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## THE SIGNAL-TO-NOISE RATIO MEASUREMENT IN CHLOROFORM DETECTION IN THE PRESENCE OF KRYPTON BUFFER GAS BY LASER PHOTOACOUSTIC METHOD

# ИЗМЕРЕНИЕ СООТНОШЕНИЯ СИГНАЛА К ШУМУ В ОБНАРУЖЕНИИ ХЛОРОФОРМА В ПРИСУТСТВИИ КРИПТОННОГО БУФЕРНОГО ГАЗА ЛАЗЕРНЫМ ФОТОАКУСТИЧЕСКИМ МЕТОДОМ

#### M.R. Mohebbifar

#### М.Р. Мохебби Фар

Department of Physics, Faculty of Science, Malayer University, Malayer 65719-95863, Iran

Кафедра Физики, Факультет Науки, Университет Малайера, Малайер 65719-95863, Иран

E-mail: mmohebifar@gmail.com

#### Abstract

The signal-to-noise ratio is a measure used in engineering and science that compares the level of a desired signal to the level of background noise. This parameter is one of the main features of the spectrometer devices. In this experimental study, a homemade photoacoustic layout used to detect chloroform vapour in the presence of krypton buffer gas. The system limit of detection for detecting chloroform was measured 475ppb at the 0.49W carbon dioxide laser power, 605Hz resonant frequency and in the presence of 1bar krypton gas. Also the system signal-to-noise ratio variations for 690 mTorr chloroform vapours in the presence of three buffer gases (krypton,  $N_2$  and He) at the various laser power and barometric pressure was measured. Results show that signal-to-noise ratio increase, when the carbon dioxide laser power increases. Also when He used as buffer gas, signal-to-noise ratio is the lowest.

#### Аннотация

Отношение сигнал/шум является мерой, используемой в технике и науке, которая сравнивает уровень полезного сигнала с уровнем фонового шума. Этот параметр является одной из основных особенностей приборов спектрометра. В этом экспериментальном исследовании использовалась самодельная фотоакустическая схема, используемая для обнаружения паров хлороформа в присутствии буферного газа криптона. Системный предел обнаружения для обнаружения хлороформа был измерен в 475 частей на миллиард при мощности лазера на углекислом газе мощностью 0,49 Вт, резонансной частоте 605 Гц и в присутствии 1 бар криптонового газа. Также были измерены изменения отношения сигнал/шум системы для паров хлороформа 690 мТорр в присутствии трех буферных газов (криптон, азот и гелий) при различной мощности лазера и барометрическом давлении. Результаты показывают, что отношение сигнал/шум увеличивается, когда увеличивается мощность лазера на углекислом газе. Также, когда гелий используется в качестве буферного газа, отношение сигнал/шум является самым низким.

**Key words:** Laser photoacoustic method, Signal-to-noise ratio, Krypton gas, Chloroform, Carbon dioxide laser power.



**Ключевые слова:** Лазерный фотоакустический метод, отношение сигнал/шум, криптон-газ, хлороформ, мощность лазера на углекислом газе.

#### Introduction

The photoacoustic effect was discovered by A. G. Bell in 1880 [Bell, 1880]. Bell focused intensity-modulated light (by chopped sunlight) falling on an optically absorbing solid substance produced an audible acoustic [Dumitras et.al., 2007]. Then in 1881, light absorption was detected with its acoustic effect in gases, solids and liquids by A. G. Bell [Bell, 1881] and other researchers such as J. Tyndall [Tyndall, 1881], W. C. Rontgen [Rontgen, 1881], and W. H. Preece [Preece, 1881]. After these scientists, a wide range of scientists studied the various aspects of this method [Kaiser, 1881; Dibaee et. al. 2015; Kreuzer, 1971; Xiong et. al., 2018; Mohebbifar et. al., 2014, Dewey et. al., 1973, Bruce and Pinnick, 1977; Terhune and Anderson, 1977. The high selectivity and sensitivity, high accuracy and precision, large dynamic range, good temporal resolution, ease of use, versatility, reliability, robustness, and multicomponent capability are the most important features for a gas sensor. Gas chromatographs are neither fast enough nor sensitive. Although there is no ideal instrument that would fulfill all the requirements mentioned above, a spectroscopic method and particularly the simple setup of LPAS provide several unique advantages, notably the multicomponent capability, high sensitivity and selectivity, immunity to electromagnetic interferences, wide dynamic range, convenient real time data analysis, relative portability, operational simplicity, easy calibration, relatively low cost per unit, and generally no need for sample preparation. LPAS is primarily a calorimetric technique and, as such, differs completely from other previous techniques, as the absorbed energy can be determined directly, instead of via measurement of the intensity of the transmitted or backscattered radiation. This method has a ppb (parts per billion)-grade or even ppt (parts per trillion)-grade sensitivity. For this reason, this technique is used to detect partial leakage in various industries, especially advanced industries. One of the most important features of a spectrometer is the signalto-noise ratio. The signal-to-noise ratio is a measure used in engineering and science that compares the level of a desired signal to the level of background noise. Signal-to-noise ratio is defined as the ratio of signal power to the noise power, often expressed in decibels. The ability of the spectrometer to make accurate measurements depends on the quality of the signal obtained from the detector and the subsequent electrical circuits. The signal-to-noise ratio provides a measure of the signal quality. The signal-to-noise ratio compares the average power available in the signal to the average power contained in the noise, which includes any signal from sources other than the target signal source. Chloroform is one of the most serious pollutants in the environment. Prolonged exposure to chloroform vapors could cause severe health effects such as headache, eyesight disturbance, kidney damage, lung congestion, cancer, and so on. Therefore, accurate and sensitive detection of chloroform is very important in different environments. One of the most sensitive methods to detect chloroform vapors is laser photoacoustic spectroscopy method [Mohebbifar, 2014]. In this paper the system limit of detection for detecting chloroform was measured. Then the system signal-to-noise ratio variations for chloroform vapours in the presence krypton,  $N_2$  and He as buffer gas at the various carbon dioxide laser powers at atmospheric pressure and room temperature was measured.



