Journal of Environmental Sciences Vol.5, No. 4, pp. 400–409, 1993 ISSN 1001-0742

Progress in atmospheric ozone detection techniques in China

Wang Gengchen

Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

Abstract— A comprehensive review on present situation of detection techniques for atmospheric ozone in China has been given in this paper. Among them, some techniques, such as chemiluminescence,ultraviolet absorption and laser differential absorption methods for detection of ozone concentration in the near-ground atmosphere,the solar of sky light spectrophotometric method for detection of total ozone in the atmosphere, ozonesonde technique, Balloon-borne ozonemeter, laser and microwave techniques for ozone measurements in the stratosphere, and so on, are focused on. It should be pointed out that 1980s is a period for overall development of ozone detection techniques in China. Setting a stereo-observation technical system in China for atmospheric ozone is a main mission in the near future.

Keywords: atmospheric ozone; ozone detection; China.

1 Introduction

At present time, an extensive attention has been paid to the variation of ozone concentration in the atmosphere and its possible climatic and environmental effects. Especially, discovery of the ozone hole at Antarctic region and the increasing trend of ozone content in the troposphere during recent years have greatly increased people's interest in ozone study. It has been recognized already, that the impact on mankind's living environment caused by atmospheric ozone change is larger than that was estimated before, Because many important problems relating directly to mankind's living, such as climate change, eco-environment change and variation of energy structure, and so on, are involved, study on atmospheric ozone has become a worldwide subject with much concern of both scientists and government officials.

For studies of atmospheric ozone, the most important problem is to develop detecting techniques for global monitor of the temporal and spacial variations of atmospheric ozone. The development of atmospheric ozone detection techniques has had more than 70 years history. Now there are about 150 observing stations around the world (including poles), at which monitoring atmospheric ozone content is being carried out according to a unified standard. Vertical distribution of ozone in the atmosphere is measured regularly or irregularly at about 40 stations. Moreover, at the end of 1960s, global observations of atmospheric ozone by means of satellites and other space flyers have begun. Besides, regional studies on atmospheric ozone are underwaying independently or cooperatively using direct and indirect methods (including lidar working at ultraviolet and infrared) at earth's surface as well as by means of balloon, airplane and rocket.

There is a relatively longer history of ozone study in China (Ny, 1933). We had begun the total atmospheric ozone content observations in 1950s. After a long and tortuous period, this work was resumed again at the end of 1970s. Two ozone observing stations on the ground were established successively in China, one being in Xianghe about 70 km away from Beijing, another being in Kunming, the southwest of China. Dobson spectrophotometer is utilized to measure the total ozone content at both stations. These two stations have been brought into the world ozone observing network. At the same time, relevant researches have been developed, such as ozone in the middle atmosphere, ozone in the troposphere, ozone in the stratosphere, total content of ozone, vertical distribution of ozone, variation of ozone layer over poles, numerical simulation of atmospheric ozone layer, effects of ozone variation on the climate and environment, relations between solar activities and atmospheric ozone, trace gases related to ozone variation and the solar ultraviolet radiations and so on. Especially, new important progress has been made in detection techniques of atmospheric ozone, that is mainly introduced in this paper.

2 Detection of atmospheric ozone in the troposphere

In recent years, more and more attention has been paid to the variation of ozone concentration in the troposphere (Bojkov, 1989). The observed data show that there is a gradually increasing trend in ozone concentration in the troposphere which will directly influcence the effect of ozone on climate and environment, speed up photo-chemical process in the troposphere, increase atmospheric pollution, and as a result, will affect directly the human health as well as the ecological environment. Therefore, to study ozone sources, sinks and balance in the troposphere, to estimate the ecological environment effect caused by the increasing of atmospheric ozone concentration in the troposphere and particularly in the near-ground atmosphere have become an important content of atmospheric ozone study at present time.

