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DESIGN AND PERFORMANCE OF A MASS-FLOW-MODULATED DETECTOR FOR GAS CHROMATOGRAPHY

GREGORY WELLS
Varian Instrument Group, Walnut Creek Division, Walnut Creek, CA 94598 (U.S.A.)
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SUMMARY

The advantages of signal modulation for improving the signal-to-noise ratio in mass-flow-rate dependent detectors for gas chromatography is discussed. A novel means of sample mass-flow modulation is demonstrated, which employs pneumatic phase shifting to double the peak response. A further increase in response by time compression of the modulation cycle is also shown. An increase in signal-to-noise by almost a factor of five is demonstrated for a flame photometric detector.

INTRODUCTION

It is common practice to reduce the noise and drift from a transducer by modulating the signal that enters the device. Subsequent narrow-band amplification followed by synchronous demodulation can result in a significant reduction in noise. The noise reduction is best obtained if only the signal of interest is modulated and not the noise.

Most detectors that are used in gas chromatography (GC) have large amounts of low frequency noise present, which is often the predominant noise source[1]. Modulating the sample flow into the detector results in a signal in which the sample response is modulated, but the inherent detector noise is not. This principle of modulation was first applied to chromatography by Lovelock[2] who used an electron-capture detector as the transducer. The sample flow was modulated by periodically destroying a portion of the sample with another electron-capture cell so that it would not respond in the transducer. The design criteria for such a system has been described in detail by Wells[3]. Clouser and Craven[4] have described a modulated thermal conductivity detector in which the sample and reference gases alternately flow over the same detector filament.

The modulated detector arrangements described thus far have several important limitations. They have only been used with concentration dependent detectors (electron-capture, thermal conductivity) and half of the sample is either destroyed or vented during the reference portion of the modulation cycle, thus wasting 50% of the potential response. This paper describes a method of sample modulation that can be applied to mass-flow-rate sensitive detectors and which uses all of the available

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sample, thus doubling the maximum response during a modulation cycle. In addition, it is possible to take the solute present during the sample portion of the modulation cycle and force it into the detector at twice its normal flow-rate, thus again doubling the maximum response. This increase in the signal response by a factor of four, along with the reduction in noise due to tuned amplification and synchronous demodulation, offers a significant improvement in the signal-to-noise ratio.

EXPERIMENTAL

The injection system has been described previously[5,6] and is capable of producing Gaussian-shaped peaks from 50 to 3000 msec in width. The detectors used were a Varian flame ionization detector and a flame photometric detector. The output current from these detectors was amplified with a Keithley Model 427 current amplifier, which has a variable time constant. The signal from the amplifier was stored in a Nicolet 1170 signal averager interfaced to a HP 1000 computer, or acquired directly with a HP 2250 20-kHz analog-to-digital converter interfaced directly to the computer. Further amplification and synchronous demodulation was accomplished with an Ithaco 391A lock-in amplifier.

DISCUSSION

Theory of modulation

An overview of the principles of modulation can be obtained by reference to Fig. 1. The ideal modulator (Fig. 1A) would vary the sample signal between the normal value (dashed line) and some reference minimum, preferably the detector background, while not affecting the detector noise either during the sample or reference portion of the cycle. This converts the sample signal into an a.c. signal (Fig. 1B), while leaving the detector noise at nearly d.c. The a.c. signal (sample) can then be amplified while leaving the d.c. (detector noise) unchanged. Synchronous demodulation (Fig. 1C) followed by low pass filtering (Fig. 1D) results in the recovery of the original waveform, with an increase in signal-to-noise ratio.

There are several important factors that must be understood in order to apply this concept effectively to GC detectors. The larger the degree of modulation, the

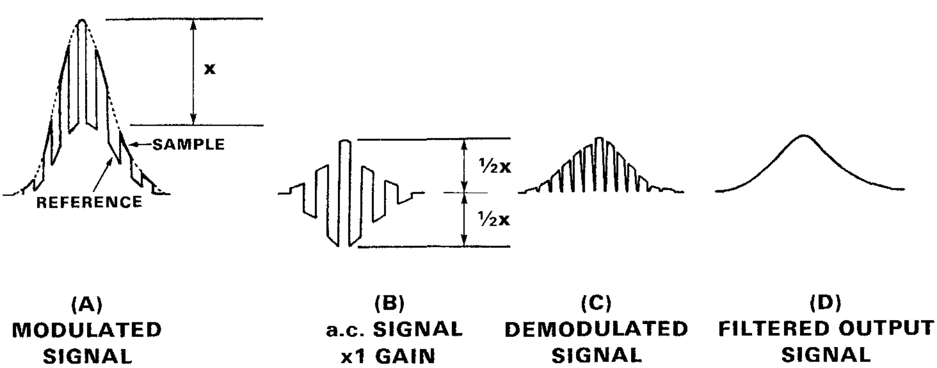

Fig. 1. (A) Modulated signal; (B) a.c. signal from amplifier, ×1 gain; (C) synchronously demodulated signal; (D) filtered output signal.

