

Design and Construction of Differential Optical Absorption Spectroscopy (DOAS) System for NO_x Remote Sensing

Dr. Mehdi M. Shellal

Laser and Optoelectronics Engineering Department, University of Technology/Baghdad

Dr. Naseer M. Hadi 

Laser Research Centre, Ministry of Science and Technology/Baghdad

Thamer M. Mohammed

Laser and Optoelectronics Engineering Department, University of Technology/Baghdad

Received on:5/10/2015 & Accepted on:4/2/2016

ABSTRACT

Differential Optical Absorption Spectroscopy (DOAS) technique is one of the methods used for measurement, analysis and managing air pollution, studying the chemical properties of trace gases in the atmosphere, identification of critical (peak) values to determine the concentration of trace gases that cause an air pollution in industrial-urban locations, and are used in evaluating criteria of photochemical or smog pollution cases of fewer days, and in analysis of wind directions. According to these issues the (DOAS) technique has been developed to become one of techniques that have high order in practical performance based on UV-Visible and near infrared region at spectral range of (200-1100nm) wavelength absorption by molecules of gases in atmosphere. The experimental work of this thesis has been focused on calibration of the system with laboratory experiments to detect many atmospheric gases which are nitrogen oxides (NO, NO₂ and NO₃ radical). DOAS technique is based on the principle of optical absorption by molecule of gas over several meters to many kilometers length, DOAS gives average concentration measurement lead's to general pollution estimation at long distances, and consequently avoids local perturbation events in point's measurements. The DOAS technique provides typical database by using the language of C # compared with results obtained from experimental measurements.

Keywords: DOAS technique, air pollution, atmospheric chemistry, Nitrogen Oxides, CCD detector, Absorption spectrum, and Spectrum analyzer.

INTRODUCTION

In the atmosphere, nitrogen oxides (NO_x) are an important trace gas, but it is also an important constituent of air pollution. It plays an important base in the chemistry of the atmosphere. The oxides of nitrogen (NO, NO₂), have an important base in atmospheric chemistry in the calculation of earth's ozone distribution. Herein, we have discussed about the sources and sinks for NO₂ in the atmosphere with some details on nitrogen oxides health effects. We have presented a short introduction to the Differential Optical Absorption Spectroscopy (DOAS) technique which is now one of the most generally used spectroscopic ways to measure atmospheric trace gases. This work includes a tool (HR4000Spectrometer) with a range of (200-1100nm) wavelength and designed in the atmosphere. Nitrogen oxides (NO_x) are an important trace gas, but it is also an

important constituent of air pollution. It plays an important base in the chemistry of the atmosphere [1, 2]. The oxides of nitrogen (NO, NO₂), have an important base in atmospheric chemistry in the calculation of earth's ozone distribution. Herein, we have discussed about the sources and sinks for NO₂ in the atmosphere with some details on nitrogen oxides health effects. We have presented a short introduction to Differential Optical Absorption Spectroscopy (DOAS) technique which is now one of the most generally used spectroscopic ways to measure atmospheric trace gases. The reasons to choose these tools are due to, high resolution, small size, powerfulness, relatively low price and light weight. DOAS is dependent on the principle of remote sensing to measure chemical species in free space or atmospheric layers, troposphere and stratosphere. In this work, the sources used include broad spectral band light such as: deuterium and halogen lamps of continuous spectrum to measure atmospheric species.

This technique is used to measure air pollution through determining the concentration of trace gases. So this technique should be more sensitive at low concentration of gases to describe few parts per billion (20ppb at pressure 1atm.295k)[3]. The high sensitivity is required to avoid the interferences with other particles in the atmosphere. This technique is very important for measuring the concentration of trace gases such as, NO, NO₂ and NO₃ radical in open path and detection limit for volcanic emissions, air pollution and bombers by using UV/VIS and NIR spectral region at the range (200-1100nm) wavelength, then to analysis type and concentration of gas. Nitrogen oxides are considered the most pollution species in the environment and urban areas. DOAS technique can be applied to several meters of distance [4]. The instrument of DOAS technique includes continuous light source and the sample is placed at over (1- 4m) distance from a light source, high resolution spectrum analyzer (HR4000 spectrometer), telescope, monochromator, photomultiplier tube detector and monitor. Finally, a comparison between the DOAS instrument and UV/Visible spectrometer technique was done [5, 6], the process is presented as shown in figure (1).