The ozone content in the troposphere is about one eighth of total content in the atmosphere, that caused some difficulties for its detection. During recent years, by combination with national major research subjects such as acid rain, atmospheric environment quality assessment and so on, measurements of ozone concentration near the earth's surface in some regions such as Beijing, Lanzhou, Guangzhou, Chengdu, Jiangxi, Xianghe and so on, and in free atmosphere of the troposphere by using airplane and tethered balloon have been made successively (Xiao 1990; Hong, 1988; Kong, 1990; Fu, 1989), characteristics of atmospheric ozone variation under different meteorological conditions were obtained, effect of the cloud, fog, rain, temperature inversion, and NO exhaust, and so on, on ozone concentration variation was also obtained. Chemiluminescence and ultraviolet absorption methods are used for this purpose. The former method is based on the formaldehyde produced by the reaction between ozone and ethylene. The excited formaldehyde instantly transferred to instantaneous-state on accompanying the light emission, whose intensity is proportional to ozone concentration taking part in reaction. For this purpose the GSH-201 chemiluminescent ozone analyzer was made in China (Wang, 1983). The analyzer consists of the gas lines, radiation reaction cell and detecting system. Gas lines include ethylene line and sample line. Under the action of pumping, ethylene and sample gas go through the reaction cell in which ozone reacts with ethylene quantitatively with 435nm light emission whose intensity is received by a photoelectric multiplier, then the electrical single is processed and, at last, the ozone concentration is given. The ultraviolet absorption method can be used to calculate the ozone content by ozone absorption of ultraviolet radiation near 253.7 nm.

An IR differential absorption technique has also been developed fqr long-path ozone monitor in near earth's surface atmosphere (Wang, 1990). This technique is based on the fact that ozone has strong absorption at some CO_2 laser lines, such as 9P(14), but no absorption or weak absorption at the other lines, such as 9P(22). Results of measurement show a possible widely applied prospect of this technique for long-path ozone monitor because of its higher sensitivity.

3 Detection of total atmospheric ozone content

At present, there is a network for total ozone content detection all over the world. This network is composed of more than 150 ground observing stations (most of them are at north middle latitude). Most instruments used are Dobson spectrophotometer and their improvers. Besides, there are also Brewer photometer (mainly used in Canada, Italy, Sweden and Greece and so on), and M-83 Ozone analyzer (mainly used in Former Soviet Union and East Europe). The main structure of Dobson spectrophotometer is a prismatic bi-monochromator, and that of Brewer ozone photometer is a mono-grating Ebert spectrograph whose working wavelength interval is 295 − 330 nm. Besides O_3, the other gases in the whole atmosphere such as NO_2, CO_2 and SO_2 can be detected by using Brewer photometer or its improver. M-83 is a kind of solar photometer utilizing a set of color filters. Although there are great difference in structure, accuracy and observation procedure, these three kinds of instruments have a same working principle from the point of ozone measurement, that is, all measurements are based on ozone absorption of the solar ultraviolet radiation. In practice, different dispersing elements (such as prism, grating or filter) are used to separate a set of given wavelengths in the UV region, then determine the ozone content in the whole atmosphere according to variations of solar radiation passing through the ozone layer. Practically, there are some factors and uncertainties such as the structure and optical properties of instruments, choice of wavelengths, influence of other components in the atmosphere, calibration and its variation, and so on are involved. Moreover, a higher sensitivity is required for the observations of total ozone content (less than 3%), so the instruments used must be high sensitive, stable and precise.

Measurements of total atmospheric ozone content were made at some places in China during solar eclipses (Barisky, 1961; Peng, 1983; Zhang, 1987; Zhao, 1990). At present time, routine observation of total atmospheric ozone by uisng Dobson spectrophotometer are going on at Xianghe and Kunming stations (Wei, 1989). Besides Dobson spectrophotometer, some other techniques have been developed in recent years to measure ozone content in the atmosphere. Among them, what should be made mention of are high resolution solar spectrometer and skylight photometer used for practical ozone observations in Beijing and Antarctic region (Mao, 1989; Hsueh, 1989; Wang, 1990). In the former case, total ozone content in the atmosphere is obtained by measuring solar spectrum at ultraviolet region (300 − 340 nm), while for the later, total ozone content is gotten by measuring intensity of the sky scattering radiation. The developed solar/skylight photometer is composed of telescope, monochromator, electronic circuits and a computer. The former two parts are set at a special sun-tracking stand, while other systems, such as driving system, controlling circuits, computer and power supply are in a movable vehicle. The whole controlling and observing systems are automated by special software. The observation results may be displayed and recorded in real-time. Spectral resolution is 0.1 nm, working wavelength range is 300 − 800 nm, so besides ozone, NO_2 and NO_3 can also be measured. The system is also equipped with a special polarization receiving system for measuring optical properties of atmospheric aerosols.

Besides measurements in the UV region, total ozone content in the atmosphere was determined by measurements of solar radiation in the visible and infrared regions (Wang, 1983; Lu, 1988; Wang, 1988; Wang, 1981; Guan, 1987; Zeng, 1974;

Wang, 1990).

