Communications in Physics, Vol. 34, No. 1 (2024), pp. 11-18
DOI: https://doi.org/10.15625/0868-3166/19360

Development of broadband ultraviolet pulsed laser using Ce:LiCAF crystal to determine SO_2 gas concentration by differential absorption spectroscopy

Minh Hong Pham[1,†], Diep Van Nguyen[1,2], Duong Van Pham[1], Tu Xuan Nguyen[1], Hieu Minh Do[1], Kieu Anh Thi Doan[1], Tiep Viet Phung[2], Luu Hong Dang[3], Dan Van Le[3], Bich Thi Vu[4], Marilou Cadatal-Raduban[5] and Trung Van Dinh[1]

[1]*Institute of Physics, Vietnam Academy of Science and Technology, 10 Dao Tan, Ba Dinh, Hanoi 11108, Vietnam*

[2]*Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam*

[3]*Tran Quoc Tuan University, Co Dong, Son Tay, Hanoi, Viet Nam*

[4]*Institute of Theoretical and Applied Research, Duy Tan University, 100000 Hanoi, Viet Nam*

[5]*Centre for Theoretical Chemistry and Physics, School of Natural Sciences, Massey University, Auckland 0632, New Zealand*

E-mail: [†]phminh@iop.vas.vn

Received 5 November 2023; *Accepted for publication 21 December 2023*
Published 05 February 2024

Abstract. *Earth's atmosphere is a mixture of many gases which include pollutants such as SO_2, NO_2, NO, and O_3 that have absorption in the ultraviolet (UV) wavelength region. Therefore, the development of broadband UV laser sources that are useful in a differential absorption spectroscopy (DOAS) system for environmental research is necessary. In this research, we present the DOAS system using the Ce:LiCAF laser for determining SO_2 gas concentration in the atmosphere. The Ce:LiCAF laser has a full width at half maximum of 2 nm with a wavelength range from 286 to 291 nm and a peak wavelength of 288.5 nm. The results show that the DOAS system accurately determines the gas concentration with a measurement error of 6%. This result can serve as the basis for developing practical DOAS systems with the ability to monitor a wide range of gasses and survey many other types of pollutants.*

Keywords: Ce:LiCAF laser; broadband laser; DOAS; concentration of gases; SO_2.
Classification numbers: 42.68.Ay; 92.60.Ta; 42.60.Da; 42.62.Cf; 42.68.-w; 96.60.Tf; *96.60.tj.

1. Introduction

Earth's atmosphere is a layer of gases, which is composed of about 78% nitrogen and 21% oxygen. Although ozone (O_3), carbon dioxide (CO_2), nitrous oxide (NO), chlorofluorocarbon (CFC), and sulfur dioxide (SO_2) only account for a small proportion of the atmospheric composition, the presence of these gases are concerning because their distribution, properties, and fluctuations greatly impact life on earth. Among these gases, SO_2 is a pollutant gas and a major threat to the health of humans and animals. SO_2 irritates the skin, eye membranes, nose, and throat. This gas can also combine with other substances and can change into small particles that go deep into the lungs and cause respiratory diseases. The natural source of SO_2 emissions is volcanic activity, but 99% of the SO_2 in the atmosphere comes from human activities such as burning coal, oil, and gas to make electricity and heat [1–4].

Research on SO_2 gas in the atmosphere can utilize differential absorption spectroscopy (DOAS), which is an advanced remote sensing technique that allows the identification and determination of the concentration of gases by measuring the narrowband absorption [5]. The DOAS technique has been demonstrated to study many atmospheric gases with large survey distances of up to 15 km, ppb-level accuracy, and low cost [4, 6–8]. A DOAS system is composed of a broadband radiation source and a spectrometer, and also includes optical devices responsible for transmitting and receiving radiation after passing through the atmosphere. The choice of radiation source depends on the absorption characteristics of the gas, sunlight, scattered light from the sun or xenon lamps with a wide emission spectrum.

