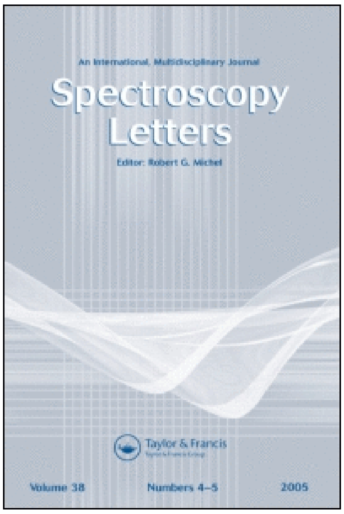

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SAMPLE INPUT MODULATION AND LOCK-IN-AMPLIFIER DETECTION FOR SIGNAL-TO-NOISE RATIO IMPROVEMENT IN INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

Key Words: Sample input modulation, Lock-in-Amplifier Detection, ICP Atomic Emission Spectroscopy

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Abstract: The effect of modulation of the sample atomization, accomplished by pulsing the nebulizer pump, and lock-in-amplifier (LIA) detection of the modulated output signal of an ICP atomic emission spectrometer is studied. The time constant of the nebulizer spray chamber allows a maximum modulation frequency of approximately 2 Hz, but optimum performance for this system is found at a modulation frequency of approximately 1 Hz. A signal-to-noise (SNR) ratio improvement approaching a factor of three is found for the arrangement employed. It is proposed that more rapid modulation, achievable through the use of a nebulization system with a shorter time constant, should lead to even greater improvement in the SNR than was accomplished in this study. The dynamic range is improved, relative to the unmodulated system, as the detection limit is lowered without any loss of linearity at high concentrations. A linear dynamic range of greater than 4 orders of magnitude is found for the modulated system.

Introduction: A wide variety of sample introduction systems for ICP spectroscopy have been reported and reviewed over the years.[1-11] These systems include the pneumatic nebulizers of various designs, ultrasonic, hydride generation, electrothermal and a number of others. The principal focus of each of these devices is to introduce as large a percentage of the sample into the plasma with as uniform and fine a droplet delivery versus time profile as possible. Each of the numerous designs has its own strengths and weaknesses that govern the types of problems for which it is most suitable. Despite the focus on pulseless sample introduction, a recent study has shown that pulses from the sample delivery pump, including supposedly pulseless syringe pumps, result in observable noise at the pulse frequency in the emission signal, at least when Meinhard nebulizers are used.[12] While pulsed flow can be viewed as a noise source when one is attempting a dc measurement, a systematic variation can be used as the basis for signal discrimination from random noise such as a light chopper is used in dispersive infra red spectrometers.

Although the development of these rather stable, efficient sample introduction systems have led to extremely sensitive and reproducible atomic analyses with excellent linear dynamic range, the resulting atomic emission signal is dc by virtue of the constant sample introduction rate and, as such, is ultimately limited by 1/f noise. Modulation followed by lock-in-amplifier (LIA) demodulation is a commonly employed technique for signal detection because of the LIA's excellent ability to reject unwanted (noise) frequencies and the decrease in the 1/f noise contribution achieved by the signal modulation. In this paper the atomic emission signal from an inductively coupled plasma atomic spectrometer is modulated *via* pulsation of the sample nebulization and the resulting ac emission signal is detected by a commercial lock-in-amplifier in an attempt to further increase the ICP sensitivity.

Experimental: A Perkin Elmer PES-40 ICP-AES spectrometer with a maximum output power of 1 KW at 40 MHz was modified for sample input modulation by cutting the ICP pump motor 24V power supply feed and inserting the transistor switching circuit shown in Figure 1. In this figure, the function generator employed was an Interstate Electronic Corporation F33 function generator with an operating frequency range of 0.03 Hz to 3 MHz. When this circuit is engaged the ICP sample pump is turned on and off at a rate determined by the frequency setting of the function generator. The function generator was set to a triangular wave shape and its dc off set adjusted to give equal on and off times for the pump. In this way, the sample introduction consists of a square wave at the function generator frequency. This method of sample input modulation was adequate for frequencies up to about 2 Hz where signal loss due to integration by the capacitance of the nebulizer body attenuated the ac signal component to unacceptably low levels. Therefore, it was not necessary to construct a more sophisticated system capable of more rapid sample pulsing for these experiments since higher frequencies would be extensively averaged out by the nebulizer body.

