Study on the measurement of isoprene by Differential Optical Absorption Spectroscopy

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Abstract. In this paper, the continuous on-line measurements of isoprene in the atmosphere have been carried out by using the Differential Optical Absorption Spectroscopy (DOAS) in the band of 202.71-227.72 nm for the first time. Under the zero optical path in the laboratory, different equivalent concentrations of isoprene were measured by the combination of known concentration gas and series calibration cells. The correlation between the measured concentrations and the equivalent concentrations was 0.9995, and the slope was 1.065. The correlation coefficient between DOAS and on-line VOCs instrument observed from 23 days field observation is 0.85 with a slope of 0.86. It is estimated that the detection limit of isoprene with DOAS is about 0.1 ppb at an optical path of 75 m, and it is verified that isoprene could be measured in the ultraviolet absorption band using DOAS method with high temporal resolution and low maintenance cost.

1. Introduction

Isoprene, named as 2-methyl-1,3-butadiene (C_5H_8), is an important BVOCs (Biogenic Volatile Organic Compounds) in the atmosphere. Its global emission rate is about 500 $TgCyr^{-1}$ (Sindelarova et al., 2014). Isoprene accounts for 70% of global BVOCs emissions (Aydin et al., 2014). Land vegetation and other natural sources contribute 90% of isoprene in the atmosphere (Zhang et al., 2016), and anthropogenic emissions mainly come from industrial activities. Isoprene, as a typical pentadiene hydrocarbon, has a higher activity than that of ordinary anthropogenic VOCs (Lian et al., 2020), and its lifetime in the boundary layer is only about half an hour (Zheng et al., 2015). Due to high volatility and reaction activity, isoprene can accelerate the reaction between atmospheric substances, and it is easy to react with strong oxidizing substances (OH, NO_3 radicals, etc.), and also affects the balance between NO_x (NO_x = NO + NO_2) and O_3 in the atmosphere. Isoprene is also the precursor of secondary organic aerosol (SOA) (Zeng et al., 2018).

Isoprene produced by plants is a byproduct of photosynthesis, its emission intensity directly relates to the abundance of plants, leaf area index, and plant species. Meteorological parameters, such as temperature, radiation intensity and humidity, can also affect the emission of isoprene (Bai, 2015). In the daytime, the chemical process oxidized by OH is the main sink of isoprene. Due to the existence of multiple double bonds, the additional reaction with OH will lead to the formation of a variety of products and the formation of RO_2. In the presence of NO_x, RO_2 can be further reacted to convert RO and HO_2, causing the mutual conversion of free radicals and the accumulation of ozone, which affects the balance of O_3 in the atmosphere (Chen et

al., 2020; Lu et al., 2018; Zhu et al., 2020). Meanwhile, the reaction of isoprene with NO_3 mainly occurs at night. Although the reaction only accounts for 6%-7% of the total isoprene oxidation, it is an important way to remove NO_3 (Xie et al., 2013).

In recent years, with the increase of urban vegetation diversity, the emission intensity of urban BVOCs has a significant upward trend. The monitoring and control of isoprene in urban ecosystem has also attracted more and more attention. Because isoprene concentration in the atmosphere is low, and the life time is short, high precision and accuracy methods are needed for monitoring. Currently, general methods, including gas chromatography-mass spectrometry (GC-MS), proton transfer reaction mass spectrometry (PTR-MS), and chemical ionization mass spectrometry (CIMS) et al. were introduced to measure isoprene.

GC-MS utilizes the high separation ability of gas chromatography to separate the components of environmental samples, and then measures the different compounds with the mass spectrometer. With the advantages of high precision and stability, GC-MS can distinguish most VOCs qualitatively and quantitatively, however, is difficult in maintaining and operating due to the complex requirements in power, temperature control, and special carrier gas. GC-MS measurement generally requires sampling, preservation, and pre-treatment before analysis. During this process, the sample may change to some extent, resulting in inaccurate results.

