

# **SIMULTANEOUS DETERMINATION OF OZONE BY DIFFERENTIAL ABSORPTION LIDAR AND CONVENTIONAL SPOT ANALYSERS DURING PHOTOCHEMICAL SMOG EPISODES**

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## **ABSTRACT**

Within an extensive summer measurement campaign performed in the Czech Republic, ozone concentration values were acquired simultaneously with Differential Absorption Lidar (DIAL), aircraft, and automatic immission monitoring stations.

The measurements were performed in two countryside locations (at a distance of 40-50 km from Prague), during days when increased ozone concentrations were presumed to be in the atmospheric boundary layer. The campaign's aim was twofold: to investigate ozone generation during the transport of atmospheric pollution from the greater Prague urban area and to verify the DIAL measurement methodology itself. We employed the mobile LIDAR 510M system (ELIGHT Laser Systems GmbH, Germany), based on the Titan-Sapphire laser technique, together with calibrated spot monitors in order to estimate the error of the DIAL O<sub>3</sub> determination.

A very good agreement between the data obtained simultaneously by the DIAL method and the calibrated analyser placed in an aircraft deck was observed. The best conformity in particular altitude layers was found in the case of homogeneous distribution of aerosols across the monitored area; the average relative error of the DIAL determination of O<sub>3</sub> in a vertical profile did not exceed 5%.

Data analysis further confirmed a very strong stochastic relationship (94.4 % and 97.5 % respectively) between ground ozone concentration values determined simultaneously by the DIAL method and the spot analyser of the automatic immission monitoring station. The average relative error of the DIAL determination of O<sub>3</sub>, in the concentration range from 50 µg·m<sup>-3</sup> to 190 µg·m<sup>-3</sup>, was about 10%, at meteorological visibility  $V_M \geq 15$  km.

## **INTRODUCTION**

Differential absorption LIDARs [1] do not yet belong to the group of instrumentations commonly used in air quality monitoring. To calibrate or verify the DIAL method, two complementary techniques can be used:

- (a) calibration using a cell of calibrated test gas;
- (b) *in-situ* comparison with other calibrated techniques.

The ability of the DIAL LIDAR 510M system to determine ozone concentrations was already confirmed using a calibration cell [2]. The testing method used, however, does not allow verifying the direct correlation between measured signal and pollutant concentration in the atmosphere under miscellaneous meteorological conditions.

Within an extensive summer measurement campaign performed in the Czech Republic (during days when increased ozone concentrations were presumed to be in the atmospheric boundary layer), ozone concentration values were acquired simultaneously with DIAL LIDAR 510M, aircraft, and automatic immission monitoring stations. In addition to others, these measurements served to prove the entire function of the LIDAR 510M system and to verify the measurement methodology used.

