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Research Article

A Computational Method for Analysis of EPR Spectra Based on Image Processing

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Abstract: In this study, it was aimed to finish the analysis process much quicker and make the error margin minimum. Image processing technique was applied to the spectra of gamma irradiated diammonium hydrogen citrate single crystals recorded in the electron paramagnetic resonance (EPR) spectrometer. The peak values in the analogue spectra were detected and transferred to digital environment by using the image process technique. The analogue structures of the spectra were reobtained by using curve fitting methods after the digital spectra were implemented some basic morphological image processing techniques. The spin-Hamiltonian parameters were calculated by using the spectra acquired in our calculation and a comparison made with the results of manually resolved spectra. In this way, the aim of the study was achieved by minimizing the loss of time spent in the analysis stage and the errors related to humans.

1. Introduction

Human factor plays an important role in the analysis of scientific spectra. It can cause the analysis to last longer and the error margin to increase more during the analysis. Since the mistakes made during the measurements of both scan field and amplitudes in the spectra affect the results of analysis, making the errors minimum and having the same success in all spectra are very important at this stage [1].

There are a lot of studies on the spectra since they are used in many different scientific fields such as physics, chemistry, medicine, and engineering. Some researchers studied about peak detection [2], curve fitting methods [3], and image enhancements [4]. A group of researchers from the field of engineering analyzed the electromyography signal by using spectrogram in 2013. In the study, they investigated the effect of signal analysis on image size [5].

It is very important to obtain the spectra correctly for paramagnetic centers having different hyperfine values and line intensities in EPR spectroscopy. It lasts weeks even months to calculate the hyperfine values and g factors of paramagnetic centers, which has a lot of lines in its EPR spectra. Taking care of distribution of line intensities in typical EPR spectra, the spectra can be converted to digital medium and used image processing techniques to evaluate both g factors and hyperfine values in a very short time.

In this study, our aim was to minimize human errors in the analysis of spectra by using image processing techniques. A software was developed to analyze the spectra and the results were compared with those obtained manually.

2. Material and Method

There are five algorithmic steps in the study and these steps are explained in detail as below.

2.1. Obtaining Spectra

The images used in the study were obtained from the EPR spectra of gamma irradiated diammonium hydrogen citrate single crystals. The spectra were recorded on an EPR spectrometer between 0° and 180° at 10° steps for each three mutually perpendicular axes, i.e. x, y, z axes.

2.2. Preprocessing

After first step, the spectra were transferred to a computer by a scanner. The digitized images had 2480*1753 pixels resolution. The images transferred to computer were cleaned from environmental noises and factors that can cause incorrect results by using Matlab (R) R2012a (7.14.0.739) 32-bit (win32). One of the important parts in the analysis of spectra is to locate the center point. To overcome this problem, the center point was marked. This mark would be used in detection of center points of the other spectra. A spectrum after completing pre-processing step is shown in Figure1.

2.3. Image Processing Techniques

Some image processing techniques were required to analyze the spectra in best way. To make the detection of points in spectra easier and more precise, all images were converted from RGB (red-green-blue) to BW (black-white). A morphological process named the erosion was applied to remove linear noises. After these processes, the spectra were provided to be more linear. Since the spectral images were based on pixels, the points of the spectra were detected by scanning both x and y axes. In BW image, "0" shows background and"1" shows the points of the spectra.

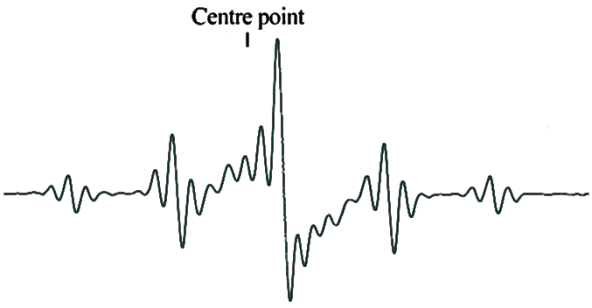

Figure 1. *One of the spectra after preprocessing step.*

2.4. Point Extraction

In the preceding part, the general outline of the spectra was somewhat appeared. To continue resolving the spectra, we need to know the corresponding values of all points. Hence, the points were converted from pixels to gauss (magnetic field unit) as well as intensity and new coordinate values were assigned for each points. The central gauss value in the spectra was taken into account when converting pixels to gauss value. For example, if the magnetic field magnitude is chosen as 3000 gauss when recording the spectra, then the central gauss value is 3000 gauss and the value will increase or decrease due moving to the right or left of the center, respectively.

2.4.1. Curve Fitting

After all these steps, the spectra are still composed of points. Hence, to continue analyzing the spectra, the points have to be combined together by using correct curve fitting method. In this study, we used smoothing spline method, which is a polynomial method. Previous studies showed that smoothing spline method is also successful at image enhancement [6]. We applied different curve fitting methods before using smoothing spline and noticed that the smoothing spline method had a greater successful rate than the other methods. We selected '0.94' as sensitivity value since it gave the best results. The digitized images which are very similar to the original spectra were obtained by using the smoothing spline method.