Recently, the development of ultraviolet laser sources for DOAS systems has been carried out. By frequency conversion of dye lasers emitting in the visible region, ultraviolet laser radiation operating in the wavelength range of 224-229 nm has been used to determine NO gas concentration [9]. Meanwhile, a lidar system using wavelengths of 282.9 nm and 286.4 have been used to determine the structure in the vertical direction of ozone [10]. However, the small output energy and dependence on the nonlinear crystal limits the scope of the investigation. DOAS systems that apply sources from the sunlight or xenon lamps for research on SO_2 gas have also been implemented. However, these light sources have limitations such as low power or high divergence [11, 12].

Figure 1 shows the characteristic absorption spectrum of SO_2 gas. SO_2 gas strongly absorbs in the wavelength range of 280 to 320 nm with spectral peaks located close to each other. Therefore, developing UV laser sources with a wavelength range of 280 to 300 nm for DOAS systems is necessary to investigate SO_2 gas in the atmosphere [5, 13]. Recent work has shown that Ce^{3+}:$LiCaAlF_6$ (Ce:LiCAF) laser is a UV solid-state laser source with many advantages such as broad emission bandwidth from 280 to 320 nm [14–16] and high conversion efficiency (up to 46%) when pumped by the fourth harmonics of a Nd:YAG (266 nm) or Nd:YLF (262 nm) laser [17]. The application of this Ce:LiCAF laser to study the distribution and density of O_3 in the atmosphere has also been carried out [18]. In Vietnam, a Ce:LiCAF laser emits UV and broadband radiation by using the Fabry-Perot resonator configuration has developed [19]. However, the low output laser energy has limited the application of the source.

In this report, a differential absorption spectroscopy (DOAS) system has been presented using the Ce:LiCAF ultraviolet laser. We developed an ultraviolet broadband amplifier using

Ce:LiCAF crystal. Furthermore, this amplified Ce:LiCAF laser radiation has been applied to the DOAS system to determine the SO_2 gas concentration.

