

Stability of Diode-Laser Spectrometer for Monitoring of OCS, C₃H₄, CN Molecular Systems Concentrations

J. Skrinsky, M. Skrinska, and Z.Zelinger

Abstract—This paper describes the assessment of infrared detection technique by the Allan variance method. In particular, the results demonstrate how to determine the optimal averaging time in such experiments. The experimental technique is diode laser spectroscopy. Several molecules were studied including stable molecules (OCS, C₃H₄) and a short-lived free radical (CN). Three types of Allan variance are mathematically defined, and then their behavior is extensively tested on experimental data. Simultaneously, the integral formula for the direct conversion from the frequency to the time domain is used to get results for comparison. The stability analyses were determined by 2000 s measurements. Results show the possibilities of the presented procedure that is going to be used for the evaluation of direct time domain laser frequency stability measurements. Results are focused on the area of influence of the reactivity on the optimal averaging time for the minimum detectable concentration is demonstrated where a question of the frequency stability is very important.

Keywords—Allan variance, CN radical, OCS, C₃H₄

I. INTRODUCTION

THE technique is universally applicable to smaller infrared active molecules and the same instrument can easily be converted from one species to another by changing the laser and calibration gases. The time resolution of TDLAS measurements can be traded off against sensitivity and this allows fast measurements with millisecond time resolution. In order to improve sensitivity various types of modulation spectroscopy have been employed in which the diode laser

This work was prepared in the frame of the project Opportunity for young researchers, reg. no. CZ.1.07/2.3.00/30.0016, supported by Operational Programme Education for Competitiveness and co-financed by the European Social Fund and the state budget of the Czech Republic and the project Innovation for Efficiency and Environment, reg. no. CZ.1.05/2.1.00/01.0036, supported by Operation Programme Research and development for Innovation and financed by Ministry of Education, Youth and Sports of the Czech Republic.

J. S. is with Energy Research Center, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, 708 33, Ostrava, Czech republic (e-mail: jan.skrinsky@vsb.cz).

M. S. is with Energy Research Center, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, 708 33, Ostrava, Czech republic (e-mail: maria.skrinska@vsb.cz).

Z. Z. is with Department of Spectroscopy, J. Heyrovsky Institute of Physical Chemistry of the ASCR, Dolejškova 2155/3, 182 23 Praha 8, Czech Republic (e-mail: zdenek.zelinger@jh-inst.cas.cz).

wavelength is modulated while being scanned across an absorption line [1]. One of the key issues in the instrument detection ability is identification of the difference between sample data and instrument drift in time. Such identification is possible using numerical methods for instrument stability characterization. The information about dispersion of pollutants could be obtained by two basic approaches. The first one is the direct monitoring of pollutants concentration levels in the atmosphere. The second one is based on the results of numerical solutions of mathematical description of simulated processes. The noise plays a very important role in today's laser based systems. A frequency-stabilized diode laser has become a fundamental tool in a variety of research fields such as optical communications, frequency standards and absorption spectrometry. Even if the noise is always included, it is possible to improve the noise performance and develop the system with a better quality. The detection limit is calculated on the basis of the variance of this mean. Stability tests based on the Allan variance method have become a standard procedure for the evaluation of the quality of an instrument. The stability of the diode-laser is analyzed in this paper in terms of the modified [2-5] and overlapping [5-8] Allan variance.

II. PREVIOUS STUDIES

Werle et. al in 1993 first utilized the concept of the Allan variance to analyze the stability of a FM TDLAS spectrometer with White cell. As a result of their study they obtained the detection limit for NO₂ molecule of 34 pptv at 6 Hz detection bandwidth with the optimal averaging time of 60 s [1]. In 1996 Werle continued his research with Jänker. They primarily identified that sensitivity improvement by signal averaging is limited by 1/f noise contributions from a turbulent gas flow. This conclusion has been supported by measured time series data from the differential pressure sensor for an air flow 1, 3, 5, 7, and 10 liters/min through the White cell. The corresponding Allan plots show 1/f characteristics for integration times above 30 s, indicating that further averaging does not reduce the noise [9]. Freed et al. presented merits of Allan variance approach in an aircraft FM TDLAS system with Herriott cell [10]. Formaldehyde (CH₂O) was used as the target gas. The measurements indicated the detection limit of 18 pptv that is within a factor of two of that reported by Werle