larger is the a.c. signal that will be amplified. This means that during the reference portion of the modulation cycle no sample should enter the detector, so that the reference signal is comprised only of the detector noise.

To quantitate the foregoing concepts better, let us assume that the original signal has a Gaussian shape and a width at half height of $W_{1/2}$. It can be shown[7] that in order to maintain a 98% peak height fidelity the detector time constant, τ, must be:

$$\tau \leqslant W_{1/2}/10 \quad (1)$$

This time constant implies a frequency (or information) bandwidth[8] of:

$$\Delta f_S = \frac{1}{2\pi\tau} \quad (2)$$

where the subscript refers to the signal. Thus, in order to have less than a 2% loss in fidelity the electronics must be capable of passing frequencies in a bandwidth of

$$\Delta f_S = \frac{5}{\pi W_{1/2}} \quad (3)$$

For example, a 1-sec wide peak can be synthesized by a Fourier expansion[9] which includes all signal frequencies within a bandwidth of $\Delta f_S = 1.6$ Hz.

The process of modulation can be thought of as multiplying each of the signal frequencies within Δf_S by a modulator, or carrier, waveform of frequency f_C. For the purpose of illustration, let us choose a representative signal frequency:

$$S(t) = A_S \cos(\omega_S t) \quad (4)$$

and multiply it by the carrier frequency:

$$C(t) = A_C \cos(\omega_C t) \quad (5)$$

where $\omega_S = f_S 2\pi$ and $\omega_C = f_C 2\pi$.

The result is a modulated signal:

$$M(t) = S(t) \cdot C(t) = \frac{A_C A_S}{2} \cos[(\omega_C - \omega_S)t] + \frac{A_C A_S}{2} \cos[(\omega_C + \omega_S)t] \quad (6)$$

The effect of this can be seen in Fig. 2A, which shows the Fourier transform components of the signal in frequency space.

The information in the original signal, the Gaussian shaped peak, which can be described by the frequencies within the bandwidth $\Delta\omega_C$, is moved by the process of modulation to higher frequencies around ω_C. Upper, $\omega_C + \omega_S$, and lower, $\omega_C - \omega_S$, sideband frequencies are thus created. The detector noise which was not modulated still remains at the lower frequencies.

Amplifying the signal with an a.c. amplifier (BW, Fig. 2A) of bandwidth $2\Delta\omega_S$ and center frequency ω_C, results in the signal being selectively amplified but not the low frequency detector noise (Fig. 2B). The degree to which the signal-to-noise ratio is increased depends on $\Delta\omega_S$, ω_C and the detector noise bandwidth.

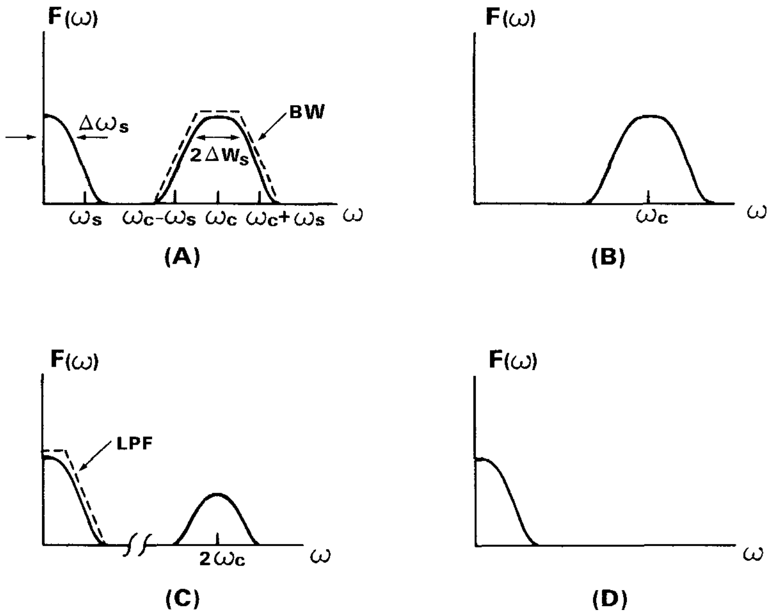

Fig. 2. Frequency space representations of signals. (A) Original signal frequency distribution $\Delta\omega_S$ and modulated distribution $2\Delta\omega_S$; (B) frequency distribution after a.c. amplification; (C) frequency distribution after synchronous demodulation; (D) frequency distribution after low pass filtering.