## EXPERIMENTAL

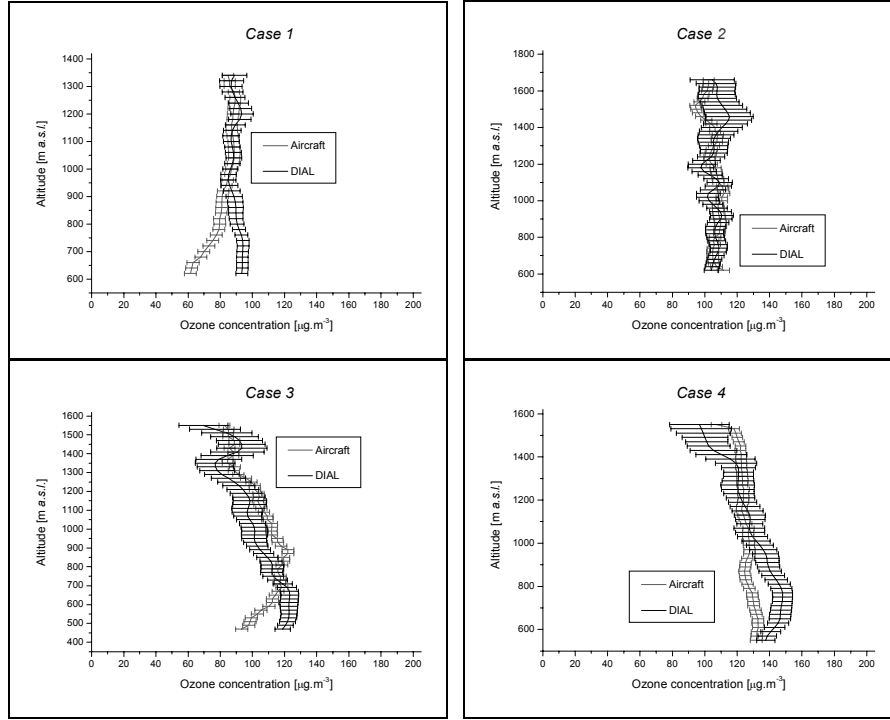
DIAL LIDAR 510M [3] uses a tunable pulse Titan–Sapphire ( $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ ) laser pumped by xenon flash lamps with the repetition rate of 20 Hz. The laser tuning range is 700 – 900 nm. The pulse duration with a Q-switch is less than 40 ns. A specially designed ‘double oscillator’ permits alternating between two wavelengths,  $\lambda_{\text{ON}}$  and  $\lambda_{\text{OFF}}$ , with a bandwidth of less than 0.3 nm each. Nonlinear crystals are employed in order to generate the second and third harmonic frequency. The laser pulse energy, after the third harmonic generation, is more than 0.5 mJ. In the case of  $\text{O}_3$  concentration measurements,  $\lambda_{\text{ON}}$  is 282.4 nm and  $\lambda_{\text{OFF}}$  is 286.3 nm. A rotating periscope enables measurement in any direction. Thus, the creation of horizontal or vertical maps of pollutant concentration is possible from one standpoint. The DIAL system is integrated in a van and equipped with a diesel-powered trailer generator, which makes it fully mobile. Moreover, the van is also equipped with a Doppler SODAR PA2 system (sound detection and ranging), manufactured by Remtech Inc., France ([www.remtechinc.com](http://www.remtechinc.com)). This device enables continuous measurement of the speed and direction of movement of individual atmospheric layers at heights ranging from 20 m to 1500 m. Meteorological data acquired by SODAR enable better interpretation of pollutant concentration profiles measured simultaneously by LIDAR.

The ground spot monitors, the measurement results of which were considered as the result of a reference analytical method, were equipped with a Thermo Electron analyser, model 49 (Thermo Electron Corporation, Environmental Instruments Division, Franklin, Massachusetts, USA), which meets the U.S. EPA standards for continuous monitoring of ambient  $\text{O}_3$  concentration in the range of 0 ppmV to 1 ppmV. The same type of analyser was also installed in the aircraft deck of a L410 Turbolet. The plane sampled the atmosphere in an ascending spiral at a climbing speed not exceeding  $2.5 \text{ m}\cdot\text{s}^{-1}$  (up to the altitude of 1700 meters above sea level). The spot monitors were operated in continual mode, with 5 s sampling intervals, or 10 s in the case of the aircraft sampling, respectively. The DIAL measurements were carried out by means of repeated two-dimensional vertical scans across the monitored areas. Particular 2D scans were composed of ten beams sent in directions forming an angle of 2, 5, 10, 15, 20, 25, 30, 35, 40 and  $45^\circ$  with the ground surface. Each single beam measurement lasted approximately 90 s. Resulting values of ozone concentration were obtained through a mathematical projection [3] of sequential 2D scans onto a one-dimensional vertical profile. That means the resulting values represented arithmetic means of ozone concentrations measured at corresponding altitudes of particular 2D scans performed within a corresponding time interval.