et al. for integration time of about 87 s. At the same year Werle et al. [11] have found the detection limit of FM TDLAS with Herriott cell for CO₂ molecule of 0.87 ppm obtained at an integration time of 0.1 s. Werle and Lechner [12] published the comparison of the FM TDLAS technique and the FM-Stark TDLAS modulation technique. FM spectra and FM-Stark spectra were obtained together with time series data from a 4.6 ppm (25 mbar) CH₂O calibration gas and corresponding Allan plots. For both measurement series the optical density was adjusted to 4.1×10^{-4} at 25 mbar and the detection bandwidth was 2 Hz. The optimal integration time 120 s for FM Stark spectrometer and 24 s for FM spectra were achieved with 35-cm path. In 1999 Werle and Popov [13] presented measurements of CH₂O and CH₄ with a selected antimonite laser device. From first experiments they determined a detection limit for HCHO of 120 pptv with a 40 s integration time, corresponding to 5×10^{-6} at $\Delta f = 5$ Hz, and for CH₄ was obtained 2 ppb with a 20 s integration time, corresponding to 2.7×10^{-4} at $\Delta f = 1$ Hz. Werle et al. [14] used FM-Stark TDLAS with 35 cm single pass cell to detect the concentration about 0.6 ppm for H₂¹⁷O measurements at the optimal integration time of 60 s. Further improvements for the aircraft applications are being discussed. Combined use of a multipass cell and modulation to suppress the background signals was applied by [15]. The target molecule was CH₂O with concentration 361 ppb. The authors used rapid background subtraction in which an external electric field was turned off on alternate scans. Such double modulation experiment show drift free, white noise limited characteristics up to the integration times of more than 1000 s.

III. EXPERIMENTS

The diode-laser absorption spectroscopy is frequently used for monitoring of very small concentration levels [11, 16-17] of different species – stable, unstable including radicals. The description of the diode laser spectrometer employed was presented in [18-20]. The diode laser (Laser Components GmbH) was placed in a laser head cooled by the He cryostat. The laser was temperature and current controlled using Laser Photonics units, model L5731, at a temperature of 30 - 70 K. A lens focuses laser beam into a (Czerny-Turner) monochromator to separate single laser modes from the spectrum. The radiation leaving the monochromator was directed either into a reference cell, a Ge etalon (0.04 cm^{-1}) or into an absorption cell loaded with the gas being studied. The absorption spectrum was recorded with a photoconductor InSb detector operated at the liquid nitrogen temperature. The signal from the detector was fed into a lock-in amplifier. Diode-laser spectrometer was tested by means of the modified and overlapping Allan variance of stable molecule OCS and unstable molecule of CN radical.

IV. ANALYSES

The Allan variance is the most common time domain measure of frequency stability. It is a measure of the fractional frequency fluctuations, and it has the advantage of being

convergent for most types of diode-laser noise. There are several versions of the Allan variance that provide better statistical confidence, can distinguish between white and flicker phase noise, and can describe time stability. In the present paper we have tested simple non-overlapped, overlapping and modified Allan variance. The original non-overlapped Allan, (two-sample) variance, is the standard time domain measure of frequency stability. The calculation of the expected value for the time average of non-overlapped simple Allan variance $\langle \sigma_A^2(k) \rangle_t$ is defined for a set of $m-1$ independent measurements to obtain a more precise estimate for the detection limit. The assumption for this calculation is that data set is sorted according to the measurement time. Simplified calculation of subset average value for measured elements $A_s(k)$ is given by:

$$A_S(k) = \frac{1}{k} \sum_{l=1}^k x_{(s-1)k+l} \quad (1)$$

Simplified calculation of Allan variance for measured elements of time series $\langle \sigma_A^2(k) \rangle_t$ is defined as:

$$\langle \sigma_A^2(k) \rangle_\tau = \frac{1}{2(m-1)} \sum_{s=1}^{m-1} [A_{s+1}(k) - A_s(k)]^2 \quad (2)$$

$\langle \sigma_A^2(k) \rangle_t$ is the time average of Allan variance [a.u.]; A_S is the arithmetical mean of measured elements [a.u.]; k is a number of averages [-]; m is a number of subsets; N is a total number of elements [-]; t is the integration time [s]; s, l are the indexes ($s = 1, \dots, m-1$ and $l = 1, \dots, k$).