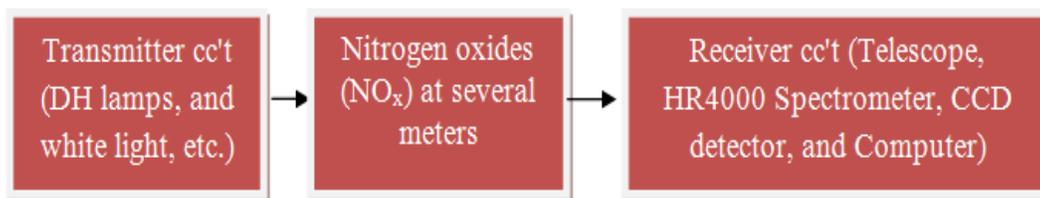


Figure (1): Steps of DOAS Set-up

The DOAS technique has many applications [6] as shown in the following:

- Monitoring of air pollution to observe the performance of active DOAS
- Monitoring distribution of trace gas in atmosphere (troposphere and stratosphere) by measuring the concentration.
- Diagnosis composition of the stratosphere passive spectroscopy.
- To study the atmospheric chemistry.

Experimental setup

The DOAS system consists of the following parameters:

- 1) Broad spectral band UV-Vis and Nir light source, deuterium and halogen lamps.
- 2) Telescope to collect beam divergence toward detector.
- 3) A target cuvette to the liquid sample or gas chamber to the gas.

- 4) Spectrum analyzer high resolution type (HR4000) connected to the computer for saving absorption spectra for target (liquid and gas).
 - 5) Personal computer to control the detector to save the absorption spectrum.
- These components are shown in Fig. (2)

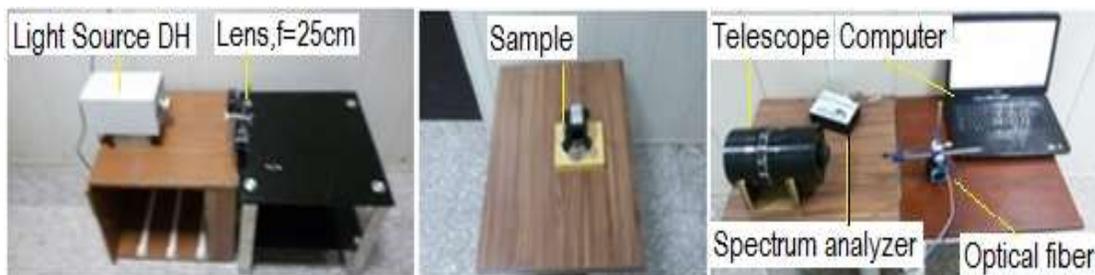


Figure (2): Overall devices of the DOAS system model

The advantages of DOAS system are:

- 1) Broad spectral band has a feature that Rayleigh and Mie of scattering are canceled [5].
- 2) There is no need to estimate the incident intensity [7].
- 3) High sensitive, specification and quantum efficiency at long path length [8,9].
- 4) The scientific studies require parameters such as low detection limit, more or large degree flexibility and specific detection [8].