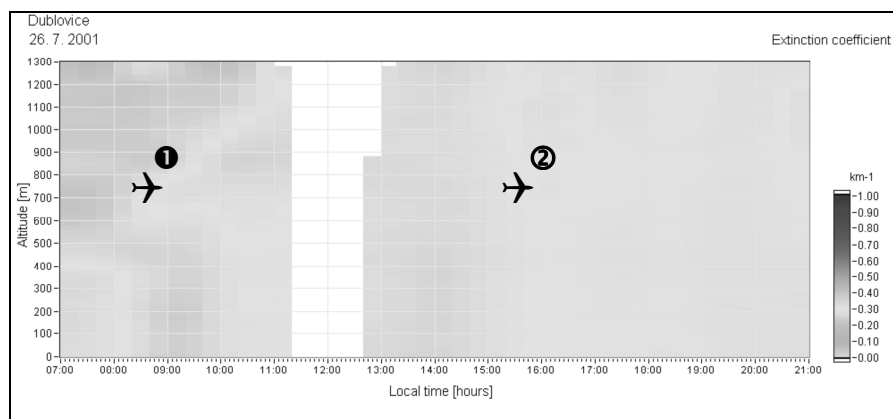
## RESULTS AND DISCUSSION

A very good accordance between the data obtained simultaneously by the DIAL method and the spot analyser placed in the aircraft deck was observed (*Figure 1*). More apparent differences were found at the lowest monitored altitude layers above the ground surface in the case of the 1<sup>st</sup>, 2<sup>nd</sup> and 4<sup>th</sup> synchronously performed monitoring. The vertical gradient of aerosol distribution across the measured area can be considered in these cases as one of the main causes of discrepancies found. For the first approximation, the vertical variability of values of the atmospheric extinction coefficient  $\alpha(r, \lambda)$  can serve as a good indicator of a potential aerosol layer in the air: the sectors with apparently higher values of  $\alpha(r, \lambda)$  correspond to a higher reflection or absorption of

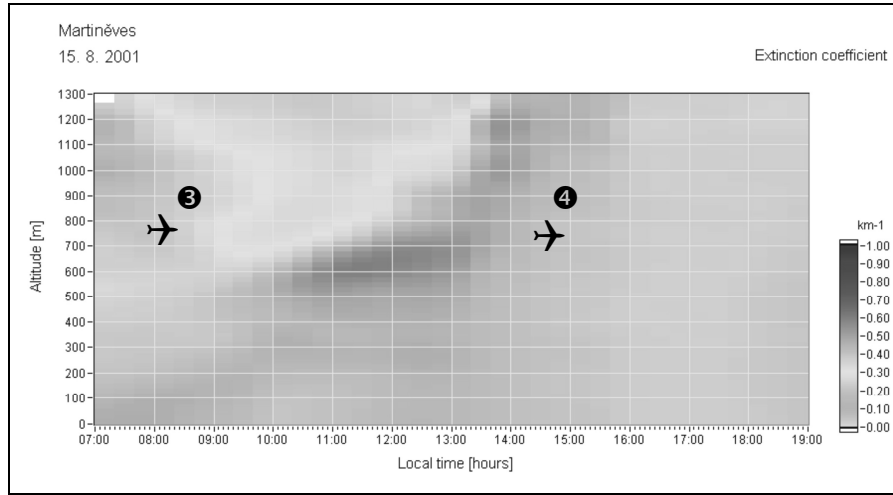
radiation by aerosol particles present. With notably inhomogeneous vertical distribution of aerosols, the condition of only slightly changing the value of backscattering coefficient  $\beta(r, \lambda)$  along the whole path of the radiation beam, as it is assumed to properly determine pollutant concentration using DIAL, is met just partly. In such cases, concentration values determined by the DIAL method are loaded with a systematic error caused by uncertainty of the approximate Mie scattering correction [4] of measured data.



*Figure 1.* Comparison of  $O_3$  concentrations determined in the vertical profile simultaneously by the DIAL method and conventional spot analyser located in the aircraft deck. The data measured by the DIAL method were averaged within a 60-minute time interval and 100 m height interval.



*Figure 2a.* The time-height cross-section of the atmospheric extinction coefficient  $\alpha(r, \lambda)$  obtained by the lidar measurement in the first locality. The height on the vertical axis is measured from the ground (0 m  $\equiv$  360 m above sea level).



*Figure 2b.* The time-height cross-section of the atmospheric extinction coefficient  $\alpha(r, \lambda)$  obtained by the lidar measurement in the second locality. The height on the vertical axis is measured from the ground (0 m  $\equiv$  250 m above sea level).

It can be concluded from time-height cross-sections of  $\alpha(r, \lambda)$  measured by lidar during the days the plane flew across the monitored areas (*Figure 2*) that the most homogenous aerosol distribution was during the second of all four cases of synchronous monitoring (in the first locality, between 3:32 – 3:42 p.m.). The best conformity in particular altitude layers was found in this case; the average relative error of the DIAL determination of  $O_3$  in a vertical profile was approximately 5%. Remarkably, at levels of about 1450 m above sea level, a decrease in signal-to-noise ratio has already started to emerge, causing the deviation of concentration values obtained by the DIAL method from the values obtained by aircraft sampling.