PTR-MS is the chemical ionization of gas sample through proton transfer in drift tube. The proton source is usually H_3O^+. The fixed length of the drift tube provides a fixed reaction time for the ions as they move along the drift tube. The sample air is continuously pumped through the drift tube and the VOCs in the sample react with H_3O^+ to be ionized, and then enter the mass spectrometer to be detected. The disadvantage of PTR-MS is that it completely relies on mass spectrometry to provide the identification of mixtures. VOCs as a class of substances, it is possible to have the same molecular weight or the same mass of fragment ions and parent ions. In this case, it is difficult to determine all species present and their respective concentrations. A solution to this is to combine GC with PTR-MS (Robert et al., 2009).

CIMS (Leibrock & Huey, 2000) retains the qualitative ability of mass spectrometry, and coupling the traditional air sampler with mass spectrometry technology. However, this method is not sensitive to low concentration isoprene. In addition, the VOC composition in the atmosphere is complex, and the unknown composition may react with benzene reagent to interfere with the measurement results. Table 1 lists the comparison of performance of these three methods for isoprene measurements together with DOAS method in this study.

Table 1. Comparison of different on-line methods for isoprene measurement.

	DOAS (this study)	GC-MS (Gong et al., 2018)	PTR-MS (Eerdekens et al., 2009)	CIMS (Leibrock et al., 2003)
Time resolution	1 min	30-60 min	0.5-2 min	1.65 s
Accuracy (Correlation with GC-MS/GC)	R=0.85	R>0.99 (with offline)	0.95	R=0.78
Detection Limit	10 ppt	4 ppt	100 ppt	<30 ppt
Platform	Stationary / conditional mobile	Stationary / mobile	Stationary / mobile	Stationary / mobile
Advantages	No sampling Easy operation Simple instrument	High precision Accurate quantification	Fast responses High precision	High time resolution Good sensitivity

Disadvantages	Impacts by weather conditions Impacts of interferences	Time consuming Calibration needed Difficult operating and maintaining	Molecule or fragment ion of the same mass cannot be differentiated	Interference of unidentified components Expensive equipment

In addition, a portable gas chromatograph (iDirac) equipped with photo-ionization detector to measure isoprene was proposed by Conor et al. (2020) in Cambridge University. The instrument is an improved technology for GC-MS, which can work independently weeks to months in the field environment. Previous studies rarely mentioned the measurement of isoprene by spectral method. Brauer et al. (2014) measured the infrared spectrum of isoprene by Fourier transform spectrometer, and found that isoprene has a strong absorption near 11000 nm, which provides a new possibility for the measurement of isoprene by spectral technology. So far, however, few people have mentioned the measurement of isoprene by ultraviolet spectroscope. In this paper, an on-line measurement method with high temporal resolution for isoprene in the atmosphere is proposed by using the DOAS technology in the far ultraviolet band.

2. Measurement method

2.1 Instrument introduction and spectral analysis

DOAS technology was proposed by Platt et al. (1979, 1980) in 1970s for the first time. The principle of the instrument was detailed in other literature (Platt & Stutz, 2008), here is the description of deep UV-DOAS. The system is mainly composed of light source, transmitting telescope, receiving telescope, spectroscope, and computer, etc. (see Figure 2). The transmitting and receiving telescopes are located at both ends of the measuring optical path with a distance of 75 m. Since the measurement of isoprene is in deep ultraviolet, we choose deuterium lamp (L6311-50, Hamamatsu, 35 W) as light source. The aperture of the transmitting telescope is 76 mm, with a UV enhanced spherical mirror with a focal length of 304 mm. The aperture of the receiving telescope is 152 mm with a UV enhanced spherical mirror with a focal length of 608 mm. A spectroscope (B&W TEK Inc. BRC741E-1024) with a spectral range of 185-400 nm, a spectral resolution of 0.75 nm FWHM (Full Width Half Maximum), and a 1024-pixel photodiode array was used as detector to record the spectrum. The measurement routine is that the light emitted by the light source is collimated by the transmitting telescope and then sent out, after a certain distance of transmission, it is collected by the receiving telescope and focused on the incident end of the optical fiber. The optical fiber feeds the light into the spectroscope, which detects the light signal and sends it to the computer for spectral analysis.

