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ALLANOVY VARIANCE - FOTOAKUSTICKÁ SPEKTROMETRIE ETHANOLU

ALLAN VARIANCE - PHOTOACOUSTIC SPECTROMETRY OF ETHANOL

Abstrakt

Fotoakustická spektrometrie s CO_2 laserem je velmi efektivní nástroj pro monitorování stopových množství plynů. Zlepšení citlivosti fotoakustického spektrometru je nezbytné pro měření minimálních detekovatelných koncentrací polutantů. Pro zlepšení citlivosti spektrometru je potřebné celkový šum rozlišit na jednotlivé části a určit jednotlivé typy šumu. Fotoakustický spektrometr s CO_2 laserem byl upraven k detekci lehkého polutantu etanolu. Allanovy variance fotoakustického signálu byly použity k testování stability spektrometru. Byly porovnány detekce laminárního a turbulentního proudění etanolu. Je popsán postup pro studium vlivu turbulence na optimální dobu průměrování pro minimální detekovatelné koncentrace.

Klíčová slova: allanovy variance, CO_2 laserová fotoakustická spektrometrie, ethanol.

Abstract

The photoacoustic spectrometry with CO_2 laser is a very effective tool for monitoring of trace gases. An improvement of sensitivity of a photoacoustic spectrometer is necessary for monitoring of the minimum detectable concentrations. For improvement of the spectrometer sensitivity it is desirable to resolve the over-all noise figure into its individual parts and evaluate individual noise type. The photoacoustic spectrometer with CO_2 laser was adapted for detection of light pollutant ethanol. Allan variances of the photoacoustic signal have been utilized to test the stability of the spectrometer. The detection of laminar and turbulent flow of ethanol has been compared. An approach for studies of the influence of the turbulence on the optimal averaging time for the minimum detectable concentrations is described.

Key words: allan variance, CO_2 laser photoacoustic spectrometry, ethanol.

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Introduction

Photoacoustic spectrometry is selective, sensitive, and nondestructive laser-based analytical method [1]. This method has been steadily more employed to physical modeling of trace amounts of pollutant gases present in the atmosphere [2]. Wind tunnel experiments combine with photoacoustic spectrometry are used to investigate the motion of pollutants in urban scale models [1].

The output data of all measurements are often obscured by noises which negatively influence the instrument sensitivity. An improvement of sensitivity of the photoacoustic spectrometer depends on the determination of optimal integration time. Allan variance method becomes a standard procedure for evaluation of optimal integration time of the analyzed instrument [3, 4, 5, 6].

An approach for investigation of optimal integration time of diode laser and CO_2 laser photoacoustic spectroscopy was described in [7]. The urban scale models used establish the turbulent and laminar flow fields. Investigation of dependence of optimal integration time on the sample flow leads to further methodological advances.

In present article the concept of the Allan variance has been utilized to test detection abilities of both laminar and turbulent flow. In our preliminary analysis we demonstrate that the flow influence the optimal averaging time for the minimum detectable concentration.

Experimental details

As a model pollutant was used ethanol (company: Sigma Aldrich; purity: 99.8 %). Spectroscopic experiment aimed at application of photoacoustic spectrometry to physical modeling was performed within a low speed (~ 1 $m.s^{-1}$), straight open wind tunnel (constant 1.5x1.5 m cross-section, length of 20.5 m, a working section 2 m).

Experimental set-up aimed at the application of mid-infrared (IR) photoacoustic spectrometer with CO_2 laser is described in previous works [1, 8, 9, 10]. The photoacoustic cell was a thermally stabilized brass tube with the length of 38 cm and the diameter of 8 mm. Detection was performed on longitudinal acoustical resonance (modulation frequency 1.2 kHz, the phase is set on the maximum of the photoacoustic signal).

Analysis

The description of the Allan variance method was published previously [6, 7]. The Allan variance σ^2_A is calculated for a set of *m-1* subgroups of k classes (where $k = N/m$) which contains x values of measured data (N) and plotted over the integration time t:

$$\left\langle \sigma_A^2(k) \right\rangle_t = \frac{1}{2(m-1)} \sum_{s=1}^{m-1} (A_{2,s} - A_{1,s})^2 \tag{1}$$

$$A_s(k) = \frac{1}{k} \sum_{L=1}^{k} x_{(s-1)k+L} \tag{2}$$

The concept of Allan variance has been utilized to test the detection ability of both flow systems.