The original signal can be recovered by synchronous demodulation, which is equivalent to multiplying the modulated signal, eqn. 6, by a reference frequency of the form in eqn. 5, and having the same phase. The result is the demodulated signal:

$$D(t) = M(t) \cdot C(t) = A_S \frac{A_C^2}{2} \cos(\omega_S t) + A_S \frac{A_C^2}{2} \cos(\omega_S t)\cos(2\omega_C t) \quad (7)$$

The first term is the original signal, while the second term represents higher order

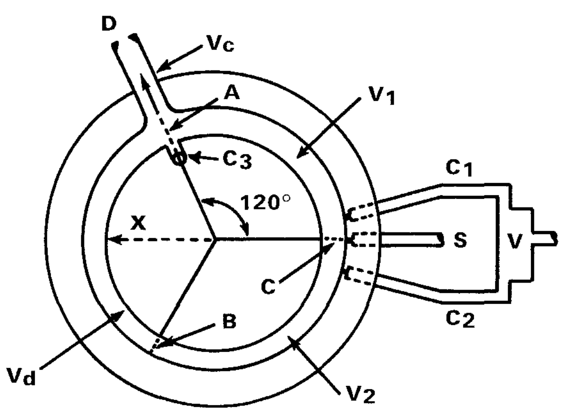

Fig. 3. Fluid modulator cell. S = Sample inlet; C1, C2, and C3 = control flow ports; D = detector flame tip.

harmonics (upper and lower sidebands centered at $2\omega_C$) which are easily removed by low pass filtering (LPF, Figs. 2C and 2D).

Non-synchronous noise inputs to the demodulator which do not have a fixed phase relative to the reference frequency are attenuated, even though they may have the same frequency as the reference. For practical reasons it is easier to use a square wave[10] as the reference waveform. The results, however, are unchanged since only the fundamental (eqn. 5) of the square wave makes any significant contribution to the demodulated signal. In addition, information theory[11] requires that the modulation frequency, ω_C, be at least twice that of the highest frequency component (or bandwidth) of the original signal.

Modulation cell

From the discussions in the previous section, it is clear that if one wishes to have a modulated detector capable of handling a 1-sec wide peak, that a modulation frequency of at least 3.2 Hz is required. A higher frequency would be desirable from the viewpoint of signal-to-noise ratio. For the purpose of this work, a frequency of 5 Hz was choosen.

The pneumatic modulator cell used in this study is shown in Fig. 3. It consists of a circular channel with a sample inlet, S, and a sample outlet, D, being either the flame tip of a flame photometric or a flame ionization detector. The body is fabricated from stainless steel and the top of the channel is sealed with a thick gasket made of polyimide. A flow of control gas, the same as the sample carrier gas, is alternately applied at ports C1 and C2. The gas flow to the control ports is determined by a pressure regulator and a restrictor. Flow is applied to C1 and C2 alternately, and for equal time intervals by means of a three-way valve (Linear Dynamics). if the sample flow F_S, from the column is small compared with the control flow, F_C, then when flow is applied to C1 a flow of $F_C/2$ of pure carrier gas enters volume V_1, while a flow of $F_C/2 + F_S$ enters V_2. If the sample mass flow were to be measured awt point A (Fig. 3) it would be modulated at a frequency, f_C, determined by the value V. The mass flow at point B would be similar, except that it would be phase-shifted by 180°, or $1/2f_C$ in time. If an additional delay volume, V_d ($V_d = V_1 = V_2$), is introduced after V_2, then the sample mass flow through V_2, when measured at point A, is phase-shifted by 180°. The result is that the sample flows through V_1 and V_2 arrive at point A in phase, and the instantaneous mass flow at point D will be twice that through either V_1 or V_2.