The measured atmospheric spectrum contains the absorption information of molecules in the atmosphere. After removing the Rayleigh scattering and Mie scattering, as well as the broadband absorption of molecules by high pass filtering, the so-called differential absorption spectrum is obtained. This high pass filtering is performed by a high pass binomial on the spectrum using the iterations of 500 twice aiming to eliminate the broadband structures. The concentration of the corresponding atmospheric components can be retrieved by fitting the differential absorption spectrum with the differential absorption cross section of the measured molecules. The reference spectrum during laboratory experiments was recorded by receiving the light beam close the transmitting device, suggesting the zero light path and none absorption of isoprene. In the field measurements, the measured atmospheric spectrum collected at 00:00 LT on July 1, 2018 was used as the reference spectrum considering it is “clean” without isoprene absorption.

Isoprene has strong absorptions between 200.0-225.0 nm, among which there are relatively obvious absorption peaks (Martins et al., 2009) near 210.0 nm, 216.0 nm and 222.1 nm, as shown in Figure 1(a). After high pass filtering, the

differential absorption spectrum (1 ppb*km) of isoprene is shown in Figure 1(b). According to its differential absorption characteristics, the fitting band of isoprene is 202.71-227.72 nm. Within this band, there are also absorptions of NH_3 (Chen et al., 1999), SO_2 (Wu et al., 2000), NO, NO_2 (Mérienne et al., 1995), C_6H_6 (Dawes et al., 2017), C_7H_8 (Serralheiro et al., 2015), etc. These high-resolution absorption cross sections are convoluted with the instrumental wavelength before introducing into the spectral fitting. The absorption of NO used here was measured in laboratory with known concentration gas by using the same instrument. Therefore, the absorption of these components is also considered in the process of spectral retrieving. Figure 2 displays an example of the spectral fitting of an actual atmospheric spectrum (measured at 2018-07-08 12: 47). In Fig.2 (a). the black line is the measured spectrum and the red line is the fitting spectrum (0.79 ppb isoprene, 2.83 ppb NH_3, 1.85 ppb SO_2, 1.42 ppb NO, 4.94 ppb NO_2, 0.01 ppb C_6H_6, 2.20 ppb C_7H_8), while the fitting residual (standard deviation is 4.76E-4) is shown in Fig. 2(i). The differential optical density of isoprene and other interference trace gases were displayed in Fig. 2(b) to (h), respectively, of which the measurement error of isoprene is about 10.6% according to the method proposed by Stutz and Platt (1996).

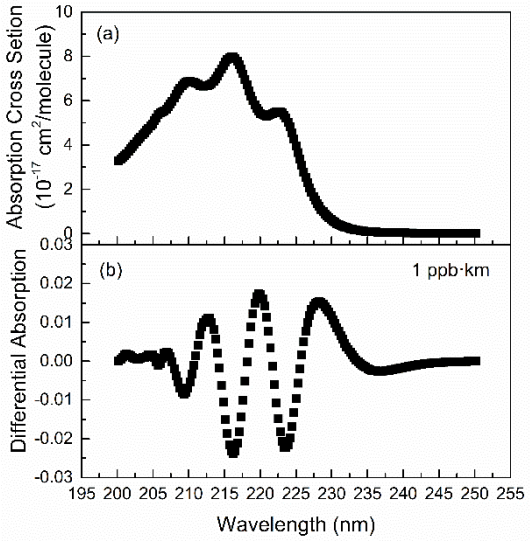

Figure 1. The absorption cross-section and differential absorption spectrum of isoprene in 1 ppb*km, together with other trace gases with absorptions.