Results and Discussions

In this part, the DOAS technique study of absorption spectroscopy for many solutions with approx. different concentrations will be tested. The results of the experimental work and their discussion are to be shown here. This work includes the measurement of absorption intensity in the UV-Vis and Nir region produced by the interaction of a light beam with material. The target is the water solutions of nitrate compositions (NaNO₃), nitrite composition (NaNO₂) and vapor gases NO, NO₂ and NO₃ radical. For studying the effect of the light beam parameters in using DOAS applications, we introduced many experiments for identifying the impact of these effects of light beam parameters:

Effect of the light beam on the absorption Intensity for sodium nitrite (NaNO₂) solution

Figures (3 a, b, c, d, e and f) show many of concentrations for sodium nitrite (NaNO₂) solution of the atmospheric pressure in the range (200-1100 nm) wavelength, continuous light power 25watt. The spot size diameter of the light beam is equal to 1cm to cover target area. The concentration of the NaNO₂ exhibited an almost linear increase with absorbance.

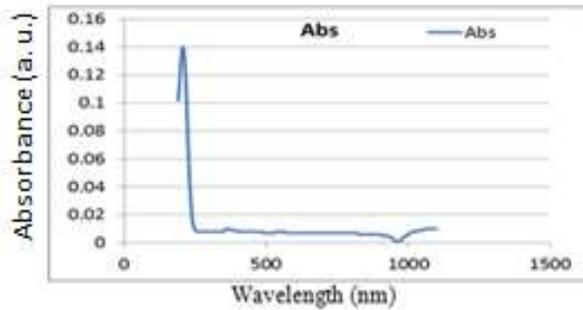


Figure (3a) The absorption spectrum of the NaNO₂ at concentration 15 ppm

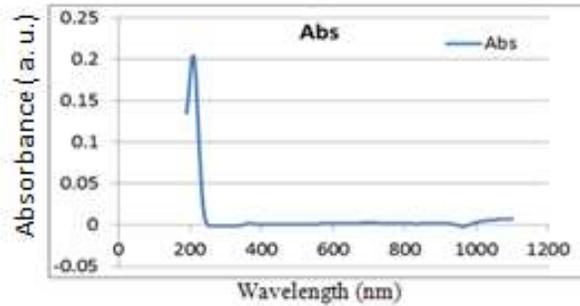


Figure (3b) The absorption spectrum of the NaNO₂ at concentration 20 ppm

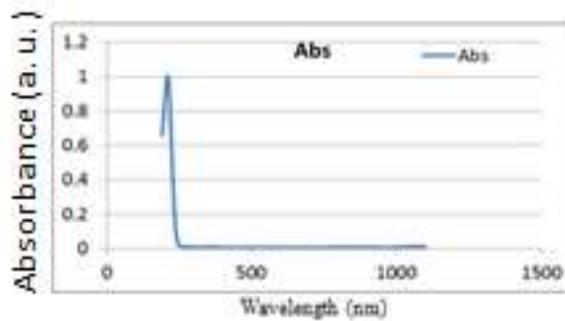


Figure (3c) The absorption spectrum of the NaNO₂ at concentration 55 ppm

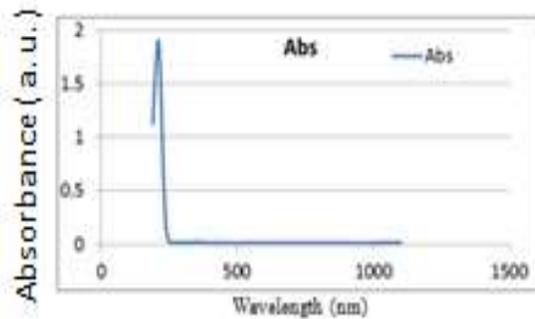


Figure (3d) The absorption spectrum of the NaNO₂ at concentration 100 ppm

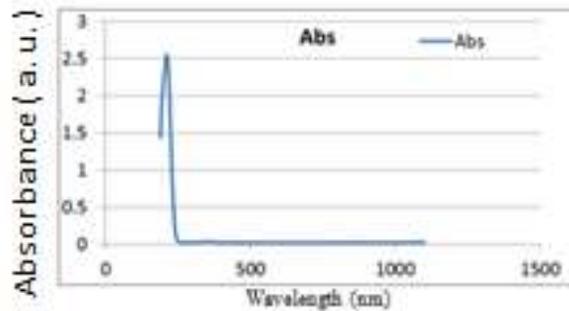


Figure (3e) The absorption spectrum of the NaNO₂ at concentration 125 ppm

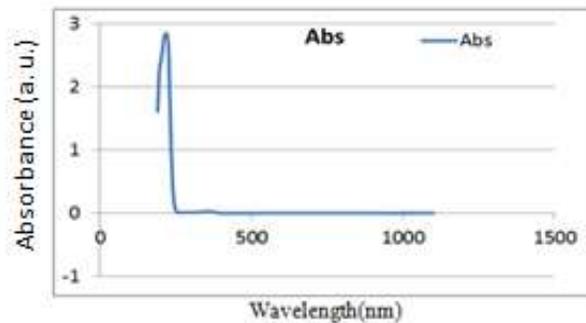


Figure (3f) The absorption spectrum of the NaNO₂ at concentration 150 ppm

Effect of the light source on the barium nitrate BaNO₃ solution absorption Intensity

Figures (4 a, b, c and d) show, the different concentrations of barium nitrate (BaNO₃) solution at normal atmospheric pressure and room temperature (1 atm., and 298k) in the range (200-1100 nm) wavelength, of continuous light power 25 watt. The spot size diameter of the light beam is equal to 1cm to cover target area.

