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# Cross-Correlation Noise Studies in Atomic Magnet-Optic Rotation Spectroscopy<sup>\*</sup>

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Analytical signals in an Atomic Magneto-Optic Rotation spectrometer are buried in noise at the limit of detection. The noisy analytical signals were analysed by carrying out mathematical correlation of their time domain waveforms. The noise components of signals were removed by auto-correlation to simplify the study. If noise interferes in analytical signals whose source is unclear, a cross-correlation of the output waveform with noise source may identify the source, e.g., mains frequencies and background radio signals. A cross-correlation will reveal whether the two signals are derived from the same source. This can also lead to an improvement in the signal detection limit. Either of the two above situations can occur in studying analytical signals. In this study, both auto-and cross-correlation studies were carried out on analytical signals which had discrete noise sources present in their waveforms.

Key Words: Atomic magneto-optic rotation spectrometer, auto-and cross-correlation

## Introduction

The detection limits of analytical spectroscopic measurements are ultimately limited by the presence of broad band system noise. An analytical spectrometer designed to measure Atomic Magneto-Optic Rotation (AMOR) of light through analytes was found to suffer considerably from interfering frequencies on detected spectroscopic signals<sup>1-4</sup>.

The presence of noise in analytical signals can be reduced if their sources are identified. This often is a trial and error procedure, and is time consuming. A more systematic approach is to mathematically correlate the signal waveforms with suspected sources of noise in the system or those present in the surroundings. Auto-correlation and cross-correlation can both be carried out on the signal waveforms. Correlation can identify sources of interfering frequencies related to each other; others have even improved the signal-to-noise ratio of the analytical signal<sup>5</sup>. The purpose of this paper is to describe this method of analysis, which is largely independent of the instrumentation<sup>5</sup>.

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Cross-Correlation Noise Studies in Atomic Magnet-Optic..., A. T. INCE,

## Theory

Similarity and association are good intuitive definitions for the mathematical operation of correlation. The mathematical definition of correlation in the time-domain is given  $by^6$ ,

$$r(\tau) = \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{T} x(t) y(t+\tau) dt$$
(1)

Where r ( $\tau$ ) is the correlation function formed by summing the lagged products of two waveforms x (t) and y (t), and  $\tau$  is the time lag between x (t) and y (t).

Correlation is a mathematical similarity test between waveforms, it is simplified using a Fast Fourier Transform (FFT). In the frequency domain, it may be represented as<sup>7</sup>

$$R(f) = X(f) * Y(f)$$

$$(2)$$

R (f) is the frequency correlation, and \* is used to denote conjugation.

R (f) is then inverse transformed back to the time domain to give r ( $\tau$ ).

If the two waveforms are the same, i.e., x(t) = y(t), then an auto-correlation is performed. If the two waveforms are different, i.e.,  $x(t) \neq y(t)$ , a cross-correlation is performed.

The FFT of a correlation function is a power spectrum. The FFT of an auto-correlation function is an auto-spectrum, noise power spectrum or power spectral density (PSD). The FFT of a cross-correlation function is a cross-spectrum.

## Experimental

The studies presented here involve investigation in the time domain of the noise sources within a 200 Hz spectral range for an AMOR spectrometer set-up in the Faraday configuration and employing an offset polariser method ( $\theta$ =45°). The experimental set-up and D.C. power supply circuit used for the magnet assembly are shown in Figures 1 (a) and (b) respectively. A Rochon prism was used as the analysing polariser since it generates two orthogonally polarised beams with a small angle of separation from the incident beam. These two rays are focused onto the entrance slit of a monochromator, one above the other. On leaving the exit slit of the monochromator, they are reflected by a plane mirror and thus further separated into two rays. Each ray then enters identical side-window PMT tubes. The output of the PMT tubes form the input to a Solartron 1200 model signal processor. Details of the AMOR apparatus are explained in a previous paper<sup>2</sup>. Magnesium was the analyte used to carry out the correlation studies. When the rotated plane polarised light traverses the offset polariser, light is split into two rays and the noise sources carried by the rotated plane polarised light are split between these two rays.