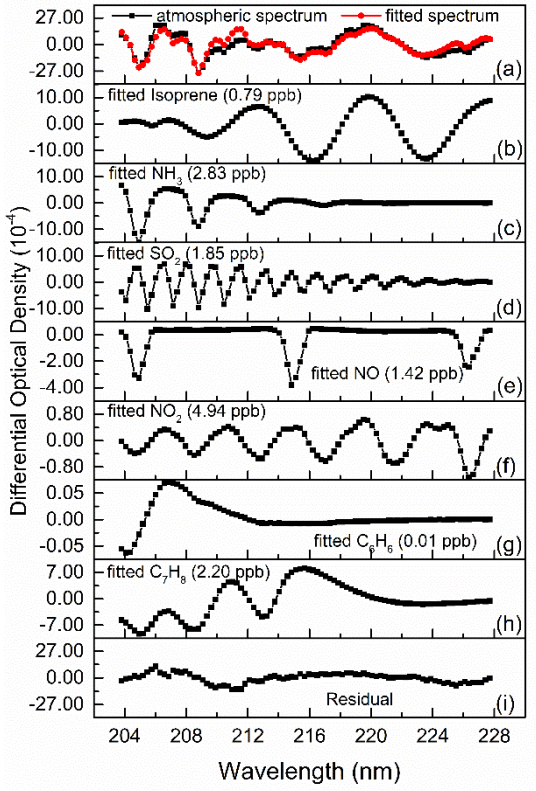

Figure 2. Example of the spectral fitting of an actual atmospheric spectrum (measured at 2018-07-08 12: 47).

2.2 Calibration experiment

In order to verify the accuracy of measurement results, isoprene gas with known concentration is used to calibrate the instrument in the laboratory. The method is to close the emitting telescope and receiving telescope (close to zero optical path) in the laboratory, and then a series absorption cell was placed between the telescopes. 10 ppm isoprene gas was injected into the cells at a constant flow rate of 100 ml/min, and then the corresponding concentration under different cell combinations was measured, as shown in Figure 3.

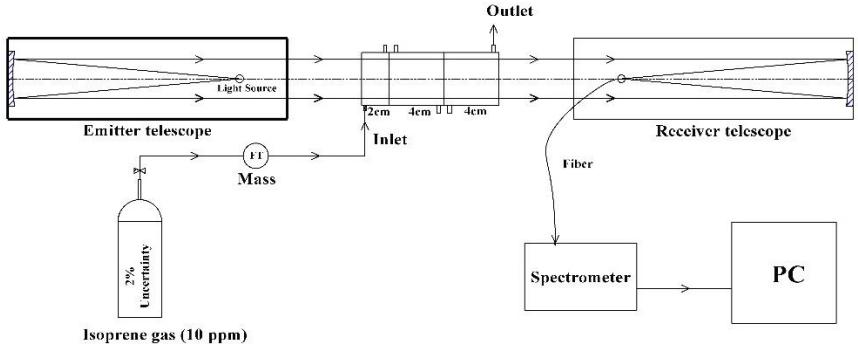

Figure 3. The scheme of the calibration system

The absorption cell group is composed of one 2 cm and two 4 cm long cells in series. When using different combination of cells, different equivalent concentrations (C_E) (equivalent to the average concentration in the 100 m optical path) can be obtained. The specific combination and corresponding equivalent concentrations, as well as the actual measurement concentrations (C_M) are shown in Table 2.