The instrument operation in pulsed mode consisted of setting the monochrometer wavelength to the wavelength of maximum emission for the

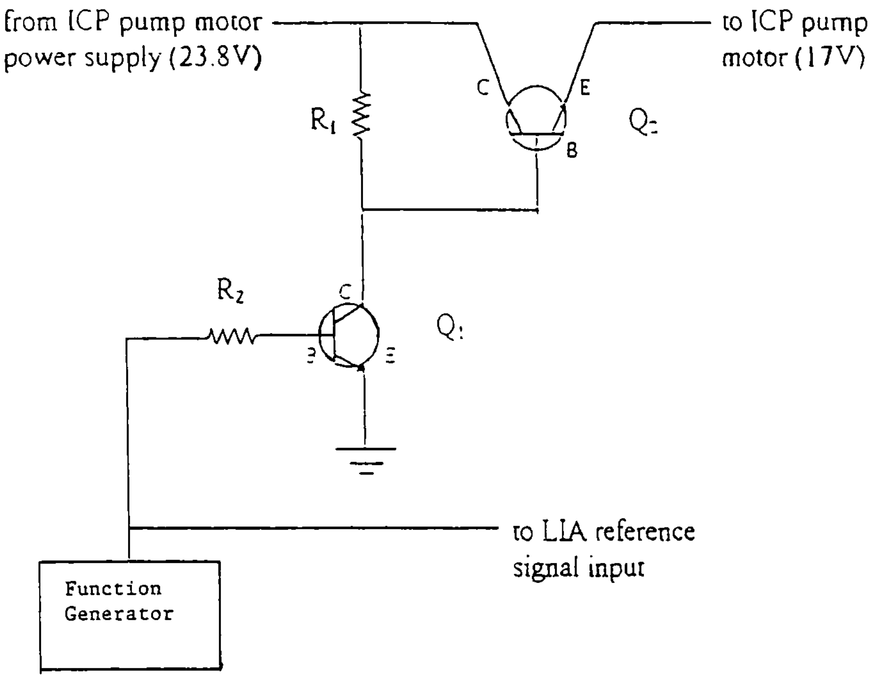

Figure 1: Electronic pump motor switch circuit. R1 = 3.9 K Ohms; R2 = 16 K Ohms; Q1 = ECG 128; Q2 = NTE 130.

element of interest and monitoring of the ac signal from the photomultiplier tube by connection of the LIA input to the recorder output of the PES-40. The PES-40 recorder output provides an operational amplifier buffered output signal from the photomultiplier tube. The time constant for this circuit is in the millisecond range and, therefore, has a negligible effect on the time response of the 1 Hz modulated signal. The maximum emission wavelength was determined each day by measurement of the emission from a 1 ppm standard, followed by setting of the monochrometer to the peak maximum obtained. A slight variation from the tabulated values for emission lines was usually noted in this process. For example, the 214.432 nm cadmium line was routinely measured as 214.436 nm on this instrument. A Princeton Applied Research model 186 lock-in-amplifier with a frequency range of from 0.5 Hz to 100 KHz was employed as the modulated signal detector. The output of the LIA was recorded on a OmniScribe model B5217-1 linear chart recorder. Each day the phase setting of the LIA was adjusted to yield a maximum output signal while observing the modulated emission from a standard 1 ppm solution. Once adjusted, that phase setting was utilized for all of the measurements on that day. However, only slight day-to-day variation of the phase setting was noted (±0.5°). To operate the system in normal mode, the pulsing circuit was simply shut off completing the power supply connection. Normal instrument operation controlled by an Amax Ps/2 30/286 computer and Perkin Elmer software (version 4.0) was then obtained as if no modification had been made to the instrument. Thus, the instrument modifications made for this study are easily and completely reversible.

