the assumed signal model is proposed. It consists of two sequential stages, the first is an impulsive noise filter that detects and removes the spikes principally caused by cosmic rays [1]. The second stage is a denoising filter designed to make a good estimate of the signal s[n] from the measured signal $\hat{x}[n]$.

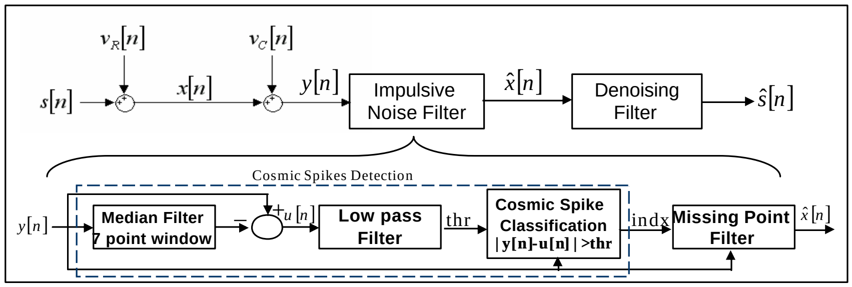


Figure 3. Preprocessing system proposed and impulsive noise system implemented

IMPULSIVE NOISE FILTER

Cosmic spikes (impulsive noise) are produced by high energy radiation that affects the CCD detector and result in sharp peaks in the measured spectra. The shape of the peaks is diverse, some examples are shown in Figure 4

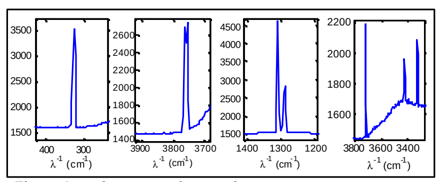


Figure 4. Real cosmic spike samples

The impulsive filter is composed of two parts. The first part is a Cosmic Spike Detector (see Figure 3), and the second part replaces the detected spikes with an estimated spectra.

The detection system is based in the median filter. Different authors use other algorithms [4,5,6] but the median filter was selected because of its good impulsive noise rejection. After filtering the spectrum (Figure 5, blue), the difference is calculated |y[n]-u[n]| (red). The absolute value of the difference is lowpass filtered, and threshold is set based on this filtered signal (the lower black line in figure 5). The peaks above the threshold are candidates for being cosmic spikes. Each peak is evaluated, and classified as being a spike or non spike depending on its normalized area.

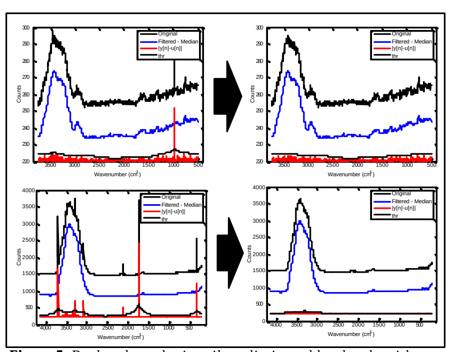


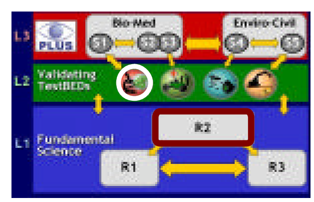
Figure 5. Real and synthetic spikes eliminated by the algorithm

Once detected, the cosmic spikes are replaced by the Missing Point Filter and added noise. The filter is a polynomial interpolator [7], and the noise is added in order for the replaced points to have the same statistics as the rest of the signal.

OPPORTUNITIES FOR TECHNOLOGY TRANSFER

The algorithms are useful for any commercial software that processes Raman spectroscopy signals. The de-noising of Raman spectroscopy signals is essential to classification or unmixing algorithms, since cosmic spikes in the data tend to cause incorrect results. In addition to helping machine based classification or unmixing, these algorithms produce visually cleaner spectrums which make analysis by a spectroscopist easier.

RELEVANCE TO CenSSIS STRATEGIC RESEARCH PLAN



The algorithms will help to improve the processing and the understanding (R2) of Raman spectrums used in the estimation of chemical and physical properties of biological materials (BioBED).

REFERENCES

[1] R. L. McCreery, *Chemical Analysis: Raman Spectroscopy for Chemical Analysis*, Vol 157, Wiley, New York, 2000.
[2] J. LUO, K. YING, P. HE, J. BAI, Elsevier – Digital Signal Processing 15, 2005. p. 122-136
[3] F. EHRENTREICH, L. SUMMCHEN, Analytical Chemistry, Vol. 73, No. 17, Sep 1, 2001. p. 4364-4373
[4] K. J. DIEN HILLIG, M. D. MORRIS, Applied Spectroscopy, Vol. 36, No. 6, 1982. p. 700-701.
[5] W. HILL, D. ROGALLA, Analytical Chemistry, Vol. 62, No. 21, Nov 1, 1990. p. 2351-2357.
[6] Y. KATSUMOTO, Y. OZAKI, Applied Spectroscopy, Vol. 57, No. 3, 2003. p. 317-322.
[7] G. R. PHILLIPS, J. M. HARRIS, Analytical Chemistry, Vol. 62, No. 21, Nov 1, 1990. p. 2351-2357.

CenSSIS, the Center for Subsurface Sensing and Imaging Systems, under the Engineering Research Centers Program of the National Science Foundation (Award Number EEC-9986821).