Table 2: the calibration results in different gas cells combination

Length of cells	C_E (ppb)	C_M (ppb)

empty	0	0.01±0.005
2 cm	2.00	1.88±0.004
4 cm	4.00	3.61±0.019
2 cm + 4 cm	6.00	5.40±0.009
4 cm + 4 cm	8.00	7.44±0.030
2 cm + 4 cm + 4 cm	10.00	9.42±0.010

Figure 4 shows the linear fit of calibration results. The ordinate in the figure is the equivalent concentration, and the abscissa is the measured concentration. For six measuring points including the zero point, the linear fitting correlation coefficient R is 0.9995. The relationship between the equivalent concentration and the measured concentration is shown in the following equation (1). For future measurement results of the actual atmosphere, equation (1) will be used to calibrate the measured data.

$$C_E = (0.061\pm0.024) + (1.067\pm0.004) * C_M \quad (1)$$

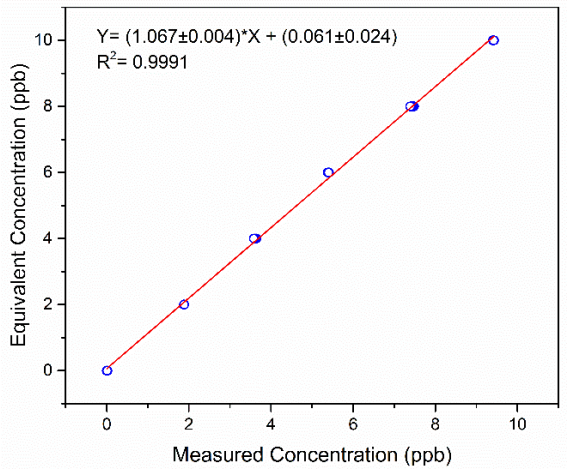

Figure 4. The linear fitting of calibration results for isoprene measurement

3. Field comparison experiment and discussion

3.1 Comparison with on-line VOCs results

In order to further verify the reliability of the DOAS method in actual atmospheric measurement, in July 2018, the field measurement results of the DOAS were compared with the on-line VOCs (TH-300B on-line VOCs monitoring system) analyzer (Zhu et al., 2020), which is based on the GC-MS technology. DOAS instrument is installed on the 7th floor of the Environmental Science Building (31.344 ° N, 121.518 ° E) in Jiangwan campus of Fudan University, as shown in Figure 4. The optical path is about 25 m above the ground. The transmitting telescope is at the west part of the building (A in Figure 5), while the receiving telescope is at the east part (B in Figure 5). The distance between the telescopes is 75 m. The on-line VOCs instrument is located in Xinjiangwan City monitoring station of Shanghai Environmental Monitoring Center (C in Figure 5). The straight-line distance is about 0.5 km to the south of the DOAS instrument. The coverage rate of plants around the observation sites is high, mainly including pine, camphor, etc., and a large number of lawns are also distributed. Meteorological parameters were recorded by the automatic weather station (CAMS620-HM, Huatron Technology Co. Ltd) co-located with the DOAS instrument.

Figure 5. Field measurement sites of DOAS and on-line VOCs, A is the transmitting telescope, B is the receiving telescope, and C is the on-line VOCs, the yellow arrow is the light path of DOAS. This map is sourced from © Baidu

The comparison experiment was carried out from July 1st to 23rd, 2018. The temporal resolution of DOAS was 1 min, while that of on-line VOCs was 1 h. In order to match the temporal resolution, DOAS data were averaged hourly. Moreover, the measured spectra with low light intensity and high integration time were excluded from the spectral fitting and data processing, which are mainly due to the unfavorable weather condition influencing the measurements. The spectral were also corrected for offset before introducing fitting. Figure 6(a) shows the time series of the isoprene data measured by these two instruments, which are in a good agreement. The average values of DOAS and on-line VOCs were 0.325 ppb and 0.217 ppb respectively, and the standard deviation (SD) was 0.254 ppb (N=551) and 0.257 ppb (N=466), respectively. The average value of DOAS results is higher than that of the on-line VOCs mainly because, at night, DOAS can still detect a certain concentration in most cases, most of which are between 0.02-0.10 ppb, while most of on-line VOCs data are between 0-0.05 ppb. Due to the missing of some data of on-line VOCs during the comparison period, totally 466 sets of hourly data were used to analyze the correlation between these two instruments. As shown in Figure 6(b), the correlation coefficient is 0.85 and the slope is 0.86.