4 Direct detection of vertical distribution of atmospheric ozone

Study of vertical distribution of ozone in the atmosphere and its variation is one of important subjects of ozone studies. This is because not only of its relation to temperature structure and dynamic process in the stratosphere, and hence, to climate and weather in the troposphere but also of its contribution to the greenhouse effect. For a long time, because of lacking atmospheric detecting techniques, information on ozone vertical profile in the atmosphere was obtained only by indirect methods. Götz inverse method is a more common used one (Götz, 1934). This method has been used until now since it was proposed in 1930s with its successive improvement at about 20 stations over the world. At present, information of the vertical distribution of ozone is obtained more regularly by using this method. At the same time, some kinds of direct methods for detection ozone vertical profile by using rocket, airplane and balloon have been developed in some countries.Ozonesonde is one of such methods having a more applied prospect. Now several kinds of ozonesondes are working at about 20 stations all over the world, such as ECC (electrochemical type), Brewer-mast (electrochemical type), Regener (chemiluminescent type), and KC-79 (electrochemical type). Since 1970s, for ozone measurement, a great attention had been paid to remote sensing by satellites with which the global information of atmospheric ozone is obtained.

Since 1980s, Götz inverse method is constantly used for calculating vertical distribution of ozone in the atmosphere at Xianghe Station in China (Wei, 1989; 1988). It is only until the end of 1980s, when the balloon-borne ozonemeter and IAPI ozonesonde were developed, the direct detection of ozone vertical distribution between 0 to 32 km had just been realized. IAPI ozonesonde is a electrochemical type (Kong, 1990; Wang, 1989), its working principle is based on iodide redox reaction, the free iodine liberated from the reactions is proportional to the ozone passing through the reaction cell. Whole system of the IAPI ozonesonde is constituted by sensors (including ozone, temperature, and pressure), data collecting, converting and transmitting systems, ground receiving and data processing systems. Ozone sensor is a key component which is formed of a single reaction cell and relevant gas pipes. During flying of the balloon, signals coming from all sensors are amplified, converted and transmitted to the ground receiving station, where the vertical distributions of ozone and temperature in atmosphere is calculated, printed and recorded.

5 Detection of ozone in the stratosphere and mesosphere

Detection of ozone in the stratosphere and mesosphere holds a special place in the atmospheric ozone study. The ozone layer in the atmosphere is formed by decomposition of oxygen molecules due to solar ultraviolet radiation, so the ozone is mainly concentrated in the stratosphere. The ozone content and its variation is an important factor determining the physical, chemical and dynamic states in the stratosphere. For this reason, the ozone study is included in all international and national scientific projects on the middle atmosphere. But such study is not as easy as it seems to be, because of rather complicated theory and technology involved. So this technique was developed slowly over a long period of time. During the last twenty years, an obvious progress in ozone study in the middle atmosphere have been made due to application of satellite remote sensing and laser sounding techniques. Until now there are more than 20 kinds of instruments at satellites and other space flyers, and more than 10 kinds of special or multi-purpose lidars on the ground for the ozone remote sensing in the stratosphere. There are two kinds of satellite remote sensing techniques. One is to detect intensity of back scattering solar ultraviolet radiation from the sky by using satellite-borne instruments, and the ozone information at different altitudes can be obtained by choosing different ultraviolet wavelengths. SBUV is such a model instrument placed at Nimbus 7. Another is to measure the limb emission or absorption intensities in the infrared regions to get the ozone information at different altitudes, whose model instrument is LRIR and LIMS placed at both Nimbus 6 and 7. Generally, satellite remote sensing is an effective method for getting ozone information at altitudes from the tropopause to 70 km. Laser remote sensing technique used to detect ozone is mostly based on the differential absorption principle with distance resolution. In this aspect, Xe-Cl pulsed lidar is used most extensively because of coincidence of laser emission wavelength of 308 nm with the ozone absorption line. We have done nothing on detection of ozone in the stratosphere for a long time. Until the middle of 1980s, along with development of some advanced techniques, such as microwave, lidar, stratospheric balloon and computer, and application of these techniques in atmospheric sciences, the detecting techniques for ozone in the middle atmosphere had gotten much progress too in China.