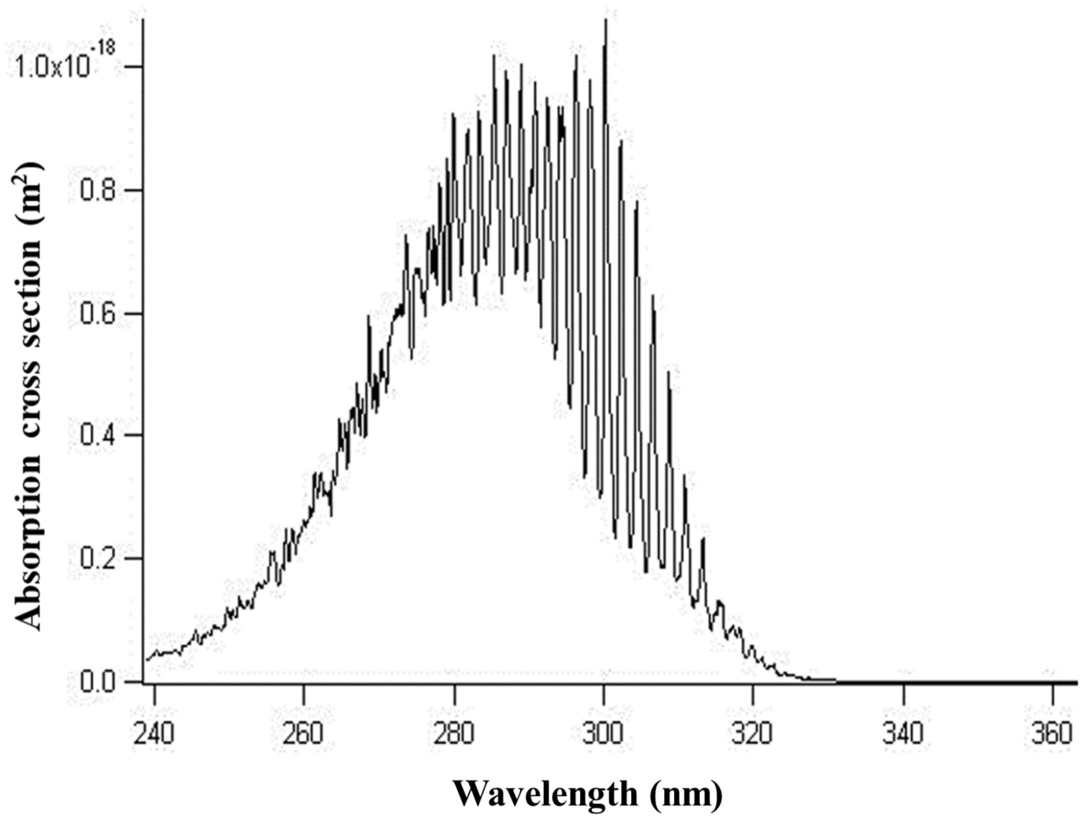


Fig. 1. Absorption cross section of SO_2 gas in the ultraviolet region [5].

2. The 4-pass amplifier system of UV laser pulses using Ce:LiCAF crystal

The 4-pass amplifier of broadband UV laser pulses using Ce:LiCAF crystal is shown in Fig. 2. A seed pulse having power of 7 mW, 3 ns pulse duration and full width at half maximum (FWHM) of 2 nm with a peak spectrum at 288.5 nm. The pumping source is the fourth harmonics (266 nm) of a Q-switched Nd:YAG laser operating at 10 Hz repetition rate and 7 ns pulse duration and a pump laser power of 160 mW.

The amplifier has an output power of up to 54 mW, corresponding to an amplification factor of 8. The output spectrum has a FWHM of 2 nm, a wavelength range from 286 to 291 nm, and a peak of 288.5 nm (Fig. 3a). The output pulse duration is 3.1 ns as shown in Fig. 3b. This laser amplifier is applied for a DOAS system to determine the concentration of pollutant gases, which have absorption spectrum in the range of 286 to 291 nm.

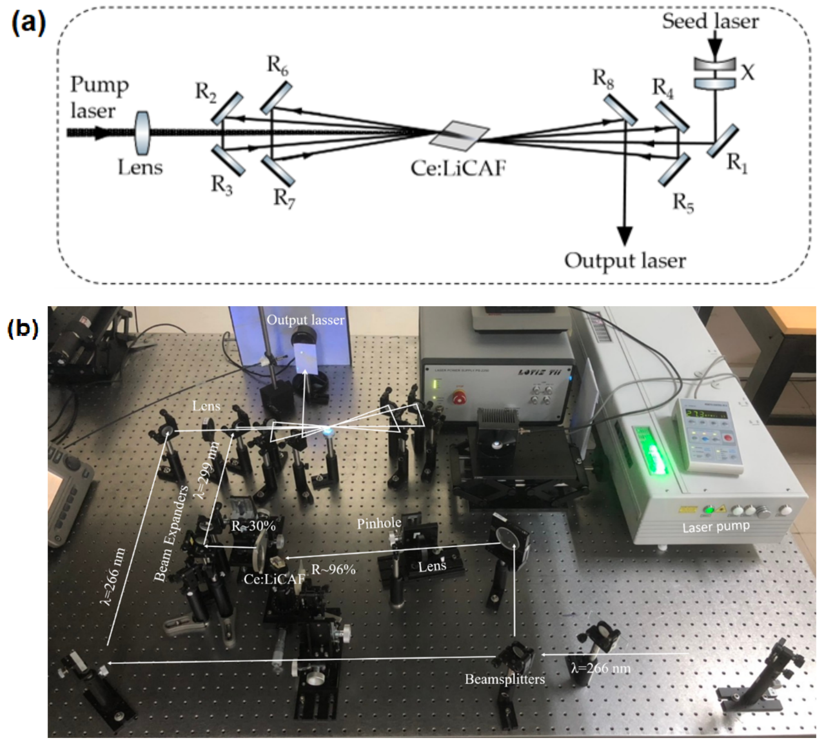


Fig. 2. (a) Schematic diagram and (b) experimental system of the 4-pass amplifier using a Ce:LiCAF crystal.