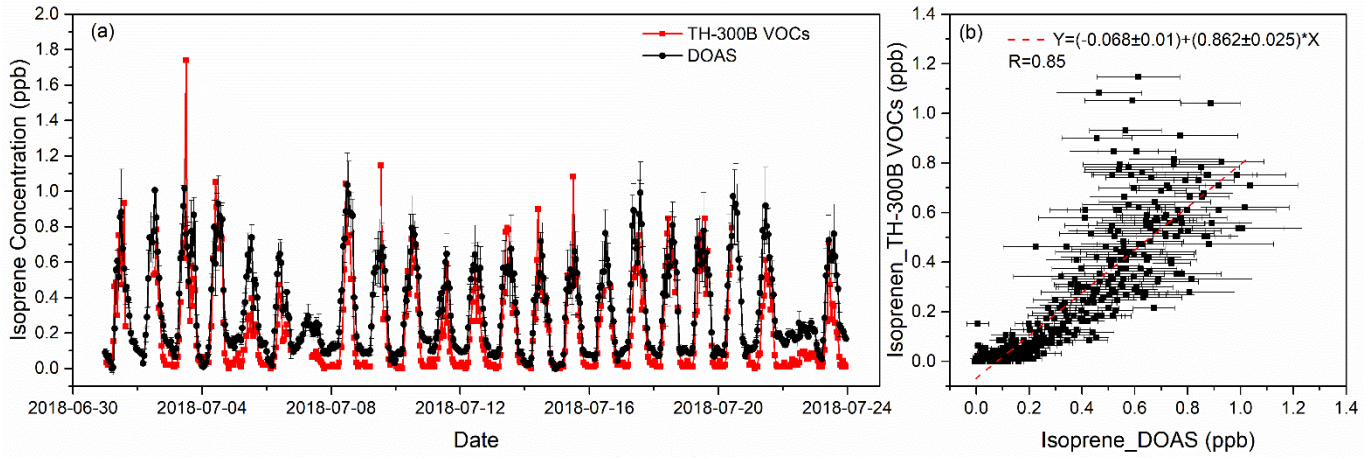

Figure 6. The comparison of hourly isoprene measured by DOAS and on-line VOCs during the field measurement

The main reason for the difference of DOAS and on-line VOCs results is that the sampling and measurement heights of the two instruments are different. The light path of DOAS is about 25 m above the ground, while the sampling height of on-line VOCs instrument is about 10 m. In addition to the 500 m distance between these two sites, the air sampled by VOCs

analyzer or penetrated by DOAS light beam are completely different. Considering the inhomogeneity spatial distribution of isoprene, this will lead to different data results between two instruments. Considering the sampling of on-line VOCs is through the sampling tube, isoprene will be more or less lost during the sampling process, which could be up to 10% for some high carbons VOCs (EPA, 2019). In order to ensure the authenticity and accuracy of the observed data, the working status and response of the TH-300B monitoring system were inspected every day. Daily calibrations were performed automatically at 00:00 to 01:00 LT. In addition, the external standard method for the FID and the internal standard method for the MS were adopted. The daily calibration operated at midnight could make the on-line VOCs observed value close to the zero point, which may deviate from the real abundance. Since the observation is in summer, there is also a very high temperature at night during the observation period, i.e. 27.1℃ (19:00-06:00 next morning). In addition, the release of isoprene produced by the leaves of plants in the daytime is delayed to some extent, resulting in a certain concentration of isoprene remaining at night, so that we think the data of DOAS is more reasonable. Those two reasons will eventually lead to DOAS measurement results higher than online VOCs instruments, especially when the isoprene concentration is very low at night, the difference is more obvious. On the other hand, the error of DOAS method would also be the possible reason causing the difference with VOCs analyzer.