Stability calculations can utilize fully overlapping samples, whereby the calculation is performed by utilizing all possible combinations of the data set, as shown in the formulae below. The use of overlapping samples improves the confidence of the resulting stability estimate, but at the expense of greater computational time.

$$\langle \sigma_O^2(k) \rangle_\tau = \frac{1}{2M^2(m-2M+1)} \sum_{j=1}^{m-2M+1} \sum_{s=j}^{j+m-1} [A_{s+1}(k) - A_s(k)]^2 \quad (3)$$

$\langle \sigma_O^2(k) \rangle_t$ is the time average of overlapped Allan variance [a.u.], A_S is the arithmetical mean of measured elements [a.u.], k is a number of averages [-], m, M are a number of subgroups, N is total number of elements [-], t is an integration time [s], s, l are the indexes ($s = 1, \dots, m-2$ and $l = 1, \dots, k$).

In the frequency domain the data is often affected by systematic effects such as frequency offset or frequency drift. Therefore, the frequency stability is more easily specified through the characterization in the time domain.

The modified Allan variance, Mod $\sigma^2 y(\tau)$, is the time domain measure of frequency stability [2-5]. These variances based on square of 2nd differences of averaged phase deviation values. It is estimated from a set of M frequency measurements for averaging time $\tau = m\tau_0$, where m is the averaging factor and τ_0 is the basic measurement interval, by

the expression.

$$\text{Mod}\langle\sigma_A^2(k)\rangle_\tau = \frac{1}{2m^4(M-3m+2)} \sum_{j=1}^{M-3m+2} \left\{ \sum_{i=j}^{j+m-1} \left(\sum_{k=i}^{i+m-1} [A_{s+m}(k) - A_s(k)] \right) \right\}^2 \quad (4)$$

$\text{Mod}\langle\sigma_A^2(k)\rangle_\tau$ is the time average of modified Allan variance [a.u.]; A_s is the arithmetical mean of measured elements [a.u.]; i, j, k are the number of averages [-]; m is a number of subsets; N is a total number of elements [-]; t is the integration time [s]; s, l are the indexes ($s = 1, \dots, m-1$ and $l = 1, \dots, k$).

The modified Allan variance is the same as the normal Allan variance for $m = 1$. It includes an additional phase averaging operation, and has the advantage of being able to distinguish between white and flicker PM noise. The confidence interval of a modified Allan deviation determination is also dependent on the noise type, but is often estimated as $\pm\sigma_y(\tau)/\sqrt{N}$. Use the modified Allan deviation to distinguish between white and flicker PM noise.

In the frequency domain the data is often affected by systematic effects such as frequency offset [21]. Therefore, the frequency stability is more easily specified through the characterization in the time domain.

For the Allan variance, the transfer equation has the form:

$$\langle\sigma_A(k)\rangle_\tau = 2 \cdot \sum_0^\infty S_y(f) \cdot \frac{\sin^4(\pi \cdot \tau \cdot f)}{(\pi \cdot \tau \cdot f)} \cdot df \quad (5)$$

The mathematical form of power spectral density estimate:

$$S_y(f) = \sum_\alpha h_\alpha f^\alpha \quad (6)$$

α is an integer that runs from -2 to 2, h_α is the transfer function proportional to the power of α

The frequency domain could be characterized by five noise categories: (1) white phase noise, (2) flicker phase noise, (3) white frequency noise, (4) flicker frequency noise and (5) random walk frequency noise [21]. This model adequately describes most of the observed noise processes. These five noise categories are grouped into three parts, thus the calculation can also be spread into the sum of these fractional calculations:

$$\langle\sigma_H^2(k)\rangle_\tau = c_{\text{white-noise}} + c_{1/f} + \sum_\alpha c_{\text{drift},\alpha} \tau^\alpha \quad (7)$$

$\langle\sigma_H^2(k)\rangle_\tau$ is the Allan variance [a.u.], $c_{\text{white-noise}}$ is a constant characterizes white noise [a.u.], $c_{1/f}$ is a constant characterizes flicker noise, $\sum c_{\text{drift},\alpha} \tau^\alpha$ characterizes the type of the system drift [-], τ is the integration time.