Results and discussion

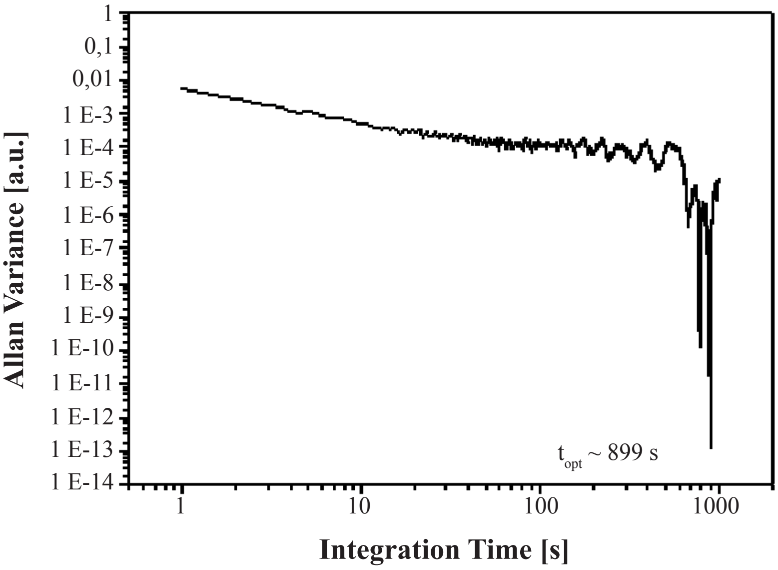

Figure 1: *Results of photoacoustic spectrometer tested by means of Allan variance with no sample flow*

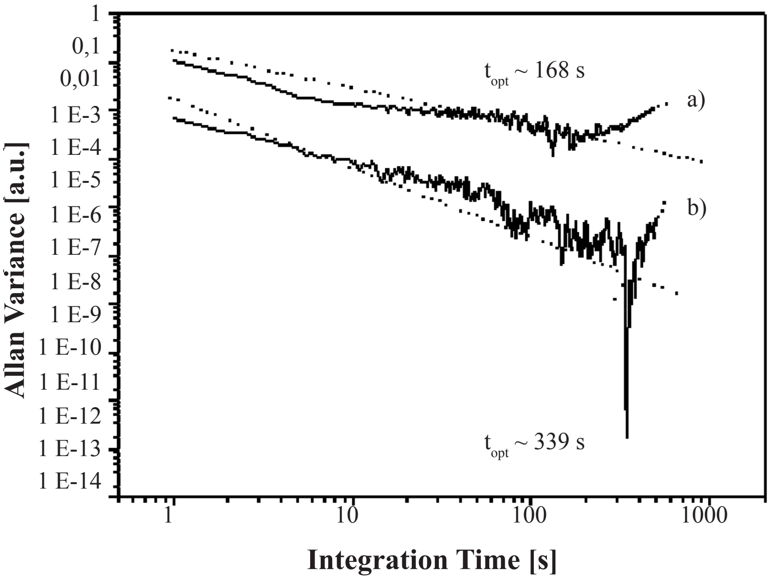

Figure 2: *Results of photoacoustic spectrometer tested by means of Allan variance with a) turbulent flow and b) laminar flow of ethanol (C_2H_5OH).*

The Allan variance was obtained at a time interval of 2000 s (Fig. 1) and 1000 s (Fig. 2). The Allan-plot shows how the noise influences the measurement. The optimum integration time (obtained on the basis of Allan variance) is in the minimum of the Allan-plot.

At low integration times White noise ($\langle\sigma^2_A(k)\rangle_t \sim 1/t$) dominates (decreasing part - see in Figures 1 and 2). After the optimal integration time the influence of the linear drift $\langle\sigma^2_A(k)\rangle_t \sim t^\alpha$, $\alpha = 1\text{-}2$) starts (increasing part - see in Figures 1 and 2). The Allan plots at Fig. 2 are the main results of the testing of both considered flow systems applied in the photoacoustic detection of ethanol.

The optimal integration time (result of four measurements at the same experimental condition) for laminar flow is between 100 - 200 s and the optimal integration time for turbulent flow is between 300 - 400 s.

Conclusion

This study conducted with the previous study [7] introduces step-by-step development of a methodology for the evaluation of the optimal integration time in laser-based analytical instruments. The stability and the resulting detection ability of the instrument depending on the sample flow with different degree of the turbulence can be described by the Allan variance. The Allan plot provides information about the optimum averaging time. This studies show that the Allan variance can also be used to analyze the performance of a detection system in the case of detection of species with different flow.

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