It can also be seen from Figure 6(b) that when the isoprene concentration is higher than 0.5 ppb, the measurement results of the two instruments show large scattering. The different measurement principles, especially the difference of sampling time can also cause the scattering of the results of two instruments. On-line VOCs only has about 50% of the time (1h) to be used to sampling, while the rest of the time is used for analysis. But DOAS is almost continuous measurement with just a little part of time to be used for analysis (about 1s per minute), this difference will affect the consistency of results. Meanwhile, there are various vegetations between the instruments, when the wind direction changes, the emission of this part of vegetation will also cause the difference between the results of the instruments. But in general, DOAS and on-line VOCs analyzers show a good agreement in the comparison of mean and correlation of measured data.

3.2 Detection limit evaluation

The detection limit of DOAS mainly depends on the signal-to-noise ratio of the spectrum. Under the condition of zero light path in the laboratory, the zero noise (standard deviation of the results) of isoprene is 0.005 ppb, the detection limit can be definite as two times of zero noise, so that the detection limit of the system is 0.010 ppb (HJ 654-2013). However, in the real atmospheric measurement, it is difficult to determine the actual detection limit due to the varied environment and the interference of other gases. The detection limit of DOAS in real atmosphere is mainly determined by the residual of spectral fitting. The residual mainly comes from the absorption of interfering substances, the change of lamp spectral intensity and structure, the spectral shift caused by the change of ambient temperature of the spectrometer, and the noise of the detector. Since the stability of light source and spectrometer will influence the fitting residual and instrumental performance, temperature control was adopted for the spectrometer and operating ambient. In order to reduce the influence of these factors on the measurement, in the process of spectra fitting, the absorption of interfering substances and the spectral structure of lamp are necessary to be considered together with the isoprene absorption spectrum. The lamp spectrum will be also introduced into the fitting process if obvious lamp spectral structure was observed in the residual. At the same time, it is also necessary to calibrate the spectral drift. However, there are still some residual remain after the spectral fitting due to possible imperfect reference spectra. Overall, the averaged measurement errors of isoprene were estimated lower than 20%.

In the fitting band of isoprene, the absorption of NO, benzene and toluene are the main interference factors. The reason for the influence of NO is that there are three obvious absorption peaks of NO in the fitting band. After high pass filtering, there is component in the differential absorption cross section of NO similar to the variation frequency of isoprene's differential

absorption spectrum. After the analysis of the measurement results, the impact of NO on isoprene is about 0.3% of its concentration. But the effect of NO is mainly in the morning and evening rush hour. The influence of benzene and toluene is mainly due to their strong absorptions in the fitting band of the spectrum. Their presence will lead to a significant reduction in the spectral intensity in this band, resulting in a reduction in the signal-to-noise ratio of the spectrum. During the comparison experiment, high concentration of benzene or toluene occasionally occurs, resulting in a large fitting residual. Other aromatics, such as xylene and styrene, also absorb strongly in the fitting band, but because of their lower concentration in the natural atmosphere, their impacts on isoprene are significantly smaller than that of benzene and toluene. Although NH_3, SO_2 and NO_2 have absorption in the fitting band, their differential absorption variation frequency is significantly higher than that of isoprene, and only overlaps in parts of fitting band, so that they have little influence on the isoprene measurement. Fig. 7a shows the absorption cross section of benzene, toluene and isoprene, while Fig. 7b illustrates the differential absorption spectra (1 ppb*km) of NO, SO_2, NO_2, NH_3 and isoprene obtained by applying high filter pass same as the spectral fitting process. Moreover, the employment of the "clean" atmospheric spectrum, instead of the reference spectrum without any absorption under zero optical path, also introduces the uncertainty into the spectral fitting, because it may contain few of isoprene absorption.