V. RESULT AND DISCUSSIONS

The stability of a diode-laser spectrometer has been

estimated by measuring the Allan variance with 10 sets of the 2000 s measurements. The long-time scan data were obtained by measuring line peaks and background spectra. All computations so far were restricted to a time series of arbitrary data, i.e. an individual spectrometer channel i , but they ignored that a full instrument consists of thousands of spectrometer channels which are partially, but not completely independent. The Allan variance approach is used to characterize the full spectrometer by the computation of the Allan variance channel by channel. Fig. 1 shows examples of the line peak scan containing noise and a linear slope (red line) for the OCS molecule. Time series shown in Fig. 1 has been recorded at $1901.9690 \text{ cm}^{-1}$ for 2000 s. The background noise level significantly reduced by the frequency modulation technique was obtained by the measurement of non-sample region over 2000 s free of studied molecules at the same experimental conditions that were in effect during measuring of the sample. After the background subtraction the resulting spectrum could be tested by the standard or Allan variance method. By using the (5) we are able to make the transformation of the time domain spectrum into the frequency domain and vice-versa. A closer look into a short interval of the time series resolved at for e.g. 100 s time interval shows (non-linear and linear) short-term 'trends' due to turbulence in the inertial subset and therefore a similar behavior with respect to averaging can be expected as for the long-term drift already discussed. The time-domain characterization based on a two-sample variance using an σ/τ plot shown in Fig. 2 provides the same information as the spectral characteristics of turbulence in the frequency domain. The problem with the standard variance stems from its use of the deviations from the average, which is not stationary for the more divergence noise types.

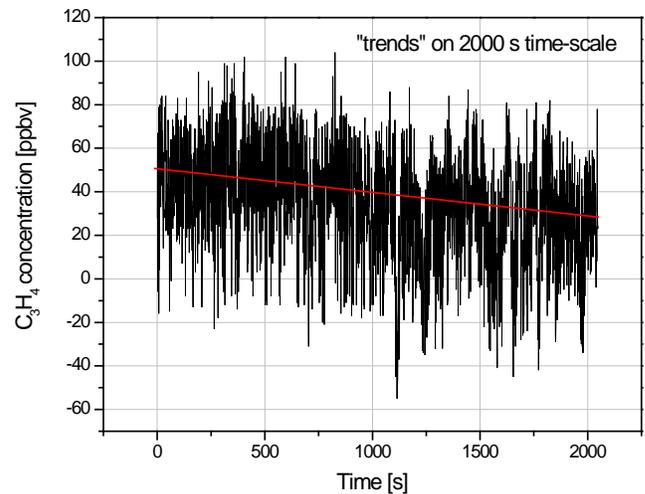


Fig. 1 OCS concentration in ambient air recorded during measurement

The following first stage σ/τ plot shows the significant reduction in variability, hence increased statistical confidence, obtained by using overlapping samples in the calculation of the Allan deviation. The problem of noise divergence can be

solved by instead using the first differences of the fractional frequency values (the second differences of the phase), as described for the Allan variance. Therefore, we will apply the overlapped Allan variance. In Fig. 2 are the non-overlapped and overlapped Allan variances plotted as a function of integration time. Stability of the tested diode-laser instrument could be discussed based on the Allan plot. First of all, the resulted plot is divided into two levels highlighted in Fig. 2 by dashed lines.

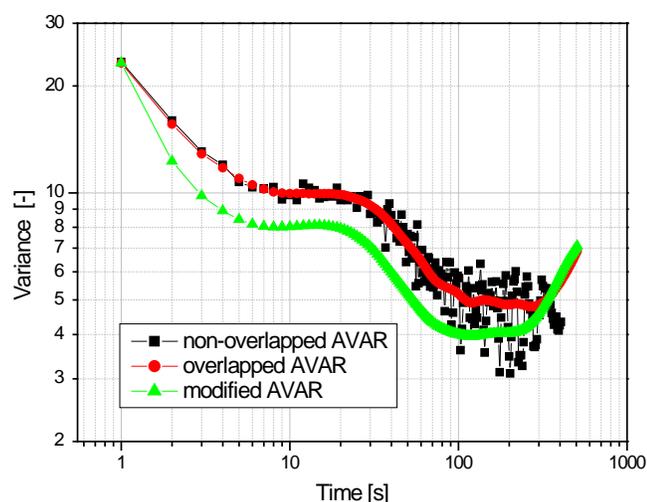


Fig. 2 Comparison of non-overlapping, overlapping and modified variances for OCS data sampling.