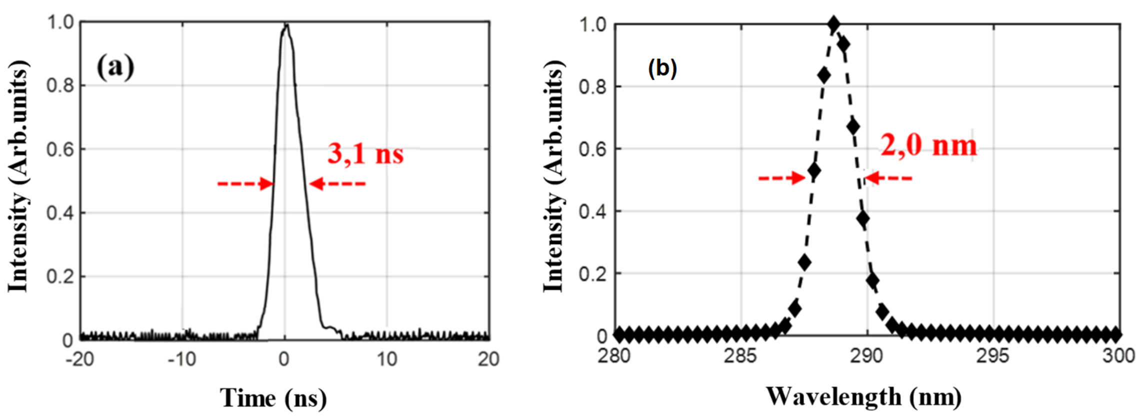
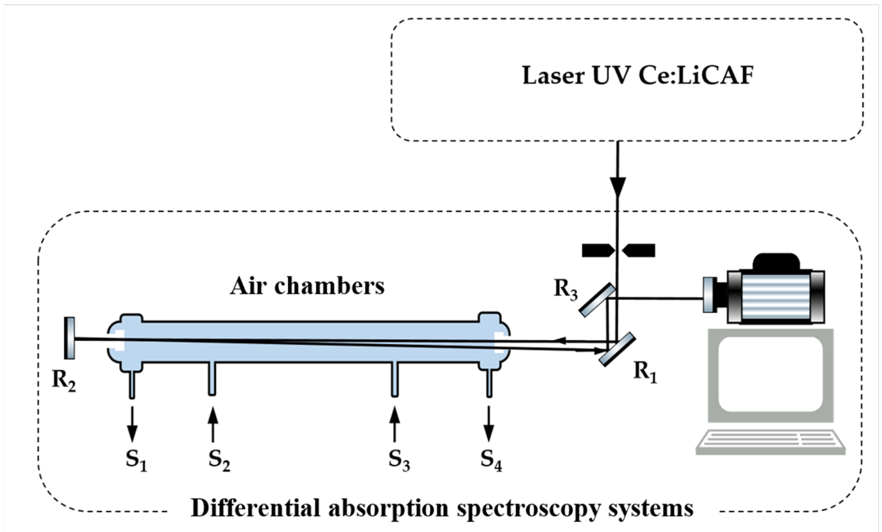


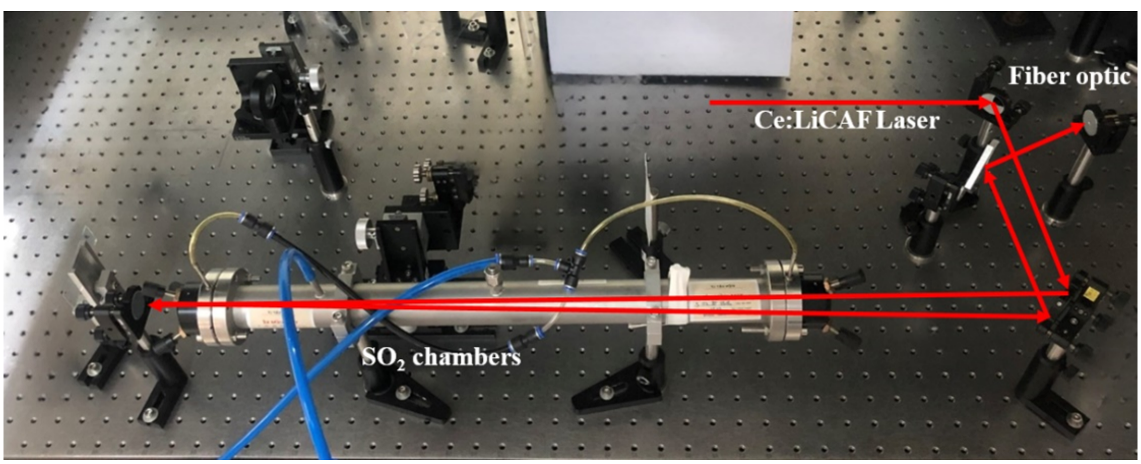
Fig. 3. (a) Pulse and (b) spectrum of output laser.