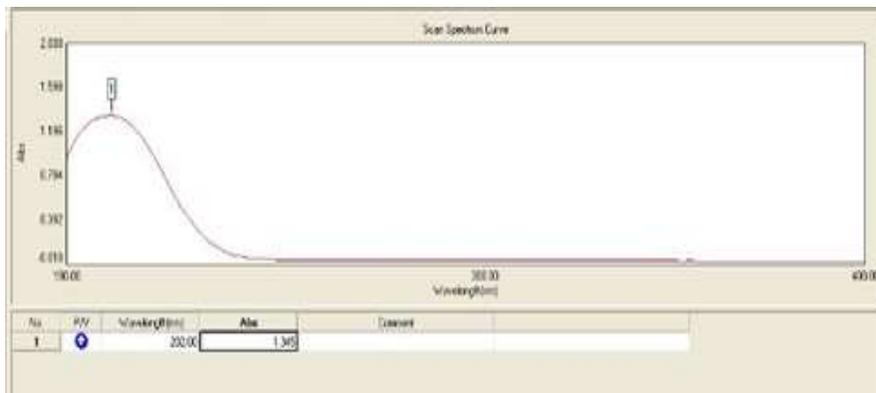


Figure (4a) The absorption spectrum of the BaNO₃ at concentration of 15 ppm

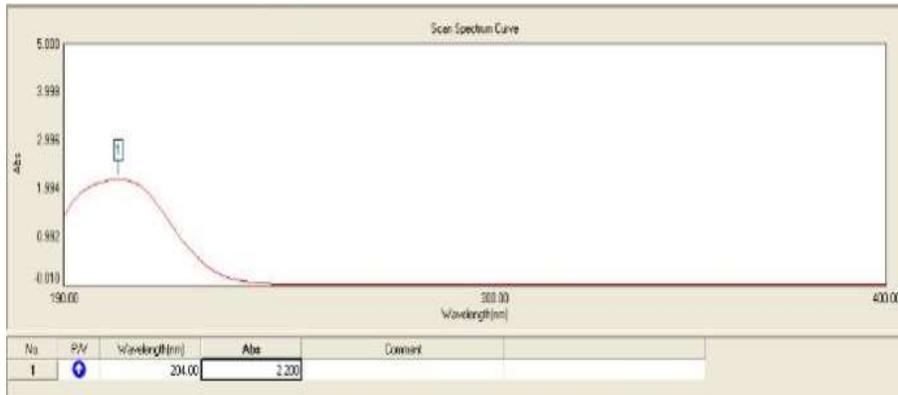


Figure (4b) The absorption spectrum of the BaNO₃ at concentration of 25 ppm

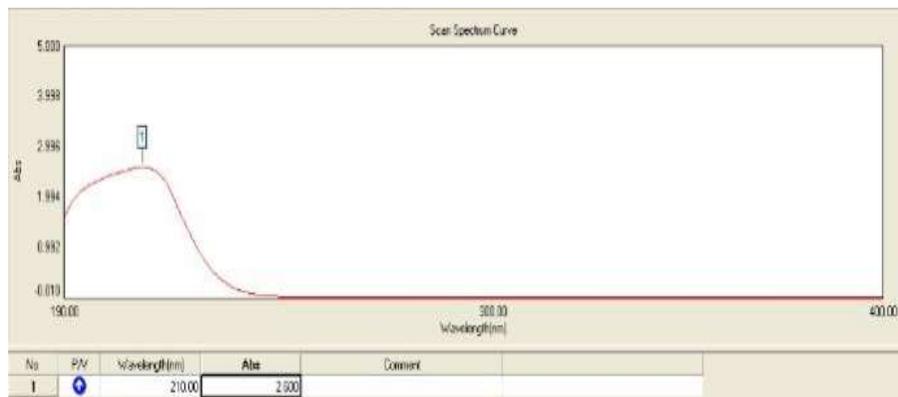


Figure (4c) The absorption spectrum of the BaNO₃ at concentration of 50 ppm

The concentration of the BaNO₃ exhibited an almost linear increase with absorption as shown in fig. 4d.

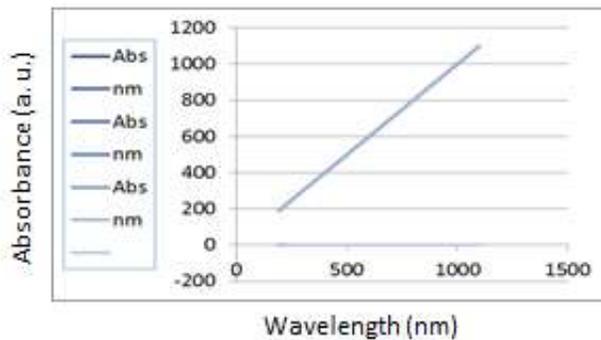
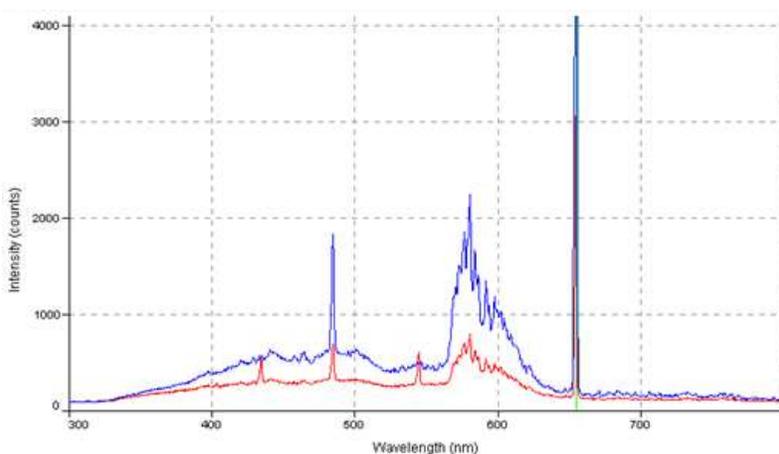


Figure (4d): Calibration curve of the BaNO₃ an absorbance as a function of concentration, 15, 25, and 50 ppm with wavelength is constant

Effect of the light source on the differential absorption for nitrogen oxides

In the vacuum chamber the light beam can subject several processes like absorption. In DOAS only those signals that are changing rapidly are analyzed as a function of wavelength (differential) in DOAS. We can investigate different species instantaneously [6, 9]. From DOAS, target species that can be retrieved are, NO, NO₂ and NO₃ radical. Some differential absorption cross-sections are shown in figure 6. The vacuum chamber evacuated down to 1atm using hand pump and diffusion pump at one time. The dissolved gas was removed by boiling the water at 90C⁰ for 8 minutes; a plastic pipe was used to transfer the gas to the gas chamber. Nitric oxides (NO_x) were analyzed by applying light beam across quartz windows; the sample is placed at variable distances.