Figure 1. (a) Block diagram showing the AMOR spectrometer arrangement. HCL: hollow cathode lamp; PSU: power supply unit; L1, L2, L3, L4 lenses; F: Flame; PMT: photomultiplier tube(b) D.C. power supply circuit used to drive the electromagnet assembly

Noise sources detected in the signals were white noise, a 50 Hz frequency (probably from the hollow cathode lamp's DC power supply), a flame feature frequency, and a 100 Hz frequency, which is thought to be due to field modulation<sup>4</sup>. The 50Hz frequency is generated outside the AMORS system by the hollow cathode lamp's power supply, and the flame feature frequency and field modulation frequency are generated in the AMORS system by the sample. These latter two interference frequencies suffer from noise introduced onto them as a result of the sample introduction system, which is not continuous, but delivers samples only intermittently into the AMOR system.

The electrical signal waveforms derived from these two rays form the inputs to a Solartron 1200 signal processor. Auto-correlation and cross-correlation studies of the noise sources were carried out. Auto-correlation of the noise sources was carried out to detect interference frequencies buried in noise. Frequencies which are not of interest may then be removed so that the signal-to-noise ratio can be improved. Frequencies found to be derived from the analytical signal may then be cross-correlated and possibly used for further analytical study. Cross-correlation of the waveforms of both rays reveal frequencies derived from a common source, where the source forms one of the input waveforms. The phase relationship between the waveforms can hence be found. If the maximum signal is at t=0 the two frequencies are in phase and at other times they are out of phase. These frequencies can either be attenuated or used to improve the signal-to-noise ratio.

Cross-Correlation Noise Studies in Atomic Magnet-Optic..., A. T. INCE,

# Results

## a) White Noise

With neither magnetic field nor a sample present in the system and the hollow cathode lamp switched on, noise power spectra of white noise on channels A and B were recorded. These are shown in Figures 2 (a)-(b), respectively. Their cross-correlation function in Figure 2 (c) indicates that no correlation exists at any time, which is characteristic of random noise.



Figure 2. Cross-correlation of white noise on channel A and B, with blank sample.

(a)-(b) Noise power spectra of channel A and B, respectively

(c) Cross-correlation of channel A and B

## b) 50 Hz Interference Frequency

The introduction of a 10 ppm magnesium sample at a magnetic field of 0.55 T causes attenuation of the auto-correlation functions in Figures 3 (a)-(b), the channel B auto-correlation function more so than that of channel A. The cross-correlation function in Figure 3(c) indicates no phase change between the two channels. The 50 Hz frequency was removed from the spectrum by replacing the hollow cathode lamp's power supply with a pure dc rechargeable lead-acid battery supply, as described previously<sup>8</sup>.



Figure 3. Auto-and cross-correlation of the 50 Hz waveform on channel A and B in the  $45^{0}$  offset polariser configuration. Atomic absorption mode, 10 ppm Mg.

(a)-(b) Auto-correlation of channel A and B respectively.

(c) Cross-correlation of channel A and B.

#### c) Flame Feature Frequency

Varying the flame parameters revealed that this was an audio frequency caused by the flow of gases from the flame past the metal cooling sheets. The 100 Hz magnetic field modulation noise was attenuated in the spectrum using a 33 mF capacitor to prevent its interference. During studies of the flame frequency, a magnetic field strength of 0.55 T was used. Polaroid pictures were also taken of the trace of channel A (upper trace) and channel B (lower trace) on the storage oscilloscope (Tekronix 466). Figures 4 (a)-(c) are traces of these Polaroid pictures for 50 ppm, 80 ppm and 100 ppm magnesium concentrations, respectively. The channel B signal is attenuated with an increase in concentration, whereas the channel A signal increases linearly with concentration. This is attributed to the dichroic and rotation effects described previously<sup>8</sup>. Correlation studies were carried out at 40 ppm magnesium as this effect is not significant at this concentration. Auto-correlation functions of the channel A and B waveforms are shown in Figures 5 (a)-(b), respectively. They also show that the channel A auto-correlation function amplitude is greater than that of channel B. The cross-correlation function of the channels (Figure 5 (c)) indicates that the time interval between each peak corresponds to 30.5 Hz. This is the frequency of the flame feature. Distortion of the cross-correlation function is due to variations in the gas flow in the sample introduction system. The flame feature frequency is carried in phase through both channels, but has a low signal-to-noise ratio due to the quality of the sample introduction system.