Given a modulation frequency, f_C, and control flow, F_C, the volume, V_1, is given by:

$$V_1 = F_C/4f_C \tag{8}$$

This is the volume occupied by either the sample or reference gas during one half of the modulation cycle. Thus, for $F_C = 0.167$ ml/sec and $f_C = 5$ Hz, $V_1 = 8$ μl. The cross-sectional area at the exit point A is twice that of the channel so as to maintain equal flows in the channels at all times. A further increase in peak mass flow can be obtained by compressing the time required for the sample mass to flow through the detector flame tip.

The volume, V_C, between point A and the end of the flame tip, D, is made equal to $2V_1$, so that the entire mass of solute during the sample portion of the modulation cycle will at some time be contained within this volume. If, at this time, an additional pulsed flow of carrier gas equal to F_C is applied at control port C3 for a period of $1/4 f_C$ sec, the same sample mass in V_C will be forced into the detector at twice the normal flow-rate. The result of this peak compression is to double again the peak mass flow of the sample portion of the modulation cycle. Since most mass-flow-rate sensitive detectors are not extremely dependent upon the carrier gas flow-rate, the inherent detector noise will be unchaged by the additional flow of the gas used to compress this part of the modulation cycle.

RESULTS

Fig. 4A shows the output from the modulator cell measured at point A (Fig. 3) with a flame ionization detector using butane as the sample. The modulation frequency is 5 Hz. When the exit port is located at point X, the flows through V_1 and V_2 are 180° out of phase. The result shown in Fig. 4B is a signal whose average value is approximately half of the peak value in Fig. 4A, and with a ripple frequency of 10 Hz. Fig. 5 shows a 2-sec wide chromatographic peak of butane modulated at 5 Hz. Also shown is the unmodulated peak that is obtained by turning off the three-way valve that directs the control gas to C1 and C2 (Fig. 3). The doubling of the peak envelope can be clearly seen.

Next, a flame photometric detector operating in the sulfur mode was used. The modulated signal is shown in Fig. 6A for a sample of SF_6. Because the sulfur response depends on the square of the mass flow, a faster time constant (1 msec) is needed[1] on the current amplifier and, hence, more noise can be seen on the signal. Partial peak comporession is obtained when the volume V_C is half of what is needed to trap all of the sample (*i.e.*, when $V_C = V_1$). Then only the last half of the sample cycle is affected when a comporession flow is pulsed on at point C3 (Fig. 3). The result of doubling the mass flow of the latter half of the sample cycle can be seen in Fig. 6B. Note the peak height increases by a factor of four because of the quadratic sulfur response. Fig. 7 shows the response to SF_6 in the flame photometric detector using both phase-shifting and full peak compression ($V_C = 2V_1$). Also shown is the re-

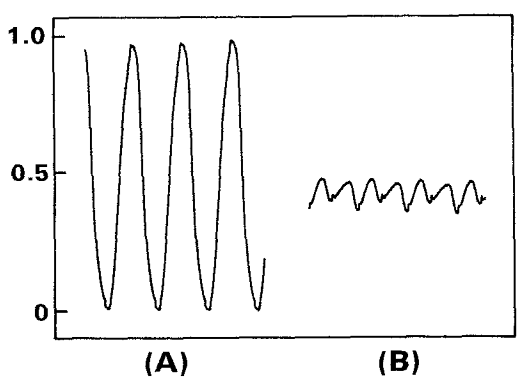

Fig. 4. (A) Flame ionization detector response measured at point A of modulator cell; (B) flame ionization detector response measured at point X of cell. Modulation frequency, 5 Hz; sample, butane.

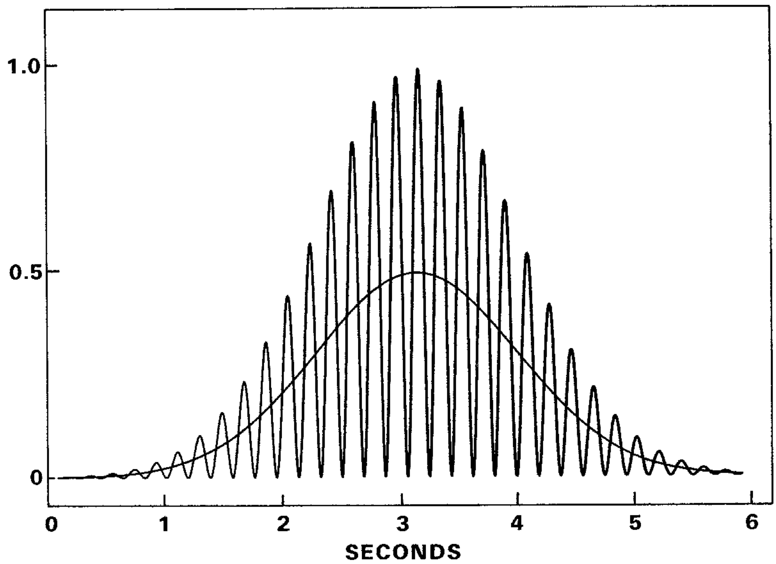

Fig. 5. Flame ionization detector response to modulated butane peak and unmodulated peak.

sponse to the same sample obtained by turning off both of the valves so that no compression or modulation occurs. The increase in the envelope of the modulated signal is nearly a factor of sixteen times the unmodulated signal.