All stock solutions were obtained from Environmental Express, Mt. Pleasant, S.C. as high purity ICP grade and were used without further purification. Working solutions were prepared by diluting either 10,000 or 1,000 ppm stock solutions with distilled water containing 3% nitric acid. The 3% nitric acid solution also served as the blank solution for these measurements.

Results and Discussion: Figure 2 shows the effect of sample modulation on the dc signal at the recorder output of the ICP. These data were recorded by connecting the recorder directly to the ICP recorder output. In the absence of modulation, the output signal is a dc level proportional to the emission signal. Examination of the ac signal in this figure shows that the modulated output signal is approximately triangular in shape. The triangular shape indicates time integration of the square wave input function. Because the electronic time constant of the instrument is much faster than the modulation frequency (time constant ~ 5 msec), it is apparent that the integration occurs in the nebulizer process. This is not surprising as the nebulizer employed is designed to have a significant capacitance so as to average out pump variations in the normal sample introduction procedure. While the large capacitance of the nebulizer precludes rapid pulsing of the sample introduction process, it is not so large that the principle can not be tested. The nebulizer time constant was measured to be 1.5 seconds by observing the time required for the PMT output signal to fall to 1/e of its value after shutting off the pump.

Because of attenuation of the modulated signal at frequencies that exceed the nebulizer time constant, low frequency modulation is indicated in this case. However, if the frequency is made too low, 1/f contributions to the noise increase and the low frequency limit (0.5 Hz) of the LIA is approached. To minimize the 1/f contribution and to avoid the low frequency limitation of the LIA requires a higher frequency modulation rate. Since there are competing factors involved, one favoring low frequencies and the other high frequencies, there exists an optimum modulation rate for this particular instrument arrangement that achieves some compromise between these contradictory requirements. The optimum modulation frequency was found by measuring the signal-to-noise ratio (SNR) at the LIA output as a function of modulation frequency. The maximum SNR was found to occur at a modulation frequency of approximately 1 Hz. Therefore, a 1 Hz frequency was used for all of the experiments reported below.

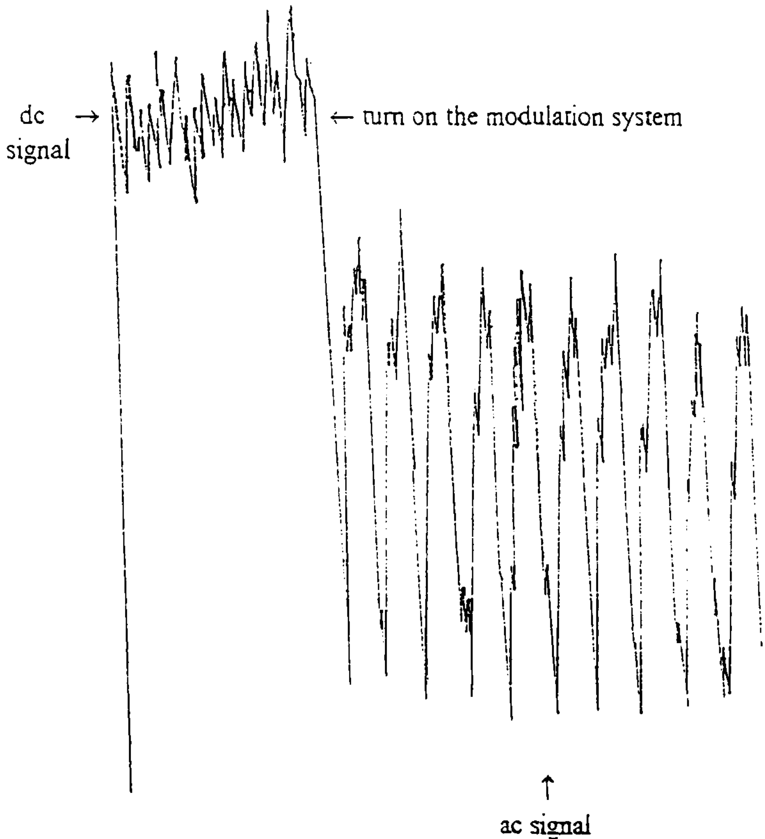

Figure 2: ICP recorder output signal with and without sample modulation.