Cross-Correlation Noise Studies in Atomic Magnet-Optic..., A. T. İNCE,



**Figure 4.** Waveforms showing phase and amplitude of the flame feature frequency on channel A and B, in 450 offset polariser configuration. Field strength 0.55 T; (a) 50 ppm Mg, (b) 80 ppm Mg, (c) 100 ppm Mg.

#### d) Correlation Study of the Magnetic Field Modulation Frequency

This interference frequency is thought to arise from incidental modulation of the AMOR signal<sup>4</sup> from the mains. This, however, is difficult to check since the mains signal is also transmitted along with the signals. The flame frequency was removed from the spectrum by narrowing the bandwidth of the Solartron 1200 signal processor to 60 Hz-260 Hz. For a 20 ppm magnesium and field strength of 0.55 T, the spectra are shown in Figures 6 (a)-(e). The power spectra are shown in 6 (a)-(b) since the analyses were all carried out from a start frequency of 60 Hz to isolate the 100 Hz frequency. Thus this 60 Hz start frequency should be added to the frequency (40 Hz) determined from the auto-and cross-correlation functions of channels A and B, Figures 6 (c)-(e), respectively. Despite the low signal-to-noise ratio of the channel B auto-correlation function, the 100 Hz signal is still observed. The cross-correlation function (Figure 6 (e)) indicates that this

frequency is in phase in both channels. However, its maximum amplitude is lower than the flame feature frequency due to the low amplitude of the interfering frequency and noise from the sample introduction system.



**Figure 5.** Auto-and cross-correlation of the flame feature frequency on channel A and channel B in the 450 offset polariser configuration. Field strength 0.55 T, 40 ppm Mg. (a)-(b) Auto-correlation of channel A and B, respectively. (c) Cross-correlation of channel A and B.

## Conclusion

In this correlation study, the phase and amplitude of four noise sources carried by the channel A and B AMOR signals were correlated. They were all carried through the AMORS system in phase.

It was observed that the two interference frequencies generated by the analyte had low amplitudes and were distorted by fluctuation noise caused by the sample introduction system. The interference frequencies were found to be carried in phase through the detection system. This means that they may easily be removed by inversion of one waveform, followed by their addition.

The correlation studies proved to be a successful method of investigating the relationships of waveforms and their possible sources of generation.





(a)-(b) Noise power spectra of cahannel A and B, respectively.

(c)-(d) Auto-correlation of channel A and B, respectively.

(e) Cross-correlation of channel A and B.

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#### References

- 1. A. T. Ince, R. D. Snook and J. B. Dawson, Anal. Proc. 29, 59, (1992).
- 2. A. T. Ince, J. B. Dawson and R. D. Snook, J. Anal. At. Spectrom., 11, 967, (1996).
- 3. A. T. Ince, R. D. Snook and J. B. Dawson, Turkish Journal of Chemistry, 24 (1), 43, (2000).
- 4. A. T. Ince and R. Ince, Spectrochimica Acta, Part B, 55, 959, July, (2000).
- 5. G. Chiorboli and M. Fontanili, IEEE Trans. on Instr. & Meas., 48 (6), 1282, December (1999).
- 6. Ramirez, R.W., "The FFT fundamentals and concepts", Prentice Hall, London, (1983).
- Wellstead, P.E., "Methods and applications of digital spectral techniques", Technical report 008/83, Solarton Instruments, Manchester, (1983).
- 8. Ahmet Ince, Ph.D. Thesis, Dept. instrumentation & analytical science, UMIST, England, (1992).