5.1 Development of balloon-borne ozonemeter

Since 1980s, altitude scientific balloon technique (ASBT) has been developed rapidly in China, and was applied in space astronomy, space physics, atmospheric physics and environmental science and so on successfully (Jing, 1988). At the same time, the detection technique for ozone in the middle atmosphere by using ASBT was developed too, and at the end of 1980s, the direct detection of ozone in the stratosphere was realized for the first time in China (Wang, 1990). The instrument used is a balloon-borne ozonemeter developed in IAP, Chinese Academy of Sciences. The ozonemeter belongs to the ultraviolet absorption type and is composed of three parts: gas collecting, photometry measuring, data gathering and processing. Its working principle is to let air sample having ozone in it go through a specially designed sample cell continuously, at the same time, choose more intensive ultraviolet radiation at wavelength of 254 nm to go through the same cell. Ozone content is determined by measuring the variation of ultraviolet radiation intensity at the chosen wavelength. In practice, balloon-borne ozonemeter telemetering and remote controlling systems, power supply system, and so on, are set in a gondola. Except the sample head, all parts are sealed in gondola by thermal insulation materials, the gondola weighing about 200−250 kg is usually drawn by a 10−30 kilo-cubic meter balloon, the special radar system follows and monitors the flying state of the balloon, and controls the flying altitude and time according to the previous plan and requirement, and at last separates the gondola from balloon by cutting operation orders. The gondola is landed by a parachute.

5.2 Lidar detection technique

Development of lidar technique and its application in the atmospheric study in China were started no later than that in other countries, and some progresses were made in laser remote sensing theory and study of atmospheric physics, such as in studies of the meteorological visibility, cloud, aerosol and pollutant and so on, but the development is rather slow, especially in detection techniques. During recent years, a considerable attention has been paid to development of lidar technique for measurement of ozone and other trace gases in the atmosphere in China, and some theory studies and technical preparations have effectively been started. For example, a concrete project on detection of ozone vertical distribution in the middle atmosphere by means of lidar has already been proposed in Chinese Academy of Sciences (Hu, 1990). As the first step, differential absorption method by using double-frequency YAG and Xe-Cl Lasers is suggested for sounding of ozone vertical distributions. At the same time, Ramann frequency shift and related detecting techniques and theory studies are also in appropriate progress.

5.3 Ground-based microwave remote sensing of ozone in the middle atmosphere

This is one of techniques recently developed in China for detecting ozone concentration and its daily variation in the atmosphere above 40 km by using a ground-based equipment (Zeng, 1991; Wang, 1986). The instrument used is actually a microwave spectrometer equipped with a telescope system (Zeng, 1991). Some advanced techniques, such as cooling, lock-in encircle and photo-acoustic receiving cell and so on, are used to increase the ratio of signal to noise. During practical measurements, brightness temperature at a given altitude is calculated firstly by means of measuring spectral profile at a chosen frequency (such as 110 GHz), then the ozone concentration is determined by an appropriate inverse method. The ozone concentration at different altitudes may be obtained by changing the chosen frequency and choosing proper weighing function.

5.4 Other techniques

Besides techniques mentioned above, there are some other techniques having been developed and used to measure the ozone in the middle atmosphere successively in China. Some techniques mainly used are as follows:

(1) Twilight observation technique: A multi-channel twilight photometer is used to measure variations of scattering radiation from the sky at different zenith distance and azimuth during the dawn and dusk. Ozone concentration in the region of 40 − 60 km in the atmosphere may be calculated according to measurement results at some chosen wavelengths within Chappius ozone absorption band (Wang, 1988; Ma, 1989).

(2) Airglow absorption technique: The excited airglow emission intensity of oxygen molecule at 1.27 μm band is measured during the dawn and dusk, then ozone distribution properties in the atmosphere above 60 km are calculated by photochemical reaction equations (Zhang, 1990).

(3) Ultraviolet radiation absorption and scattering techniques: Multi-Channel ultraviolet photometers were used at Chinese space scientific satellites to measure intensity variations of solar ultraviolet radiation at some chosen wavelengths by solar occultation method and backscattering method, respectively (Tai, 1986; Zhang, 1990; Wang, 1991). The ozone content at altitudes from 50 to 75 km is calculated.

6 Conclusion

As the attention paid to the atmospheric ozone studies is increased, there is a more overall development on atmospheric ozone detection techniques in China during the last decade, especially from the middle of 1980s. Different kinds of detection techniques have been developed for a comprehensive ozone study, such as detection of ozone concentration in both the troposphere and the stratosphere, measurements of total content and vertical distribution of atmospheric ozone and so on. The situation of atmospheric ozone study, especially of zone detection techniques has greatly been improved. The last decade is a turning period in Chinese ozone study history.

Since 1980s, two ground ozone observing stations at Xianghe and Kunming have been set up in China and continuous observation of total ozone content with high quality is being carried on. The development and experiment of balloon-borne ozonemeter and ozonesonde successfully stop the history in which there were no direct detecting techniques for either ozone vertical distribution or ozone in the stratosphere, it is a really new important progress in atmospheric ozone study in China.