In order to compare the performance of the modulated system with the standard, unmodulated, instrument the LIA integration time was set to 10 seconds. With a 10 second integration time, the time required to make a measurement with the LIA system was approximately equivalent to the time required to scan and acquire the spectrum with the normal instrument software. Experiments conducted with 30 second LIA integration times had SNR's larger than those with 10 second integrations by approximately the square root of the integration time ratio, as expected, but because 30 second integrations required considerably longer acquisition time for the LIA to reach a stable reading than the unmodulated instrument acquisition time, a 30 second integration time was considered to be too long for evaluation purposes. All results reported below were obtained with a LIA time constant of 10 seconds.

Figure 3 shows spectra of a 0.05 ppm cadmium solutions ver the spectral range 214.380 to 214.490. Spectrum A is the spectrum acquired under normal, unmodulated conditions using the standard instrument parameters for cadmium. Spectrum B shows the point-by-point spectrum acquired with a 1 Hz modulation rate by successively varying the monochrometer wavelength setting while recording the output of the LIA with all other instrument parameters identical to those of spectrum A. While the SNR improvement shown in this figure appears dramatic, the actual improvement is less than appears. The reason for this is that spectrum B, being acquired in a point-by-point basis actually represents a considerably longer integration time than the 10 second LIA integration would suggest. To fairly compare these spectra would require that the non-modulated acquisition be time averaged for the same total experiment time as the modulated spectrum. Since the system employed did not provide for spectral ensemble averaging, that comparison was not performed.

In order to make a more reasonable comparison, the SNR at the emission maximum was measured as a function of concentration under both modulated and unmodulated conditions with approximately equal total measurement time for each data point. The SNR was computed manually from the recorder traces in the case of the modulated system and from the computer stored spectrum for the unmodulated data. Figure 4 shows a plot of the observed SNR for measurements in the low ppm range. An average SNR improvement of about a factor of 3 is shown in this figure. The data points in Figure 4 are the average of 9 measurements, the error bars are the 95% confidence interval from those 9 measurements and the lines are the least squares lines through the points and 0,0. While the error bars on the modulated data are somewhat larger in absolute value than those on the unmodulated measurements, they are smaller on a percentage basis. For example, at 0.03 ppm, the unmodulated error bar is approximately 50% while the modulated one is 40%. One should also note, that no unmodulated value is reported for concentrations below 0.03 ppm while the modulated data extends to 0.01 ppm. This is because below 0.03 ppm, no peak could be identified above the noise and, therefore, no signal value could be determined. This is not surprising since the extrapolated SNR of a 0.01 ppm sample is expected to be below 1. If one examines the 0.05 ppm spectrum shown in Figure 3 it is obvious that a further factor of 5 decrease in signal size would result in the signal being indistinguishable from the noise. Thus, no value is recorded below 0.03 ppm in the unmodulated system.

Figure 5 shows the observed signal, in arbitrary units, for sample concentrations varying from 0.01 ppm to 500 ppm for the modulated system and from 0.03 ppm to 500 ppm for the unmodulated system. Examination of this