3. Measurement of SO_2 gas density using differential optical absorption spectroscopy

Before developing the DOAS system and researching gases in the atmosphere, it is necessary to evaluate the performance of DOAS at a laboratory scale. Therefore, the DOAS using Ce:LiCAF laser has been developed, the DOAS schematic diagram and experimental system shown in Fig. 4. The structure of the DOAS can be divided into three main parts, namely: (1) excitation laser, (2) air chambers, and (3) signal reception and data processing system.



(a)



(b)

Fig. 4. (a) DOAS schematic diagram and (b) experimental system for measuring actual SO_2 gas concentration.

Excitation laser: The laser system has been developed and reported in Sec. 2 [20]. To increase the absorption of SO_2 gas, the laser beam will be guided through the chambers twice by aluminum-plated mirrors R_1 and R_2 with a high reflection coefficient of over 90% in the wavelength range 280 to 320 nm.

Air chambers: The air chambers have a length of 0.5 m and diameter 0.06 m. Two windows made of quartz allow UV radiation to pass through. Two pump valves (S_1, S_2) and two exhaust valves (S_3, S_4) are responsible for continuously pumping and releasing gas in the chambers.

Signal reception and data processing system: Laser signals via fiber optic cable are guided to a spectrometer (Avaspec-HSC 1024 *x* 58TEC-EVO) with an operating wavelength range from 200 nm to 385 nm and a resolution of 0.6 nm. After that, the spectral data is processed on the computer using Q-DOAS software and gives results on the density of the gas contained in the chambers.

To evaluate the performance of the DOAS, the standard SO_2 gas with a concentration of 100 ppm ±2% (supplied by Messer Co., Ltd-Ha) was introduced into the chamber. The gas flow rate is kept constant at 3 L/min to maintain the gas concentration at 100 ppm. The spectral characteristics of the Ce:LiCAF laser when passing through the air chamber will be recorded by the spectrometer two times. The first time, the air chamber does not contain SO_2 gas. The second time, the air chamber is filled with SO_2 gas, then the laser beam will be partially absorbed by SO_2 gas. The laser spectrum characteristics of the two recordings are shown in Fig. 5.