2.4.2. Peak Detection

The most important part in spectrum analysis is to detect local maximum and minimum points (peaks) because the analysis is based on this situation. The more we choose appropriate points among the peaks in the spectrum, the more the result of analysis will be successful. To detect peaks, we used the method, with some minor changes and improvements, developed in 2012 by Billauer [7].

Two arguments were needed to detect peaks: vector and delta. The vector represents the points that create the spectrum. Delta is the threshold value for a peak. If the difference between two points is greater than delta value, the point having the greater value is detected as peak. Here the important thing is how to detect delta threshold value because the delta threshold value has different values in each spectrum. In the study, we realized that the delta threshold value has a value between 1 and 10 for all spectrum. We used an algorithm shown in Figure 2.a and detected optimal delta value for each spectrum.

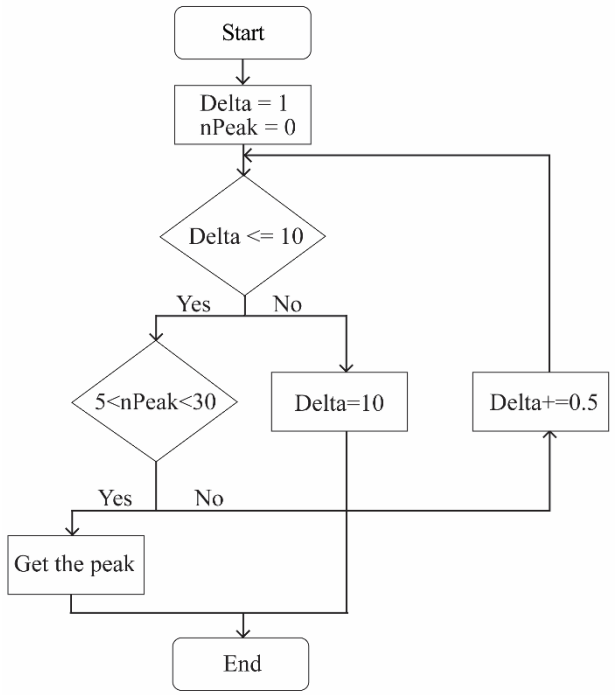

Figure 2.a. *The algorithm of detection delta threshold value.*

We detected all peaks in the spectrum after optimal delta value was found. However, in the analysis, we need only points that show sudden and major changes. To do this, we need to detect points over an identified threshold value. We determined this threshold value as the first detected value of intensity point and we realized that this method is successful for all spectra. Figure 2.b shows one of the spectra after this step.

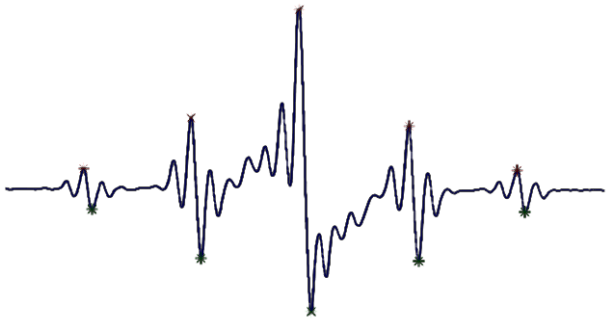

Figure 2.b. *Detected peaks over identified threshold value in one of the spectra.*

Although we detected peaks, we needed fewer points which represented the spectrum better. To select these peaks, we used a method that the points close to each other were collected in a cluster. When the distance of two points is over some specific value, which is related to hyperfine value in EPR, the points were collected in a cluster. Later, the areas under peaks were calculated in the clusters and compared with each other in its own cluster. A peak which has the largest area in its cluster was selected as point used in the analysis stage. This process was applied to all clusters and a single peak was found for each cluster. The determined peaks having the largest area are shown in Figure 2.c.

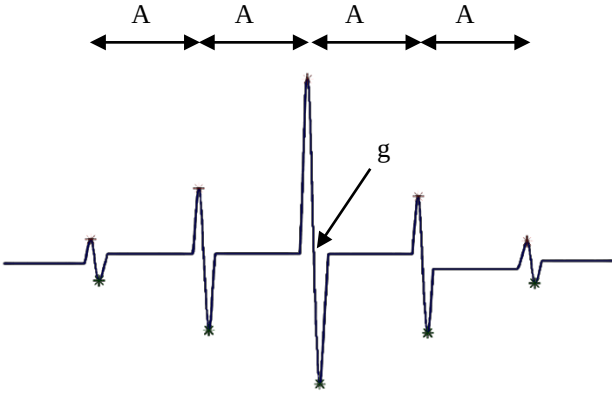

Figure 2.c. *The peak points detected with area*

2.5. Evaluation of obtained points

In the stage of detection of peaks, the peaks were selected to be used in the analysis. To analyze spectrum, the gauss values of points were saved as a text output that used in evaluation application. The signal analysis was completed after all these steps and evaluation of signal was initiated.

