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KH20, the source is a low-pressure krypton glow tube. As noted above, the emission of the krypton tube exhibits a band greater than 123.58 nm and a band less than 116.49 nm (Budovich et al. 2013). Radiation at 123.58 nm is strongly attenuated by water vapour, while absorption by other gases in the optical path is relatively weak in this wavelength. However, at 123.6 nm the water vapour absorption force is low by a factor of almost 2 compared to absorption in the Lyman-alpha line, while oxygen absorption is stronger by a factor of approximately 40 (Tillman 1965; 1996), making oxygen interference much more severe and variable with air density, a particular problem for aircraft measurements. Radiation at the shortest wavelength (116.49 nm) is also attenuated by water vapour and oxygen molecules. This means that a much greater correction is required for oxygen than for the Lyman-alpha device. In addition, a variable path length self-calibration technique cannot be applied to the krypton hygrometer, as this device works with two absorption lines, each with two absorbers. All of this reduces the accuracy of krypton hygrometer measurement. However, Campbell and Tanner (1985) determined that for their Kr lamp, this line (116.49 nm) contributes only 3% to the total lamp output. Since it is very close to the nominal limit of 115 nm for magnesium fluoride windows, they concluded that it is very dimmed. Therefore, the use of MgF2 windows installed in the source and detector tubes should help to improve the measurements. But it is necessary to keep in mind that magnesium fluoride is hygroscopic material. This material changes its transfer characteristics in humid environments by the interaction of atmospheric components with UV photons. Windows had to be cleaned manually more or less frequently. Another disadvantage is the wide range nonlinear output signal from Lyman-alpha and krypton-based systems. This requires special analog signal processing or the use of wide-range A/D converters for accurate calculations. In addition, we should keep in mind that due to the simplicity of the configuration and its signal displacement deviation, these hygrometers cannot be used for the determination of absolute concentrations. A feature of the KH20 is that the source tube window undergoes scaling when operating, especially in humid environments. This will arise through the desaturation of atmospheric components by UV photons and can be removed simply by cleaning the windows. Figure 3.33 KH20 krypton hygrometers developed by Campbell Scientific: calibration range—1.7–19.5 g/m3 (nominal), frequency response—100 Hz; Operating temperature range: from 30 to +50 °C; weight: 6.8 kg. () There is no doubt that other wavelengths in the UV range can also be used for hygrometer design. For example, the emission line (184.9499 nm) of the low hydrogen pressure lamp can be used for these purposes (Wernecke and Wernecke 2014). However, the sensitivity and accuracy of these devices will be much worse than on the devices considered above. Gersh and Matthew (1988) for their research have used radiation at wavelengths of 177 and 205 nm. A silica window flashlight filled with xenon was used as a source of UV radiation, while CsTe photocathodes, which are solar shutters, were used as detectors. They used this hygrometer to monitor and control the operation of the industrial drying chamber. The basic concept of this UV hygrometer was to measure the differential absorption by water vapour of UV radiation in two spectral bands and to relate this measurement to the absolute humidity of the air in the measurement volume. In the first spectral absorption band (at 177 nm), UV radiation is strongly attenuated by water vapour, while in the second reference band (at 205 nm), UV radiation is not affected by the presence of water vapour. The ratio of absorption to the intensities of the reference band is then a reflection of the water vapour mass per unit volume in the measurement region (which is the definition of absolute humidity). There is no doubt that this approach is correct, but the selected spectral range does not provide the necessary sensitivity. A complication arises from the fact that atmospheric oxygen also absorbs UV radiation in the same spectral region as water vapour. With respect to other light sources in the desired spectral range, which unfortunately in this particular spectral range of set of sources is very limited (Heering 2004), LEDs can be manufactured to emit light in the UV range, although practices LEDs are very limited below 365 nm. The efficiency of the LED at 365 nm is approximately 5%–8%, while efficiency at 395 nm can reach to 20%, and power outputs at these longer UV wavelengths are also better. Taoyuan Electron Lmt. (HK) only (HK) UV LED flashlight operated at 280nm (). But this source has a small power of 25 mW, strict requirements for operation and a short service life. UVDSDs should be used within three months. A similar situation is observed for UV DL. Ce:LiSAF and Ce:LiCAF DL (Lawrence Livermore National University) can generate radiation in the range of 280 to 316 nm. LaseMaster Group, Inc. provides a Solid State Laser Pumped Diode (DPSS) that work in the range of 261 to 2200 nm. Laser 2000 produces Ql262 laser with wavelength 262 nm (. Passively pulsed laser systems Q-switched laser, emitting wavelengths of 213 nm was designed by CryLAS GmbH (. Only gas lasers can generate light with a wavelength of less than 200 nm; UV argon-fluoride (ArF) excimer lasers operate at 193 nm, and the Ar2+ excimer laser can