A main aim of development of ozone detecting techniques in China at present and in the near future is to increase the number of ozone observation stations and to set up a stereo-observation technical system gradually. Among them, increasing the number of ground stations for observing total ozone content, improving the ozonesonde system and realizing laser ozone detecting system and so on, are major content of this proposed stereo-observation technical system. At the same time, development of appropriate method and technique for ozone observation by using satellite is also an important subject.

References

Barisky NN, Hu Renchao. Acta Geophysica Sinica, 1961; 10(1):1.

Bojkov RD, Fabian P. Ozone in the atmosphere, Proceedings of the quadrenial zone symposium 1988 and tropospheric ozone workshop. USA: Hampton, Virginia,A Deepak Publishing, 1989

Fu Jiming, Zheng Xianying. Global and regional environmental atmospheric chemistry. Proc ICGREAC, Beijing, China, May 3 – 10, 1989:180.

Götz FWP. Proc Roy Soc, London, A145, 1934:416

Guan Fengjun. Observations of solar eclipse of July 31, 1981. Beijing: Science Press, 1987

Hong Shaoxian. Research on Atmospheric Environment, 1988; (1):31

Hsueh Chingyu, Zhao Xuepeng. Proc of ICGREAC' 89, Beijing, 1989:398

Hu Huanling. Abstract of the workshop on techniques and methods for detection of ozone and other atmospheric composition, Beijing, October 30 – November 1, 1990:8

Jing Qiyi. Scientia Atmospherica Sinica (Special Issue), 1988:341

Kong Qingxin. Observations and studies of China on annular solar eclipse of September 23, 1987. Beijing: Science Press, 1990:475

Kong Qingxin, Wang Gengchen. Abstract of the workshop on techniques and methods for detection of ozone and other atmospheric composition. Beijing. October 30 – November 1, 1990:12

Lu Daren. Quadrennial Ozone Symposium, Abstracts, August 8 – 13, 1988, FRG: Univ of Gottingen, 1988:256

Ma Yanhua. Research of Space Physics, 1989; 4(1):84

Mao Jietai. Meteorology, 1989; 15(12)

Ny Tsize, Choong Piaw, Chin. J. Phys, 1983; 1:158

Peng Yuru. Observation and studies of China on annular solar eclipse of September 23, 1987. Beijing; Science Press, 1990:472

Tai Hunshen, Gu Yunfeng. Research of Space Physics, 1986; 1(1):27

Xiao Hui, Shen Zhilai, Huang Meiyuan. Abstract of the workshop on techniques and methods for detection of ozone and other atmospheric composition. Beijing Abstract, October 30 – November 1, 1990

Wang Gengchen. Annual report, IAP, Chinese Academy of Sciences, 1990; 9(1):97

Wang Gengchen, Sun Xiulan. Acta Meteorologica Sinica, 1983: 41(2):236

Wang Gengchen, Kong Qingxin. Publications of Yunnan Observatory, Special Issue 1, 1989:230
Wang Mingxing. Scientia Atmospherica Sinica, 1981; 5(3):318
Wang Pengju, Zhou Xiuji. Journal of Academy of Meteorological Science, 1988; 3(1):46
Wang Yingjing. Abstract of the workshop on techniques and methods for detection of ozone and other atmospheric composition. Beijing, October 30 – November 1, 1990:9
Wang Yingjian, Xu Jiyo. Chinese Science Bulletin, 1990; 25(24):1990
Wang Yingjian. Proc ISSP'86, 6 – 007, Beijing, China, 1986
Wang Yingjian, Research of Space Physics, 1988; 3(2):125
Wang Yingjian, Xu Jiyo. Scientia Atmospherica Sinica (in press), 1993
Wei Dingwen. Scientia Atmospherica Sinica (Special Issue), 1988:271
Wei Dingwen. Ozone in the atmosphere, Proceedings of the quadrennial ozone symposium 1988 and tropospheric ozone workshop (Ed. by Bojkov RD, Fabian P). USA: Hampton, Virginia, A Deepak Publishing, 1989; 177
Zeng Qingcun. Principles on infrared remote sensing, Beijing: Science Press, 1974
Zhang Zhongmou, Gu Yunfeng. Observations of solar eclipse of July 31, 1981. Beijing: Science Press, 1987
Zhang Zhongmou. Abstract of the workshop on techniques and methods for detection of ozone and other atmospheric composition, Beijing, October 30 – November 1, 1990:14
Zhang Zhongmou. Research of Space Physics, 1990; 5(2):144
Zhao Yanlian. Observations of solar eclipse of July 31, 1981. Beijing: Sciences Press, 1987

(Received July 14, 1992)