The ground ozone concentration values determined by the DIAL method were compared with data measured simultaneously by the spot analyser of the automatic immission monitoring station. The mean value  $\bar{\Delta C}_{O_3}$  and the population median  $\tilde{\Delta C}_{O_3}$  of the sets of differences  $\{\Delta C_{O_3}\}_i = \{C_{O_3}^{DIAL}\}_i - \{C_{O_3}^{spot\ analyser}\}_i$  in either locality in pairs obtained concentration values were tested. The results of our analysis indicated a difference from  $0 \mu g \cdot m^{-3}$  of both the mean value (t-test) and median value (signed rank test) for both localities investigated. The hypothesis of a systematic constant error of the DIAL determination of  $O_3$  has been verified by the Youden simple regression method, which found significant differences in individual estimations  $b$  of  $\beta$  parameter of linear regression from 1, with simultaneous negligible deviations of estimations  $a$  of parameter  $\alpha$  from  $0 \mu g \cdot m^{-3}$ . The parameters of respective linear regression relations  $\{C_{O_3}^{DIAL}\}_i = \alpha + \beta \cdot \{C_{O_3}^{spot\ analyser}\}_i + \varepsilon_i$  are specified in *Table 1* together with mean values  $\bar{\Delta C}_{O_3}$  and population medians  $\tilde{\Delta C}_{O_3}$ . Above all, the reasons for differences between simultaneously obtained ground ozone concentration values can be found in the following facts:

- Concentration values obtained by the DIAL method, unlike the values measured by the spot analyser, characterize the ozone distribution in a certain spatial sector of a non-zero length. That means the DIAL monitoring shall always map possible spatial variability of a monitored pollutant that cannot be registered by a spot monitor.
- The actual geographical conditions (terrain height zoning) does not allow to choose the lowest beam of the vertical scan so that it can directly pass through the volume

element sampled by the ground monitor. Therefore, the analysis uses two values: one obtained by the mathematic extrapolation of concentration values measured by DIAL in respective time intervals in a vertical profile; and, secondly, concentrations obtained by averaging instantaneous values measured along the beam path led in the direction forming the smallest angle possible with the ground surface (one-dimensional “1D” monitoring). The results of the analyses performed have proven a very strong stochastic relationship between extrapolated data and data measured by the reference analyser:  $D = 94.4\%$  (or  $97.5\%$  respectively) for concentrations obtained in pairs in the first (or the second, respectively) locality. In comparison with 1D monitoring, the proportional systematic error can be defined more precisely in this case; however, it reaches higher values (see *Table 1*). The deviation of the mean value  $\bar{\Delta C}_{O_3}$ , or the deviation of population median  $\tilde{\Delta C}_{O_3}$  respectively, from  $0 \mu\text{g}\cdot\text{m}^{-3}$  is lower in case of 1D monitoring. Thus, it is obvious that mathematical extrapolation of data measured by the DIAL method represents, in the respective case of monitoring, one of the sources of the systematic error revealed.

Average interval of height [m]	temporal [min.]	Number of concentration values in pairs determined [-]	$\bar{\Delta C}$	$\tilde{\Delta C}_0$	$\sigma^2$	$a$	$s_a$	$b$	$s_b$	$r$	$D$
			$[\mu\text{g}\cdot\text{m}^{-3}]$	$[\mu\text{g}\cdot\text{m}^{-3}]$	$[\mu\text{g}^2\cdot\text{m}^{-6}]$	$[\mu\text{g}\cdot\text{m}^{-3}]$	$[\mu\text{g}\cdot\text{m}^{-3}]$	[-]	[-]	[-]	[%]
100	30	81	11	8,8	70,3	4,82	4,19	1,05	0,03	0,9608	92,3
	60	65	11,5	10,9	51,3	4,22	3,93	1,06	0,03	0,9718	94,4
10		65	12,9	10,3	164,7	4,49	7,22	1,07	0,06	0,9166	84,0
"1D"	3	55	5,5	5,6	84,8	4,00	5,73	1,01	0,05	0,9473	89,7

Average interval of height [m]	temporal [min.]	Number of concentration values in pairs determined [-]	$\bar{\Delta C}$	$\tilde{\Delta C}_0$	$\sigma^2$	$a$	$s_a$	$b$	$s_b$	$r$	$D$
			$[\mu\text{g}\cdot\text{m}^{-3}]$	$[\mu\text{g}\cdot\text{m}^{-3}]$	$[\mu\text{g}^2\cdot\text{m}^{-6}]$	$[\mu\text{g}\cdot\text{m}^{-3}]$	$[\mu\text{g}\cdot\text{m}^{-3}]$	[-]	[-]	[-]	[%]
100	30	65	11,1	11,5	76,2	1,65	3,76	1,07	0,03	0,9796	96,0
	60	56	10,5	10,7	49,8	2,50	3,39	1,06	0,02	0,9874	97,5
10		56	10,0	11,2	149,6	2,10	4,92	1,08	0,04	0,9649	93,1
"1D"	3	61	5,1	4,3	106,7	2,40	5,05	1,02	0,04	0,9644	93,0