Figure(5) Differential absorption cross-sections of different gas species (NO_x) at 4m in the laboratory.

DOAS system includes some parameters that experimentally and technically can powerfully affect the analytical results. The DOAS system has been designed in this work which does not differ in principle from the origin, but some of the side effects that go out working as an ideal. DOAS has several spectrometers with wide spectral regions. There have been optical resolution (0.5 nm or lower than) to know spectral lines more. Optical chamber is designed for keeping isolation from the environment gases, distortion and optical noise level. In low power light source we need to the focus the light beam on the target for keeping on the parallel light beam to cover target area and low attenuation of the signal intensity. The intensity of the light beam on the target calculates function irradiance. It is between (69.6-2.8 lux) that gives the best intensity of the absorption spectrum on the background signal.

CONCLUSIONS:

The following conclusions were drawn:

- 1) The optical system was isolated within a closed optical cavity gas chamber to obtain high accuracy and resolution for absorption spectrum.
- 2) The night time has low noise and distortion, high accuracy of the low power source was obtained which is proportional to good alignment, high resolution in several distances and the (S/N) is high.
- 3) Spectrometer parameters (wide spectral range and optical resolution) have been very important that covers wide range of the absorption spectrum trace gases, and higher ability to split spectrum lines.

REFERENCES

- [1] Platt, U.; Stutz, J.; Differential absorption spectroscopy, Physics of earth and space environments, 2008.
- [2] Svanberg, S.: Atomic and Molecular Spectroscopy, 2nd. Springer Series on Atoms and Plasmas, Springer Berlin, Heidelberg (1992).
- [3] Edner, H., Ragnarson, P., Svanberg, S.: A multi-path DOAS system for large area pollution monitoring. In: Borrell, P.M., et al. (eds.) Proceedings of EUROTRAC Symposium 1992, pp. 220–223, SPB Academic Publishing BV, Den Haag (1992).
- [4] Davis et al ,1981, D.D., Rodgers, M.O., Fischer, S.D., Asai, K.: An experimental assessment of the O₃ /H₂O interference problem the detection of natural levels of OH via laser induced fluorescence. Geophys. Res. Lett. 8, 69–72 (1981).
- [5] Hofzumahaus, A., Aschmutat, U., Brandenburger, U., Brauers, T., Dorn, H.-P., Hausmann, M., Hessling, M., Holland, F., Plass-Dulmer, C., Ehhalt, D.H.: Inter-comparison of tropospheric OH measurements by different laser techniques during the POPCORN campaign 1994. J. Atmos. Chem. 31(1–2), 227–246 (1998).
- [6] Holland, F., Hofzumahaus, A., Schäfer, J., Kraus, A., Pätz, H.: Measurements of OH and HO₂ radical concentrations and photolysis frequencies during BERLIOZ. J. Geophys. Res. 108(D4), 8246 (2003). doi:10.1029/2001JD001393 (2003).
- [7] Hilboll, A., Richter, A., and Burrows, J.P.: Long-term changes of tropospheric NO₂ over megacities derived from multiple satellite instruments, Atmos, China Phys., (2013).
- [8] Richter, A.; Introduction of Measurement techniques in environmental physics, IUP, University of Bremen, 2006. Retrieved on 22.09.2013
- [9] <http://www.doas-bremen.de/doas-glossary.htm> - retrieved on 09.07.2014