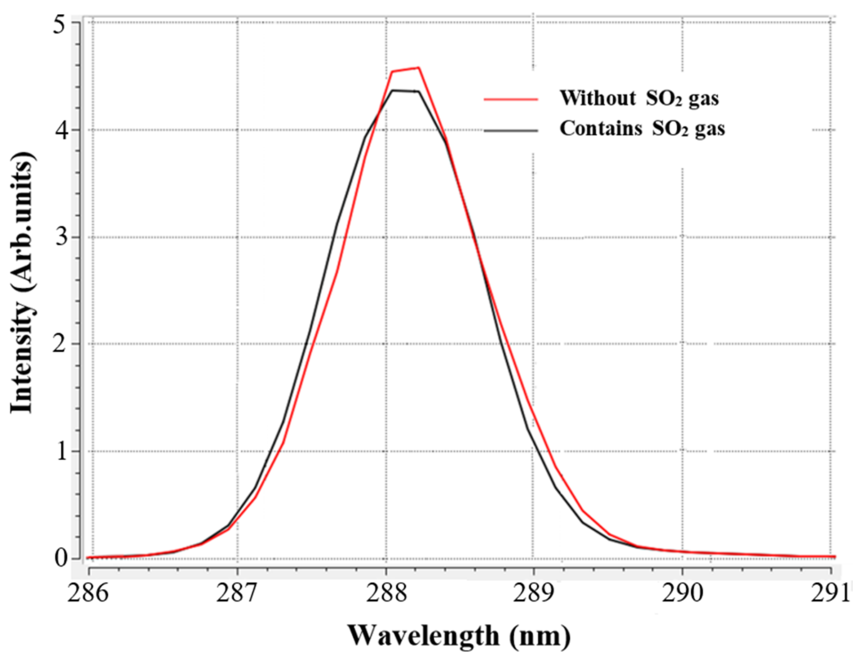


Fig. 5. Laser spectra were obtained in two cases when the chamber without SO_2 gas and the chamber contain SO_2 gas.

The experiment was performed 10 times, the spectral data were processed with Q-DOAS software. The measured gas concentration result is 100 ppm with a measurement error of 6%, which includes a error of DOAS system and standard gas. Besides, the SO_2 gas concentration is also calculated using the Beer-Lambda equation [21]:

$$I_{\text{out}}(\lambda) = I_{\text{in}}(\lambda).\exp(-\sigma_{\text{abs}}(\lambda)\text{NL})$$

where, I_{in}, I_{out} are the spectral intensity before and after passing through the air chambers, respectively. σ_{abs} is absorption cross section of SO_2, N is the SO_2 gas concentration, L is a distance traveled by the laser beam in SO_2 gas. Survey results at the wavelength of 288.5 nm show that the gas concentration determined by the Beer-Lambda law is 101 ppm with an error of 2%. This result shows good agreement between data processing using Q-DOAS software and Beer-Lambla law. The achieved results demonstrate the possibility to apply the DOAS using a Ce:LiCAF laser for investigating SO_2 gas concentrations. This is also a contribution to build a practical DOAS for large-scale observations and surveys of many different types of polluted gases.

4. Conclusions

A DOAS using Ce:LiCAF laser has been developed on a laboratory scale to determine SO_2 gas concentration. The Ce:LiCAF laser has output power up to 54 mW, the full-width at half maximum of 2 nm, and the wavelength peak of 288.5 nm. The results of measuring standard SO_2 gas concentration show that the DOAS is capable of accurately measuring SO_2 with an error of 6%. The achieved results have opened up research on applying Ce:LiCAF UV lasers to DOAS systems to research and identify or determine the concentration of gases in the atmosphere.

Acknowledgments

This research was funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED 103.03-2019.365).

References

[1] J. Fatkhurrahman, I. R. Sari, Y. Andriani, M. Romadhon, N. Zen, A. Prasetio *et al.*, *Doas calibration technique for so2 emission measurement based on h2so4 and na2so3 reaction*, J. Ris. Teknol. Pencegah. Pencemaran Ind. **11** (2020) 36.

[2] Z. Y. W. Davis and R. McLaren, *Recommendations for spectral fitting of so$_2$ from miniature multi-axis differential optical absorption spectroscopy (max-doas) measurements*, Atmos. Meas. Tech. **13** (2020) 3993.

[3] Z. Y. W. Davis, S. Baray, C. A. McLinden, A. Khanbabakhani, W. Fujs, C. Csukat *et al.*, *Estimation of no$_x$ and so$_2$ emissions from sarnia, ontario, using a mobile max-doas (multi-axis differential optical absorption spectroscopy) and a no$_x$ analyzer*, Atmos. Chem. Phys. **19** (2019) 13871.

[4] R. Zhu, J. Gao, M. Li, Q. Gao, X. Wu and Y. Zhang, *A ppb-level online detection system for gas concentrations in cs2/so2 mixtures based on uv-doas combined with vmd-cnn-tl model*, Sens. Actuators B Chem. **394** (2023) 134440.

[5] P. Dong and Q. Chen, *LiDAR remote sensing and applications*. CRC Press, 2017, 10.4324/9781351233354.