*Table 1.* The parameters of regression  $\{C_{O_3}^{DIAL}\}_t = \alpha + \beta \cdot \{C_{O_3}^{spot\ analyser}\}_t + \varepsilon_t$  (right part of the table), together with the mean value  $\bar{\Delta C}_{O_3}$  and population median  $\tilde{\Delta C}_{O_3}$  (left part of the table) of the set of differences  $\{\Delta C_{O_3}\}_t = \{C_{O_3}^{DIAL}\}_t - \{C_{O_3}^{spot\ analyser}\}_t$  in the first (upper part of table) and the second (lower part of table) locality in both measuring days of paired  $O_3$  concentrations determined at the ground level. Symbol  $\sigma^2$  represents the variance of  $\{\Delta C_{O_3}\}_t$  values round the mean value  $\bar{\Delta C}_{O_3}$ ,  $s_a$  is the standard deviation of  $a$  coefficient and  $s_b$  is the standard deviation of  $b$  coefficient. The coefficient of determination  $D = 100 \cdot r^2$ , where  $r$  symbol represents the correlation coefficient between the paired values  $\{C_{O_3}^{DIAL}\}_t$  and  $\{C_{O_3}^{spot\ analyser}\}_t$ .

Other error sources, especially errors caused by possible interferences with other pollutants absorbing radiation of the wavelengths used, can be considered as negligible due to the wise choice of measurement sites. The SODAR measurements performed, together with ground spot monitoring results, indicated no significant transport of possible gaseous interferents into the monitored areas.

With respect to the facts mentioned above, the average relative error of DIAL determination of ground ozone in a concentration range of  $50 \mu\text{g}\cdot\text{m}^{-3}$  to  $190 \mu\text{g}\cdot\text{m}^{-3}$

$$\bar{\phi} = \frac{\sum_{t=1}^n \left| \{C_{O_3}^{DIAL}\}_t - \{C_{O_3}^{spot\ analyser}\}_t \right|}{n} \cdot 100 \quad (\text{Eq. 1})$$

acquiring the value of about 10% at meteorological visibility  $V_M \geq 15$  km, can be considered as very satisfactory. Symbols  $\{C_{O_3}^{DIAL}\}_t$  and  $\{C_{O_3}^{spot\ analyser}\}_t$  in Equation 1 represent arithmetic averages within the time interval of 60 minutes ( $t - 30$  minutes;  $t + 30$  minutes) of the ground ozone concentrations obtained by both methods. It should be admitted that the mentioned concentration scale covers almost the whole range of ozone concentrations commonly observed in the atmospheric boundary layer during all periods of a year.

## CONCLUSION

Simultaneous monitoring of tropospheric ozone, performed in two countryside localities by the DIAL method and conventional spot analysers located both at the ground surface and in an aircraft deck, served to verify the DIAL-monitoring methodology and to estimate an error of the DIAL determination of  $O_3$ .

A very good agreement between the data obtained simultaneously by the DIAL method and the calibrated analyser placed in the aircraft deck was observed. The best conformity in particular altitude layers was found in the case of homogeneous distribution of aerosols across the monitored area; the average relative error of the DIAL determination of  $O_3$  in the vertical profile did not exceed 5%.

Data analysis further confirmed a strong stochastic relationship between ground ozone concentrations determined simultaneously by the DIAL method and the spot analyser of the automatic immission monitoring station. The strong correlation indicates reliable identification of time trends of  $O_3$  concentration in the atmosphere using the LIDAR 510M system.

Because of the unique information acquired by the DIAL system, the question of its accuracy and compatibility with air quality monitoring reference methods is still of great importance. Generally, simultaneous measurements carried out under miscellaneous meteorological conditions should contribute to better estimation and evaluation of error in determination of atmospheric pollutants using the DIAL technique.

## ACKNOWLEDGMENTS

This work was supported by the Grant Agency of the Czech Republic (grant no. 205/02/0898), and by the Czech Ministry of Environment (project VaV/740/2/00). In order to purchase the LIDAR 510M / SODAR PA2 system, a donation of one million DEM was granted by the German Ministry of Environment in the framework of a bilateral Czech and German project.

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