Negative slope of the dashed line indicates white type noise, on the other hand if the slope is positive, then it indicates drift. The slopes are calculated as an average value from the noise dominating in individual parts of Allan variance plot, and are used for the illustration of dominating noise type trend. According to the Allan variance plot the optimal integration time is situated in intercross of the slopes. In Fig. 2 the calculated non-overlapped Allan variance has a positive slope if the measured integration time is greater than 135 s. While the calculated overlapped Allan variance has shown that it is possible to integrate up to the value 300 s. These slopes change in the inertial integration time interval in which frequency fluctuations, according to the type of noise, dominate the Allan plot. From comparison of the Allan variance trends in Fig. 2 it is evident that the overlapped Allan variance seems to be smoother and therefore it is easily to evaluate the integration time. Experimental results have confirmed the value of 300 s thus supported the possibility to prolong the integration till the drift started dominates.

Table 1 Comparison of non-overlapping, overlapping and modified variances for sampling of OCS

Time	Model predictions (present work)					
	V_{AVAR}	V_{OVAR}	V_{MVAR}	Δ_{AO}^a	Δ_{AM}^b	Δ_{OM}^c
1	2.3344e+01	2.3385e+01	1.5048e+01	-0.0410	8.2960	8.3370
2	1.5968e+01	1.5561e+01	1.0001e+01	0.4070	5.9670	5.5600
4	1.1985e+01	1.1695e+01	7.7906e+00	0.2900	4.1944	3.9044
8	1.0390e+01	9.9723e+00	7.1734e+00	0.4177	3.2166	2.7989
16	9.7348e+00	9.7987e+00	7.3407e+00	-0.0639	2.3941	2.4580
32	8.9404e+00	8.9889e+00	6.4163e+00	-0.0485	2.5241	2.5726
64	6.4482e+00	6.1893e+00	6.3916e+00	0.2589	0.0566	-0.2023
128	4.7172e+00	4.9751e+00	8.4858e+00	-0.2579	-3.7686	-3.5107
256	5.4016e+00	4.8124e+00	1.4383e+01	0.5892	-8.9814	-9.5706

$$^a \Delta_{AO} = V_{AVAR} - V_{OVAR}; \quad ^b \Delta_{AM} = V_{AVAR} - V_{MVAR}; \quad ^c \Delta_{OM} = V_{OVAR} - V_{MVAR}$$

According to Table 1, both variances are convergent for $\alpha > -5$, unlike the Allan variance (see Fig. 2), which is convergent for $\alpha > -3$ (from the last term of equation 7). Thus it would be possible to use the Overlapped and modified variances to probe for noise beyond random walk frequency modulation. Moreover, the both variance are unaffected by linear frequency drift. This makes it an excellent tool for investigating noise types whose signatures are similar to and often confused with linear drift. By repeating this procedure we evaluated a total of 10 data sets obtained at a time interval of 2000 s and obtained an averaged value of optimal integration time by two different procedures lying in the interval from 100 to 200 s.

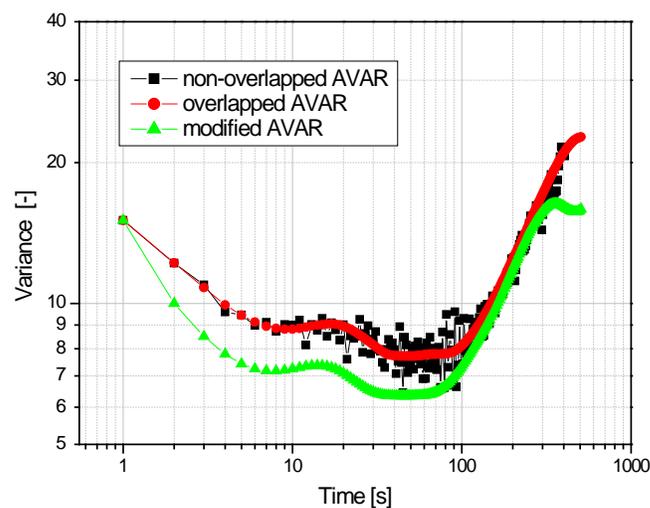


Fig. 3 Comparison of non-overlapping, overlapping and modified variances for C_3H_4 data sampling.

Similarly the unstable CN radical molecule has been investigated. In Fig. 3 are the non-overlapped and overlapped Allan variances obtained from CN radical time series measurements plotted as a function of integration time.