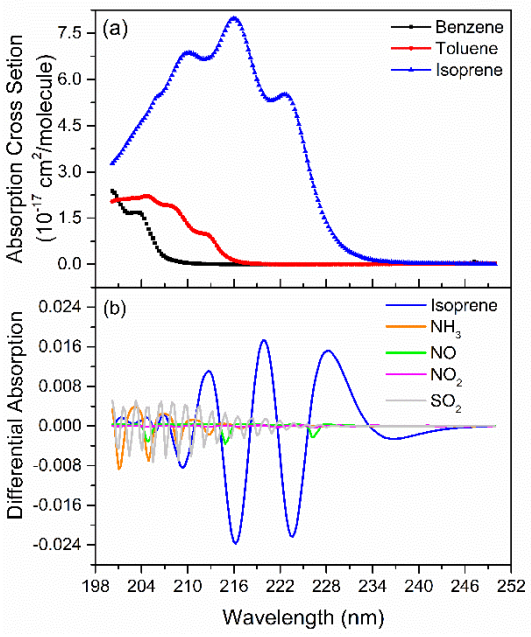

Figure 7. The absorption cross section of benzene, toluene and isoprene (a), the differential absorption spectra (1 ppb*km) of NO, SO_2, NO_2, NH_3 and isoprene (b)

Whether it is benzene, toluene, or NO, SO_2, NO_2 and NH_3, they all exist together with isoprene in the atmosphere. Therefore, their influences on isoprene measurement are common. In order to ensure the quality of results, the data with a residual of more than 0.0005 are filtered out. In a total of 33120 sets of data during 23 days observation, 1137 sets are filtered out, and the valid rate of data is 96.6%. The average residual of all valid data is 0.000234. In order to evaluate the detection limit of DOAS in the real atmospheric measurement, we made a statistic on 16387 sets of data with the concentration of isoprene lower than 0.1 ppb (assuming that the isoprene in the atmosphere is close to zero at this time), and the standard deviation is 0.0499 ppb, so the detection limit of DOAS instrument in the field measurement is no more than 0.1 ppb (twice the standard deviation).

4. Conclusion

This paper introduces, for the first time, the continuous on-line measurement of isoprene in the atmosphere by means of DOAS in the band of 202.71-227.72nm. Although the current measurements of isoprene are mainly GC-MS, PTR-MS and CIMS methods, the DOAS method has the characteristics of high time resolution, rapid temporal response and simple

operation. It is especially suitable for long-term online measurement in the field or forest where the traffic is inconvenient, and the low cost of instrument is also conducive to build monitoring network.

Under the condition of zero optical path in the laboratory, several equivalent concentrations were measured by using a series absorption cell and known concentration of isoprene gas. The correlation coefficient between the measured concentration and the equivalent concentration was 0.9996, and the slope was 1.065, indicating that the instrument has good linearity and accuracy. After 23 days of field comparison, there is a good correlation between the results of DOAS and on-line VOCs instrument, with a correlation coefficient of 0.85 and a slope of 0.86. Considering the differences in measurement principle and sampled air, the comparison results show a good agreement between these two instruments.

In order to evaluate the detection limit of DOAS instrument under the actual atmospheric measurement, this study proposes to calculate the standard deviation of all the data when the measured concentration of isoprene in the ambient air is close to zero (< 0.1 ppb, n = 16387). It is estimated that the detection limit of the DOAS is no more than 0.1 ppb under a measurement light path of 75 m. Therefore, the DOAS is suitable for long-term monitoring in cities or areas with large vegetation coverage.

Data availability. Data are published as https:// DOI: 10.17632/489mvgbsxg.3

Author contribution. The study was designed by SG and BZ. Experiments were performed by YG, RZ and YY. Data processing and analysis were done by BZ and CG. The paper was written by BZ, SW and SG.

Competing interests. The authors declare that they have no conflict of interest.

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