The noise power frequency distribution from the flame photometric detector was obtained by taking the Fourier transform of the detector background signal. A 300-msec time constant was used on the current amplifier and the data was digitized at a rate of 20 Hz. The results shown in Fig. 8A indicate that the majority of the noise power is located below 2 Hz. The results of a similar noise measurement made at the output of the lock-in amplifier, using a 5-Hz modulation frequency and a time constant of 400 msec, is shown in Fig. 8B. No time compression was used for these measurements. The absolute response of the two systems to a given amount of sample is different due to the additional gain in the lock-in amplifier. Therefore, before Four-

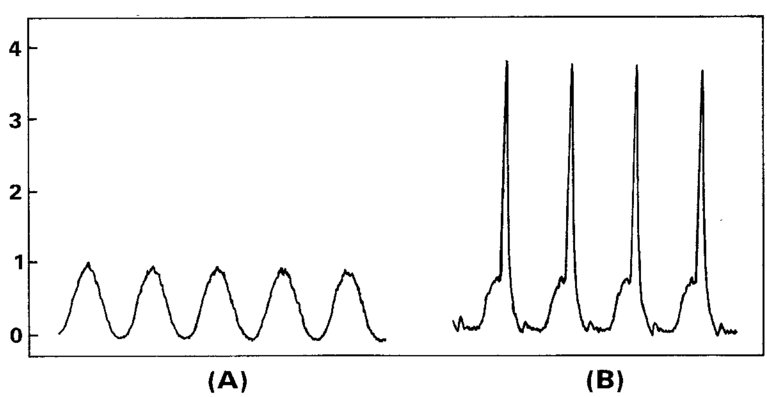

Fig. 6. (A) Flame photometric detector response to modulated flow of SF_6; (B) flame photometric detector response to modulated flow of SF_6 with one-half of peak undergoing time compression.

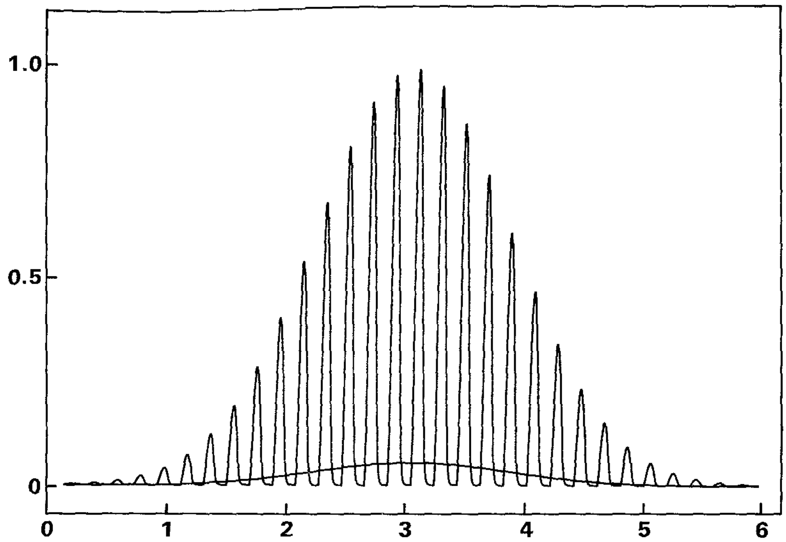

Fig. 7. Flame photometric detector response to modulated and fully time compressed SF_6 peak, and unmodulated peak.

ier transforming, the digitized detector background signal from the lock-in was multiplied by a normalization factor. This factor is the ratio of the peak response to a fixed amount of SF_6 measured from the current amplifier, to the peak response to the same amount of SF_6 measured from the lock-in. Thus, the data in Fig. 8B shows the noise power ditribution measured in the modulated system under the conditions of equal response (sensitivity) to the same amount of sample. The results show a significant reduction in the low frequency noise. To obtain a more quantitative value for the improvement in the signal-to-noise ratio (noise reduction at a constant signal), the root mean squares of the digitized values of the background signals were calculated. The resulting ratio of noise between the unmodulated and the modulated systems was found to be 4.8. Thus, an increase in signal-to-noise of almost five was obtained in a flame photometric detector by modulating at 5 Hz and using phase-shifting to double the peak mass flow into the detector.