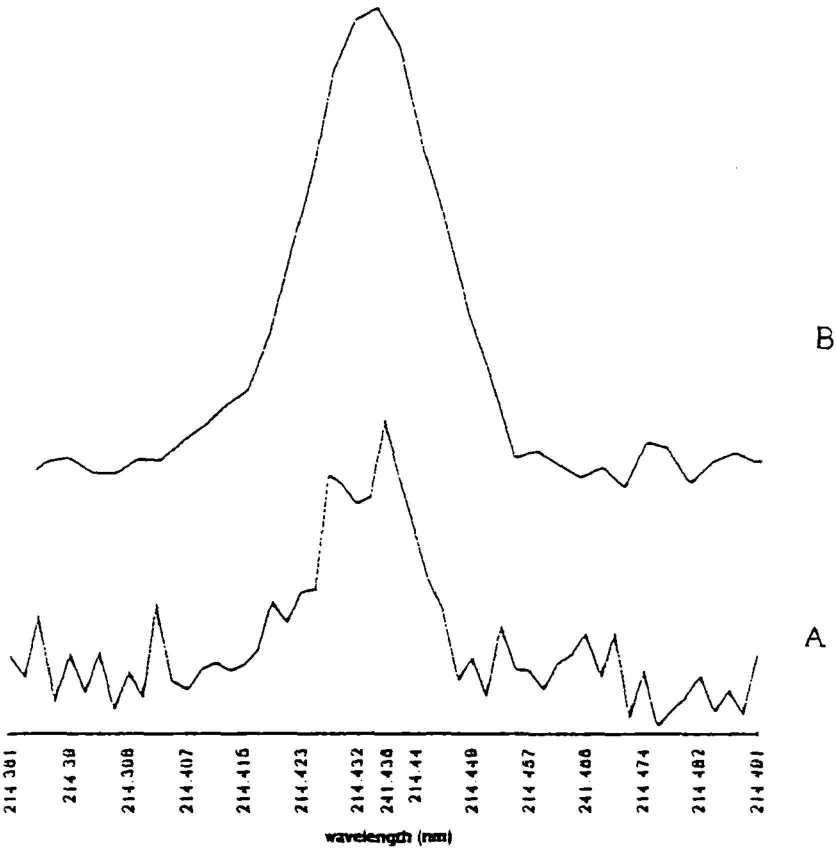

Figure 3: A. Unmodulated ICP emission signal vs wavelength for 0.05 ppm Cd^{2+} solution.
B. 1 Hz modulated signal versus wavelength for 0.05 ppm Cd^{2+} solution.

figure shows that the linear dynamic range of the spectrometer is not adversely affected by the modulation process. In fact, since concentrations as low as 0.01 ppm could be observed in the modulated system while 0.03 ppm was the lowest concentration observable with the unmodulated system, the linear dynamic range is actually somewhat greater for the LIA detected signals. Therefore, the overall SNR performance of the instrument is improved without compromise in the range of concentrations observable. However, since the instrument software does not provide for single wavelength monitoring, the data analysis is somewhat more tedious as the signal sizes and SNR's must be manually measured from the

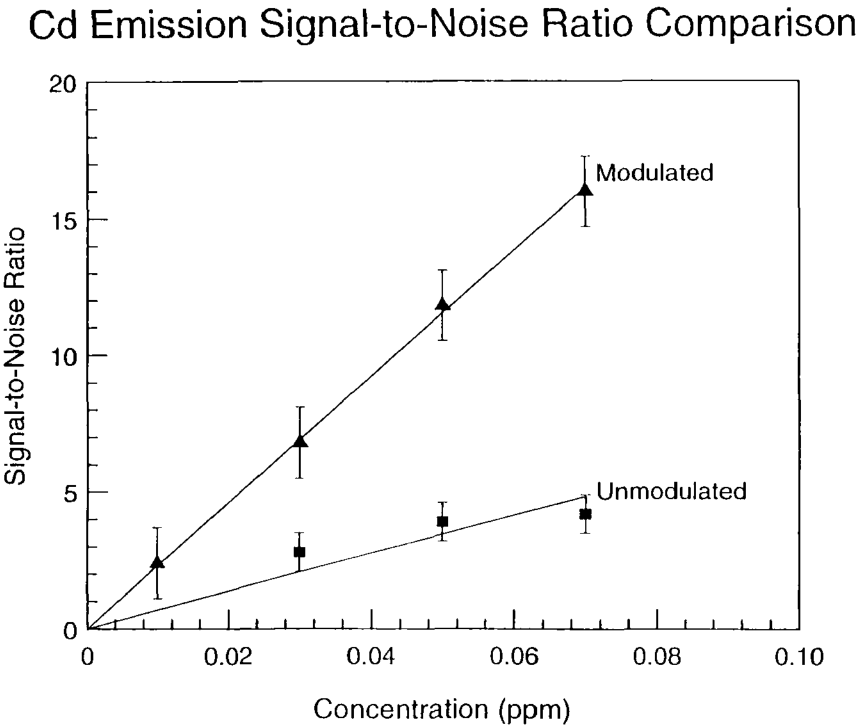

Figure 4: SNR comparison modulated vs unmodulated signals at low concentration. Modulation rate 1 Hz. Data points average of 9 measurements. Error bars 95% confidence interval.

recorder traces. This problem can, obviously, be overcome in the future with revised software or, as described below, by more rapid modulation that allows spectral scanning.