#### Theory

The photoacoustic process is mainly the consequences of the modulated light interaction with gas species to generate acoustic signal. A molecule that absorbs laser radiation is excited to a higher quantum state (electronic, vibrational or rotational state). The excited state loses its energy by radiation processes, such as spontaneous emission or stimulated emission, and by collisional relaxation, in which energy is converted into translational energy. In this technique, radiative emission and chemical reactions do not play an important role in the case of vibrational excitation, because the radiative lifetimes of the vibrational levels are long compared with the time needed for collisional deactivation at pressures used in photoacoustics, and the photon energy is too small to induce chemical reactions. Thus, in practice the absorbed energy is completely released via either fluorescence or collisions. The latter give rise to a gas temperature increase due to energy transfer to translation as heat, appearing as translational energy of the gas molecules. The deposited heat power density is proportional to the absorption coefficient and incident light intensity. As shows in the figure (1) the modulated laser beam leads to produce acoustic waves which in turn can be detected by a sensitive microphone in the center of photoacoustic cell. It gives us a measure of gas concentration.

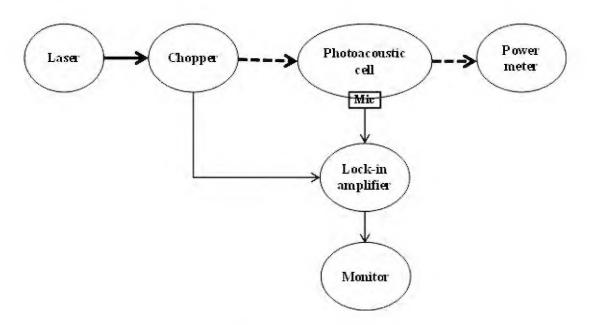


Fig. 1. A common block diagram of the laser photoacoustic spectrometer

In the laser photoacoustic spectroscopy method, the heat generation rate in the gas sample which irradiated by modulated laser, is given by Equation (1) [Dibaee et. al., 2015]:

$$dN/dt = \sigma\phi(N - N) - N/\tau. \tag{1}$$

Where in the two levels atomic model, N,  $\sigma$ ,  $\phi$  and  $\tau$  are the atomic energy density of atomic level, cross section, incident flux and relaxation time of atomic levels respectively. After modulation of incident flux  $\phi$  is given by Equation (2) and finally the heat generation rate will be as Equation (3):

$$\phi = \phi_0 [1 + \exp(i\omega t)], \tag{2}$$

$$d\hat{N}/dt = N\sigma\phi_0[1 + \exp(i\omega t)] - \hat{N}/\tau. \tag{3}$$

In the resonance spectroscopic systems, the laser is modulated by a chopper at the resonance frequency of acoustic resonator, and a phase-sensitive amplifier is locked at the chopper frequency and finally pressure changes (acoustic wave) measured by a sensitive microphone. This signal is called photoacoustic signal (Equation (4)) [Mohebbifar et. al., 2014]:

$$S = \left[\alpha C_i(\omega_i) P_0 F \exp(i\omega t)\right] / \left[\sqrt{(1+\omega^2 \tau^2)}\right]. \tag{4}$$

Where  $C_j(\omega_j)$  is the cell constant in the resonant frequency of acoustic resonator, is the microphone responsivity, is laser power and is the absorption coefficient.