[6] Y. Zhang, Y. Wang, Y. Liu, X. Dong, H. Xia, Z. Zhang *et al.*, *Optical H_2S and SO_2 sensor based on chemical conversion and partition differential optical absorption spectroscopy*, Spectrochim. Acta - A: Mol. Biomol. Spectrosc. **210** (2019) 120.

[7] M. S. Biswas, S. D. Ghude, D. Gurnale, T. Prabhakaran and A. S. Mahajan, *Simultaneous observations of nitrogen dioxide, formaldehyde and ozone in the indo-gangetic plain*, AAQR **19** (2019) 1749.

[8] W. Tan, C. Liu, S. Wang, C. Xing, W. Su, C. Zhang *et al.*, *Tropospheric no$_2$, so$_2$, and hcho over the east china sea, using ship-based max-doas observations and comparison with omi and omps satellite data*, Atmos. Chem. Phys. **18** (2018) 15387.

[9] M. Soo and N. Glumac, *Ultraviolet absorption spectroscopy in optically dense fireballs using broadband second-harmonic generation of a pulsed modeless dye laser*, Appl. Spectrosc. **68** (2014) 517.

[10] T. Pham Minh, H. Bui Van, T. Duong Tien and T. Dinh Van, *Development of uv laser source based on distributed feedback dye lasers foruse in measurement of ozone in the lower atmosphere*, Comm. Phys. **27** (2017) 345.

[11] J. Zou and F. Wang, *Simultaneous measurement of SO_2 and NO_2 concentration using an optical fiber-based lp-doas system*, Chinese Opt. Lett. **18** (2020) 021201.

[12] Q. Hong, C. Liu, Q. Hu, C. Xing, W. Tan, T. Liu *et al.*, *Vertical distributions of tropospheric so2 based on max-doas observations: Investigating the impacts of regional transport at different heights in the boundary layer*, J. Environ. Sci. **103** (2021) 119.

[13] *Laser applications to chemical, security, and environmental analysis: introduction to the feature issue*, Appl. Opt. **60** (2021) LAC1.

[14] D. W. Coutts and A. J. S. McGonigle, *Cerium-doped fluoride lasers*, IEEE Journal of Quantum Electronics **40** (2004) 1430.

[15] C. D. Marshall, J. A. Speth, S. A. Payne, W. F. Krupke, G. J. Quarles, V. Castillo *et al.*, *Ultraviolet laser emission properties of ce^{3+}-doped $lisralf_6$ and $licaalf_6$*, J. Opt. Soc. Am. B **11** (1994) 2054.

[16] M. Cadatal-Raduban, M. H. Pham, L. V. Mui, N. D. Hung and N. Sarukura, *Ultrashort Pulse Generation in Ce:LiCAF Ultraviolet Laser*. IntechOpen, Rijeka, 2018, 10.5772/intechopen.73501.

[17] V. V. Semashko, O. R. Akhtyamov, A. A. Shavelev, N. F. Rakhimov and A. V. Lovchev, *Z-scan technique to study gain properties of optically pumped media*, Laser Phys. Lett. **15** (2018) 035702.

[18] R. D. Young, W. Carrion, R. Ganoe, D. Pliutau, G. Gronoff, T. Berkoff *et al.*, *Langley mobile ozone lidar: ozone and aerosol atmospheric profiling for air quality research*, Appl. Opt. **56** (2017) 721.

[19] M. H. Pham, M. Cadatal-Raduban, D. V. Pham, T. X. Nguyen, M. V. Luong, K. Yamanoi *et al.*, *Tunable narrow linewidth picosecond pulses from a single grating gain-switched ce:licaf laser*, Laser Phys. **28** (2018) 085802.

[20] D. Van Nguyen, M. Cadatal-Raduban, T. X. Nguyen, D. Van Pham, T. Van Dinh, N. Sarukura *et al.*, *Theoretical and experimental study of ultraviolet broadband laser amplification using Ce: LiCAF crystal*, Opt. Commun. **530** (2023) 129165.

[21] T. G. Mayerhöfer, S. Pahlow and J. Popp, *The bouguer-beer-lambert law: Shining light on the obscure*, ChemPhysChem **21** (2020) 2029.