3. Results and Discussion

In paramagnetic centres, the interaction between the nucleus and the unpaired electron is called hyperfine interaction and is equal to the spacing between adjacent peaks in units of millitesla (mT) [8]. In EPR spectroscopy the g factor is a measure of the magnetic property of the paramagnetic environment and is also known as spectroscopic splitting factor [8]. These two values, hyperfine and g factor, are visualized in Figure 2.c.

The g factors and hyperfine values for gamma irradiated diammonium hydrogen citrate single crystals are evaluated first manually and then by using the image process algorithm described above. In manual evaluation, the values of each peak in recorded spectra were obtained by using a ruler and then calculations were made. The duration for the whole process is about three weeks. However, the duration for the same process is about a couple of hours by using the method we developed in the study.

To calculate g factors and hyperfine values, one needs to plot a graph g^2 against rotation angle in EPR spectra. Figure 3 shows the graphs plotted for the first plane, i.e. *ab* plane, by using both experimental and computational data. We used the fitting procedure and calculation technique as described in [8, 9]. The calculated g factors and hyperfine values

for both methods are within the experimental error range and as follows: g_{exp}=1.999, A_{exp}=3.11 mT, g_{comp}=1.994, A_{comp}=3.16 mT.

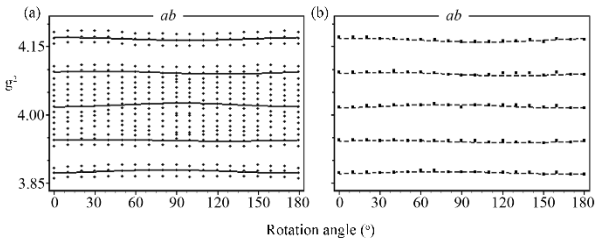

Figure 3. *Plot of g^2 vs rotation angle in ab plane by using (a) experimental and (b) computational data.*

4. Conclusion

Complex EPR spectra can be simplified by removing the noise from the spectrometer. We tried to simulate the EPR spectra recorded for irradiated diammonium hydrogen citrate single crystals. By using the algorithm provided above, the desired simple and ready to use spectra were obtained in a couple of minutes rather than weeks. One can also use the algorithm to distinguish paramagnetic centres with different hyperfine values. The paramagnetic centres can be complexes doped with transition metal ions, irradiated single crystals, or biological radical centres.

References

[1] W. Yiding, W.Yunhong, and Z. Shi, Errors analysis of spectrum inversion methods, Proc. IEEE International Conference on Signal Processing and Communications (ICSPC 2007), 24-27 November, 2007 Dubai-United Arab Emirates

[2] E. Min, M.Ko, Y. Kim, J.Joung, and K. Lee, A peak detection in noisy spectrum using principal component analysis, Proc.IEEE Nuclear Science Symposium and Medical Imaging Conference (2012 NSS/MIC), 27 October - 03 November, 2012 Anaheim, CA-USA

[3] R. Sun, H. Z. Huang, J. Yang, D. Ling, and Q. Miao, Curve fitting with weight assignment under evidence theory combination rule, Proc. 2011 International Conference on Quality, Reliability, Risk, Maintenance, and Safety Engineering (ICQR2MSE), 17-19 June, 2011 Xi'an-China

[4] S.Premkumar and K. A.Parthasarathi, An efficient approach for colour image enhancement using Discrete Shearlet Transform, Proc. 2nd International Conference on Current Trends in Engineering and Technology (ICCTET 2014), 8 July, 2014 Coimbatore-India

[5] T. N. S. T. Zawawi, A. R. Abdullah, E. F. Shair, I.Halim, and O. Rawaida, Electromyography signal analysis using spectrogram, Proc. 2013 IEEE Student Conference on Research and Development (SCOReD 2013), 16-17 December, 2013 Putrajaya-Malaysia

[6] F. Precioso, M. Barlaud, T. Blu, and M. Unser, Robust real-time segmentation of images and videos using a smooth-spline snake-based algorithm, IEEE Transactions on Image Processing 14 (2005) 910-924. DOI: 10.1109/TIP.2005.849307

[7] E. Billauer, http://www.billauer.co.il/peakdet.html, Access date, 28.09.2015

[8] B. Karabulut and R. Tapramaz, EPR study of gamma irradiated arsanilic acid single crystal, Radiation Physics and Chemistry 55 (1999) 331-335. DOI:10.1016/S0969-806X(98)00348-X

[9] R. Biyik, M. Cemberci, and R. Tapramaz, A Computer Program to Help Resolution of Complex and Poorly Resolved Cu^{2+} and VO^{2+} Ions Doped Single Crystals Electron Paramagnetic Resonance Spectra, Spectroscopy Letters 42 (2009) 436-441. DOI:10.1080/00387010903253831