#### Results and discussion

In order to design an optimum acoustic resonator, the resonant frequency and the cell dimensions were well chosen at first [Mohebbifar, 2019]. After simulation and optimization, 160mm for resonator length and 3mm for resonator radius was found as optimal acoustic resonator size and eventually home-made acoustic cell was fabricated. This resonator was made of stainless steel such that a couple of ZnSe windows were located at the both ends of the buffer volumes in order to suppress noise, coupled with the acoustic resonator. The resonator is connected to the buffer volumes to suppress the noise. The experimental setup including a continues wave carbon dioxide laser at the wave length of  $10.6\,\mu m$  and different power from 0.05 to 1 watt, Knowles EK-3024 microphone, mechanical chopper with frequency up to 10~kHz, continues wave power meter and rotary pump. The photoacoustic signal is measured in time and frequency domain by TDS3034 Tektronix oscilloscope and the SR850 Stanford Research Systems Company lock-in amplifier [Mohebbifar, 2019]. As the first step, system limit of detection to detect chloroform was measured by using Equation (5):

$$C_{min} = C/signal - to - noise - ratio. (5)$$

Where C is the concentration of incoming gas sample and signal-to-noise ratio is given by Equation (6):

$$signal - to - noise - ratio = Photoacoustic - signal/Noise - signal.$$
 (6)

The system limit of detection for detecting chloroform was measured 475ppb at 0.49W carbon dioxide laser power with  $10.6\mu m$  wavelength, 605Hz resonant frequency of mechanical chopper and 1 bar krypton as buffer gas. All measurements were performed at room temperature. In the next step of experiments, the system signal-to-noise ratio variations for chloroform vapour in terms of carbon dioxide laser power were performed. For this purpose system signal-to-noise ratio variations for 690 mTorr chloroform vapours in the presence of 1bar pressure of three buffer gases (krypton,  $N_2$  and He) at the carbon dioxide laser power from 0.05W to 1W was measured (figures 2-4). The carbon dioxide laser output power was continuously measured by continues wave power meter (EPM300 model-Coherent Company).

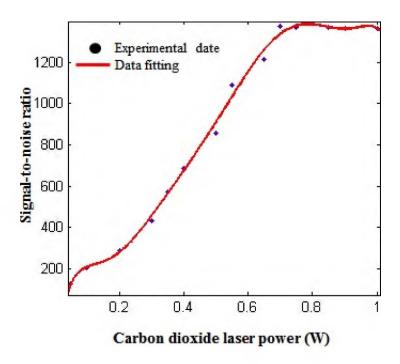


Fig. 2. Variation of the Signal-to-noise ratio of Chloroform + krypton in terms of various carbon dioxide laser powers

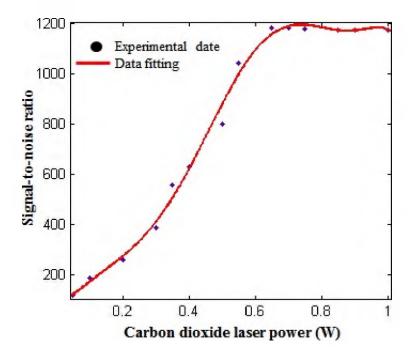


Fig. 3. Variation of the Signal-to-noise ratio of Chloroform +  $N_2$  in terms of various carbon dioxide laser powers

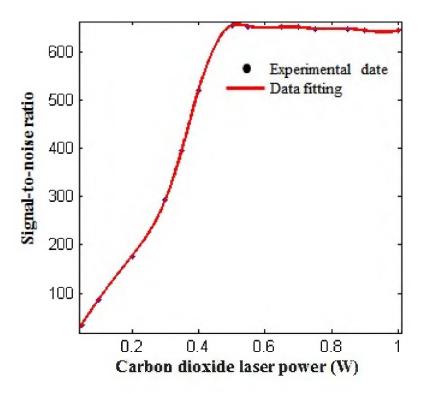


Fig. 4. Variation of the Signal-to-noise ratio of Chloroform + He in terms of various carbon dioxide laser powers

These results show that signal-to-noise ratio increases, when the carbon dioxide laser power increases. These experimental data were in agreement with the theory of laser photo-acoustic spectroscopy method. Actually increasing laser power leads to an increase collisional non-radiative processes, and thus increase photo-acoustic signal and signal-to-noise ratio. Moreover results show that when He used as buffer gas, signal-to-noise ratio of chloroform is the lowest. The different behaviour of He is because, firstly Molar mass of He is less than other buffer gases and secondly thermal diffusion of He is much faster than the other buffer gases.

#### Conclusion

This experimental study describes an experimental setup to detect chloroform vapor. For 0.49 watts of carbon dioxide laser power, 605Hz resonant frequency and in the presence of 1bar krypton as buffer gas system limit of detection to detect chloroform vapor was measured 475ppb. Also the system signal-to-noise ratio variations for 690 mTorr chloroform vapors in the presence of krypton,  $N_2$  and He buffer gases at the various carbon dioxide laser power and barometric pressure was measured. Results show that signal-to-noise ratio increase, when the carbon dioxide laser power increases. Furthermore, increasing laser power leads to an increase collision non-radiative processes, and thus increase photo-acoustic signal and signal-to-noise ratio. Also when He used as buffer gas, signal-to-noise ratio is the lowest. The different behaviour of He is because, firstly Molar mass of He is less than other buffer gases and secondly thermal diffusion of He is much faster than the other buffer gases.



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