Table 2 Comparison of non-overlapping, overlapping and modified variances for sampling of C_3H_4 .

Time	Model predictions (present work)					
	V_{AVAR}	V_{OVAR}	V_{MVAR}	Δ_{AO}^a	Δ_{AM}^b	Δ_{OM}^c
1	1.5048e+01	1.5048e+01	1.5048e+01	0.0000	0.0000	0.0000
2	1.2190e+01	1.2204e+01	1.0001e+01	-0.0140	2.1890	2.2030
4	9.5836e+00	9.9306e+00	7.7906e+00	-0.3470	1.7930	2.1400
8	8.7226e+00	8.8468e+00	7.1734e+00	-0.1242	1.5492	1.6734
16	8.5062e+00	9.0354e+00	7.3407e+00	-0.5292	1.1655	1.6947
32	7.9760e+00	8.0100e+00	6.4163e+00	-0.0340	1.5597	1.5937
64	7.2652e+00	7.7919e+00	6.3916e+00	-0.5267	0.8736	1.4003
128	9.2618e+00	9.0893e+00	8.4858e+00	0.1725	0.7760	0.6035
256	1.5503e+01	1.5107e+01	1.4383e+01	0.3960	1.1200	0.7240

$$^a \Delta_{AO} = V_{AVAR} - V_{OVAR}; \quad ^b \Delta_{AM} = V_{AVAR} - V_{MVAR}; \quad ^c \Delta_{OM} = V_{OVAR} - V_{MVAR}$$

To get a rough feeling for the spectral behavior we also look at the difference time scale line plots in Figure 3, however, the corresponding interval has to be selected arbitrarily, missing most of the statistics of the measurement, so that a single baseline can never provide all the information contained in the channel-by channel Allan variance plot.

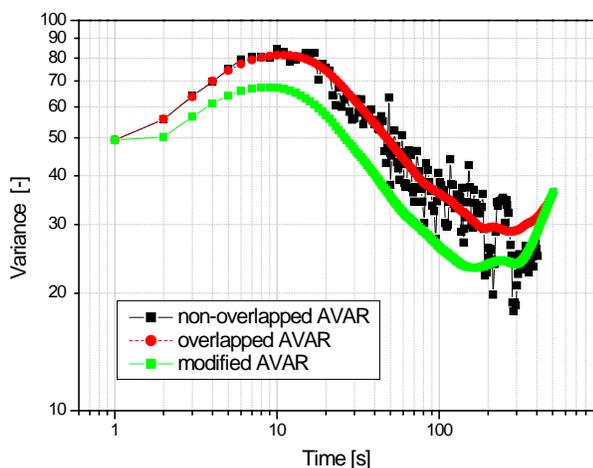


Fig. 4 Comparison of non-overlapping, overlapping and modified variances for CN data sampling.

This is the most reliable approach also applicable to observations where it is expected to distinguish White and Flicker PM noises because the modified Allan variances have additional phase averaging. At the same time if applied this type of averaging one have to avoid use with large data set gaps. Overlapped Allan variance is convergent for $\alpha > -5$, unlike the Allan variance, which is convergent only for $\alpha > -3$ (from the last term of equation 7). Therefore, the short integration time has to be applied that was confirmed by the experimental results. According to Fig. 4, both variances are convergent for $\alpha > -5$, unlike the Allan variance (see Fig. 3).

Table 3 Comparison of non-overlapping, overlapping and modified variances for sampling of CN.

Time	Model predictions (present work)					
	V_{AVAR}	V_{OVAR}	V_{MVAR}	Δ_{AO}^a	Δ_{AM}^b	Δ_{OM}^c
1	4.9350e+01	4.9350e+01	4.9350e+01	0.000	0.000	0.000
2	5.5809e+01	5.5848e+01	5.0256e+01	-0.039	5.553	5.592
4	6.9616e+01	6.9982e+01	6.1253e+01	-0.366	8.363	8.729
8	8.0460e+01	8.0363e+01	6.7315e+01	0,097	13.145	13.048
16	8.2304e+01	7.8791e+01	6.2029e+01	3.513	20.275	16.762
32	5.8018e+01	6.0617e+01	4.5310e+01	-2.599	12.708	15.307
64	4.2960e+01	4.2898e+01	3.1361e+01	0.062	11.599	11.537
128	3.6072e+01	3.3387e+01	2.4220e+01	2.685	11.852	9.167
256	3.0782e+01	2.8905e+01	2.4201e+01	1.877	6.581	4.704

$$^a \Delta_{AO} = V_{AVAR} - V_{OVAR}; \quad ^b \Delta_{AM} = V_{AVAR} - V_{MVAR}; \quad ^c \Delta_{OM} = V_{OVAR} - V_{MVAR}$$