Conclusions: The results reported in this work show that SNR improvement can be obtained by sample modulation followed by LIA detection of the ac signal. The system employed in this study is far from optimum and, therefore, the modest factor of 3 SNR improvement could probably be exceeded with a better designed system. The long integration time of the nebulizer employed in this work limited the operating frequency to a very low value where the LIA performance was marginal. Thus, one could anticipate that the use of a very low volume nebulizer or direct sample introduction to allow rapid pulsing of the sample and, therefore, operation of the LIA at a higher frequency where the 1/f noise would be lower and

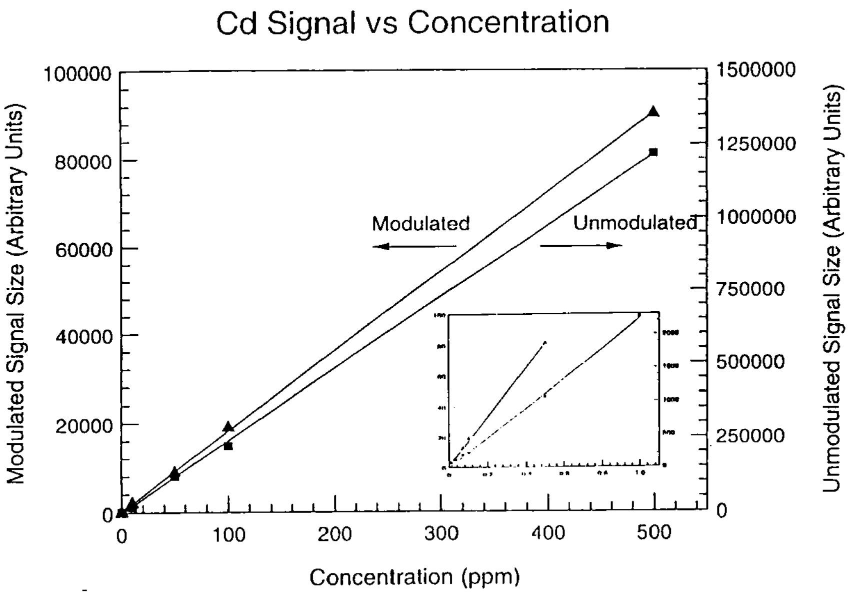

Figure 5: Signal vs concentration comparison modulated vs unmodulated. 1 Hz modulation rate.

the amplifier performance enhanced should lead to further improvement in the SNR. Rapid pulsing of the sample introduction would, however, require a mechanical chopper rather than pulsed power interruption to the pump motor. This is because the start-up and shut-off time of the pump would become another source of sample input averaging at high frequencies. In addition to providing more rapid input modulation, a suitably designed chopper would allow cycling of the input stream between sample and blank so that changes in the background signal would be minimized. The design tested in this report does not allow for such cycling and, therefore, some of the noise probably arises from the fact that the ac signal does not truly correspond to the difference between a sample and a blank but rather to the difference between a sample and no input at all. Finally, a rapidly modulated input would allow operation of the LIA at shorter integration times. With a shorter LIA integration time, it would be possible to scan the spectral region of interest instead of requiring that the monochrometer be set to a predetermined fixed wavelength. This would alleviate the problem of wavelength error and would allow use of the instrument software for analysis of the data.

Despite the limitations and suggested improvements to the system mentioned above, the simple sample modulation technique did provide improvement in the sample detection limit and comparable dynamic range and accuracy performance compared to the unmodulated instrument. Further investigation and development of modulated systems would seem to be justified.

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