CONCLUSION

Further improvements in signal-to-noise can be obtained by increasing the modulation frequency, and using a tuned amplifier and filters designed specifically for the modulation frequency and signal bandwidth that is used. The time compression of the sample portion of the modulation cycle would effect a further improvement. This approach is not limited to doubling the mass flow. The real limitation is the comporession flow at which the detector noise begins to be affected. Diffusion and mixing effects in the cell and flame tip will also limit the sharpness of the modulation peak produced by flow compression. However, to fully exploit this potential, a sample-and-hold synchronous detector is needed. This would make it possible for

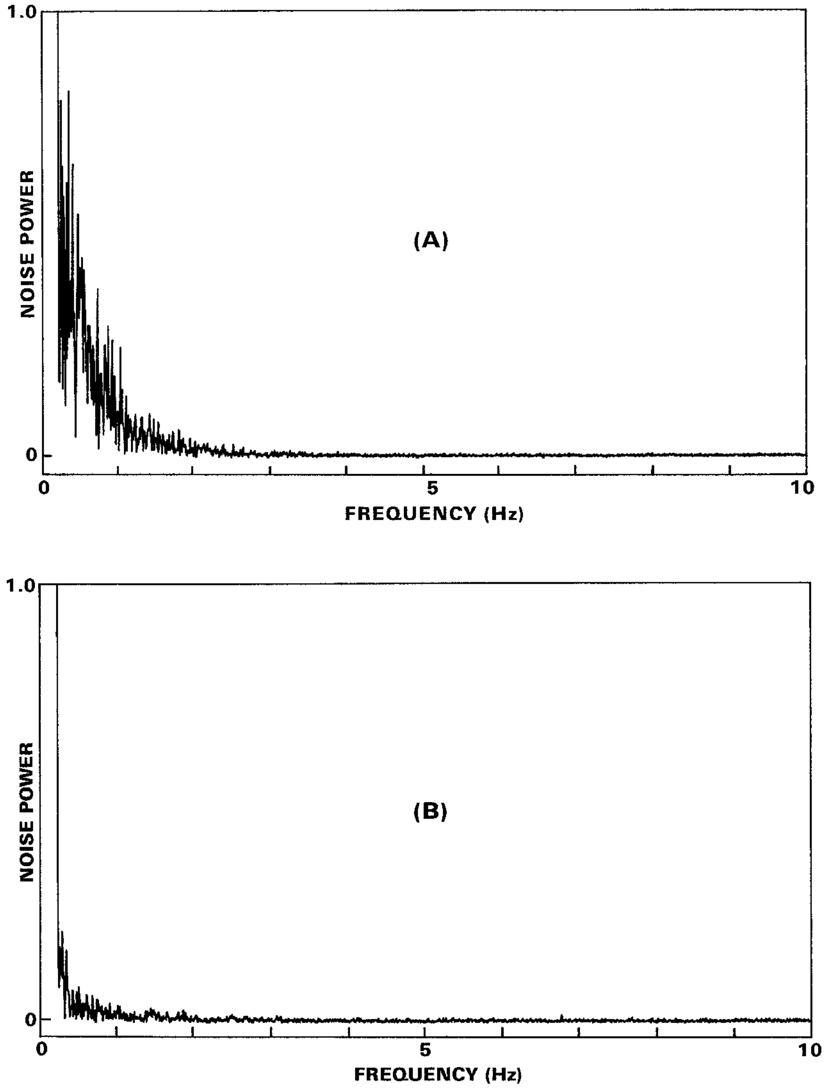

Fig. 8. (A) Noise power frequency distribution from current amplifier, 300-msec time constant; (B) noise power frequency distribution from lock-in amplifier, 5-Hz modulation frequency, 400-msec time constant, normalized to have same sample sensitivity as (A).

the demodulator to respond to the poeak of the modulation cycle where the signal-to-noise is the greatest.

The methods described in this work are applicable to any detector for GC that is fast enough to respond to the modulated mass flow. Such detectors are the flame ionization detector and flame photometric detector for sulfur, phosphorus, and chlorine[12].

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