The results of unstable molecular system record averaged over a 2000 s time interval is in Table 3. The value of optimal integration time is approximately 30-40 s in case of unstable CN radical molecule that is significantly lower than that of OCS. It means that the white noise dominated region is much lower than the white noise dominated region presented in the case of OCS molecule. It could be therefore concluded that, apart from the negative slope at the first 100 s, the Allan variance plots show expected behavior. The calculated trends of the dominant noise type are similar to the results obtained by the evaluation of experimental data obtained for the stable OCS molecule.

VI. CONCLUSION

The concept of simple, overlapped and modified Allan variances has been utilized for the stability and sensitivity analysis of described diode-laser experimental apparatus. The present investigation of optimal integration times has extended the series of studies by TDLAS. Results for OCS, C_3H_4 and CN radical molecules concerning detection limits complete the values of optimal integration times for NO_2 , CH_2O , CH_4 , $H_2^{17}O$ sample molecules obtained in previous studies. There is no simple trend in the values of integration times for TDLAS. Calculated variances plotted as a function of integration time (t) give the first stage σ/τ plot. The σ/τ plots demonstrate the noise influences of the investigated system (see Figure 2-4). The optimal integration times for the detection of trace-gas concentrations were determined by the combination of non-overlapped, overlapped and modified Allan variance methods. The analysis of Allan variances was demonstrated on a detection of gaseous OCS, C_3H_4 and CN radical molecular systems by diode-laser spectrometer with a given noise curve in the time domain. The analyzed signal is subtracted from the reference one, time dependent time fluctuations are obtained, and simple, overlapped and modified Allan variances are calculated and compared. The presented approach contributes to the analysis of performance of a detection system [21-23]. It is the case of analysis of species under different variances.

The σ/τ plots provide information about the optimum averaging time for the tested system. It would enable to make the systematic comparisons of derived integration time parameters for environmental pollutants of stable molecules as well as their unstable by-products in the future.

ACKNOWLEDGMENT

The article was prepared in the frame of the project Opportunity for young researchers, reg. no. CZ.1.07/2.3.00/30.0016, supported by Operational Programme Education for Competitiveness and co-financed by the European Social Fund and the state budget of the Czech Republic and the project Innovation for Efficiency and Environment, reg. no. CZ.1.05/2.1.00/01.0036, supported by Operation Programme Research and development for Innovation and financed by Ministry of Education, Youth and Sports of the Czech Republic.

REFERENCES

- [1] P. Werle, R. Mücke, F. Slemr, "The limits of signal averaging in atmospheric trace-gas monitoring by tunable diode-laser absorption spectroscopy," *App. Phys. B*, vol. 57, no. 2, pp. 131-139, 1993.
- [2] D.W. Allan, J.A. Barnes, "A modified Allan variance with increased oscillator characterization ability" in *Proc. 35th Freq. Cont. Symp.*, Ft. Monmouth, NJ, 1981pp. 470-474.
- [3] P. Lesage, T. Ayi, "Characterization of frequency stability: Analysis of the modified Allan variance and properties of its estimate," *IEEE Trans. Instrum. Meas.*, vol. 33, no. 4, pp. 332-336, 1984.
- [4] C.A. Greenhall, "Estimating the modified Allan variance," in *Proc. IEEE 1995 Freq. Cont. Symp.*, San Francisco, 1995, pp. 346-353.
- [5] C.A. Greenhall, "The third-difference approach to modified Allan variance," *IEEE Trans. Instrum. Meas.*, vol. 46, no. 3, pp. 696-703, 1997.
- [6] D.W. Allan, "The statistics of atomic frequency standards," *Proc. IEEE*, vol. 54, no. 2, pp. 221-230, 1966.
- [7] D.W. Allan, "Allan variance, Characterization of frequency stability," Nat. Bur. Stand. (U.S.) Tech Note 394, October 1970. Available: <http://www.allanstime.com>.
- [8] J.A. Barnes, A.R. Chi, L.S. Cutler, D.J. Healey, D.B. Leeson, T.E. McGunigal, J.A. Mullen, W.L. Smith, R.L. Sydnor, R.F.C. Vessot, G.M.R. Winkler, "Characterization of frequency stability," *IEEE Trans. Instrum. Meas.*, vol. 20, no. 2, pp. 105-120, 1971.
- [9] P. Werle, R. Mücke, F. D'amato, T. Lancia, "Near-infrared trace-gas sensors based on room-temperature diode lasers," *App. Phys. B*, vol. 67, no. 3, pp. 307-315, 1998.
- [10] P. Werle, B. Jänker, "High-frequency-modulation spectroscopy: phase noise and refractive index fluctuations in optical multipass cells," *Opt. Eng.*, vol. 35, no. 7, pp. 2051-205, 1996.
- [11] Fried, B. Henry, B. Wert, S. Sewell, J.R. Drummond, "Laboratory, ground-based, and airborne tunable diode laser systems: performance characteristics and applications in atmospheric studie," *App. Phys. B*, vol. 67, no. 3, pp. 317-330, 1998.
- [12] P. Werle, S. Lechner, "Stark-modulation-enhanced FM-spectroscopy" *Spectr. Act. A*, vol. 55, no. 10, pp. 1941-1955, 1999.
- [13] P. Werle, A. Popov, Application of antimonide lasers for gas sensing in the 3-4 μm range. *App. Opt.*, vol. 38, no. 9, pp. 1494-1501, 1999.
- [14] P. Werle, Dyroff C., A. Zahn, P. Mazzianghi, F. D'amato, "A new concept for sensitive in situ stable isotope ratio infrared spectroscopy based on sample modulation," *Isot. Environ. Health Stud.*, vol. 41, no. 4, pp. 323-333, 2005.
- [15] Dyroff, P. Weibring, A. Fried, D. Richter, J.G. Walega, A. Zahn, W. Freude, P. Werle, "Stark-enhanced diode-laser spectroscopy of formaldehyde using a modified Herriott-type multipass cell," *App. Phys.*, vol. 88, no. 1, pp. 117-123, 2007
- [16] D. Nelson, B. McManus, S. Urbanski, S. Herndon, M. S. Zahniser, "High precision measurements of atmospheric nitrous oxide and methane using thermoelectrically cooled mid-infrared quantum cascade laser and detectors," *Spectr. Acta A*, vol. 60, no. 14, pp. 3325-3335, 2004.
- [17] H. Cattaneo, T. Laurila, R. Hernberg, Photoacoustic detection of oxygen using cantilever enhanced technique, *App. Phys. B*, vol. 85, no. 2-3, pp. 337-341, 2006.
- [18] Z. Zelinger, S. Civiš, P. Kubát, P. Engst, "Diode laser application for research of molecular ions," *Infrared Phys. Technol.*, vol. 36, no. 1, pp. 537-543, 1995.
- [19] Z. Zelinger, P. Kubát, J. Wild, "Unusual Kinetics of Ions in a Discharge Plasma: ambipolar diffusion and mobilities of ArD⁺ in argon, helium and neon," *Chem. Phys. Lett.*, vol. 368, no. 5-6, pp. 532-537, 2003.
- [20] J. Skřínský, R. Janečková, E. Grigorová, M. Strižik, P. Kubát, L. Herecová, V. Nevrlý, Z. Zelinger, S. Civiš, "Allan variance for optimal signal averaging monitoring by diode-laser and CO₂ laser photoacoustic spectroscopy", *J. Mol. Spectr.* vol. 256, no. 1, pp. 99-101, 2009.
- [21] W. Todd, "A multi-variance analysis in the time domain," 24th Annual PTTI Application and Planning Meeting McLean, VA, 1992, pp. 413-426.
- [22] J. Skřínský, M. Skřínská, Z. Zeliner, "Signal Processing Evaluated by Allan and Hadamard Variances," *Int. J. Cir. Syst. Sig. Process.* vol. 6, no.7, pp. 322-328, 2013.
- [23] J. Skřínský, M. Skřínská, Z. Zeliner, "Calculation, simulation and experimental validation of Allan and Hadamard Variance" in *Recent Advances in Energy, Environment and Geology, Proc. 2nd International Conference on Energy Systems, Environment, Entrepreneurship and Innovation*, Turkey, 2013, pp. 75-81.