operate at 126 nm. However, even in this case, the emission spectrum is not optimal for hygrometer construction (Parkinson and Yoshino 2003). In addition, the use of gas lasers does not contribute to lower prices and sizes of developed hygrometers. The use of semiconductor radiation detectors in UV hygrometers is also limited due to low sensitivity in the current spectral range (Seib and Aukerman 1973; Razeghi and Rogalski 1996). The typical spectral characteristics of these photodetectors are shown in Figure 3.34. Figure 3.34 Examples of semiconductor photodetectors if optimized for operation in the UV spectral range. (From .) As demonstrated above, water vapour plays a unique role in atmospheric processes as a key chemical and radiative component. Water vapour is present in all layers of the atmosphere, including upper layers, such as the troposphere, stratosphere and mesosphere, so it is important to control the concentration of water vapour in these layers. Using for these purposes most of the methods described above, as well as most solid humidity sensors, which will be considered in Vol. 2 Electronic and electrical humidity sensors of our problem, is hindered due to the low concentrations of water vapour at these altitudes and strong temperature variations when the altitude changes. At certain altitudes, a strong temperature jump is possible. Currently, a limited number of techniques can be used for on-site measurements of the upper troposphere and stratosphere moisture. Among them, the fluorescence technique, which offers high precision and fast response, has proven to be reliable (Meyer et al. 2015). The devices that used this technique worked well when used in dashboard balloons, high-altitude aircraft and rockets. Fluorescence is radiation that is emitted after a chemical species receives radiation. UV radiation is being used for fluorescence excitation. It is the result of instantaneous deactivation that occurs after the species goes to a higher energy state in the absorption of incident radiation. The species has a lifespan of approximately 1–100 ps, and returns to its ground state (not excited) through the radiation emission: 3.4 () A* → A + h - where: A* is an excited state of an A substance is the constant plank is the frequency of the photon The emission occurs in all directions, and is of a longer wavelength than incident radiation. The wavelength of the radiation emitted is influenced by the chemical structure of the fluorescent species. Quantum fluorescence performance provides the efficiency of the fluorescence process. It is defined as the relationship between the number of photons emitted and the number of photons absorbed: 3.5 () - quantum yield - number of photons reissued number of photons absorbed The radiant intensity of the emission transmits information on the concentration of fluorescent species. For a weak absorber system (i.e. A < 0.05), fluorescence intensity (I F) is linearly related to the concentration (C) of the fluorescent species, as expressed in the following equation: 3.6 () I F to F I 0 C where: I 0 is the intensity of the incident radiation k F is a constant that depends on the absorption characteristics of the species, the quantum efficiency of fluorescence, and the configuration of the instrumentation system In relation to water vapour, the theory of fluorescent-based technique has been developed by Kley and Stone (1978) and Bertaux and Delannoy (1978). Subsequent refinements were carried out by Keramitsoglou et al. (2002). The fluorescent method of water vapour detection is based on the photodissociation of H2O at wavelengths below 137 nm and the subsequent fluorescent relaxation of the oh* radical produced (Yushkov et al. 1995; 2000). For Lyman-alpha dissociation of water vapour, the process can be expressed as 3.7 () H 2 O + h (121.6 nm) → OH*(A 2 +) + H (2 S) with a quantum performance well below 1. About 10% of absorbed photons result in oh-OH fragment excitation to electronic state A 2+. The oh* radical electronically excited at 310 nm 3 80 OH*(A 2 +) → OH*(X 2) + h (305 to 325 nm) or is shutting down by collisions with air molecules 3 9 () OH*(A 2 +) + N 2, O 2 → products → OH(X 2) + M Fluorescence is observed in both bands (0 - 0) and (1 - 0), but the strongest fluorescence comes from highly excited rotation levels (N to 20–22) of the band (0 - 0). A photomultiplier with an interference filter measures the intensity of fluorescence that is the signature of H2O's stem molecules. The intensity of fluorescence is obtained as 3.10 () J OH * + ? A? H 2 O ? ? F - · · H 2 O · C · A + h k · q · ? air · exp 4 0 Q 2 · ? Or 2 ? · L - where: L is the length of absorption between the lamp and the interaction region [OH*], [H2O], [O2] are the numerical densities of OH*(A 2+), H2O, air and respectively A is Einstein S's probability of transition is photon flow from the light source o H 2 O and o O 2 are vapor cross sections and for Lyman-alpha, respectively q is the quantum performance of the photo dissociation ka cooling coefficient Therefore, by measuring fluorescence radiation you can determine the abundance of H2O. Of course, for a correct measurement of photon flow, oxygen absorption should be taken into account. However, at an air pressure below 10-1 hPa air quenching and oxygen absorption are negligible (Kley and Stone 1978) and the intensity of fluorescence becomes 3.11 () J - H 2 O ? · F · to · o H 2 O · q In the other case limiting P air > 10 hPa, i.e. in the atmosphere up to 20–35 km, ka [air]> > A and therefore 3.12 () J to H 2 O ? · air · F · to · o H 2 O · C · A + h k · q · exp 4 0 Q 2 · ? Or 2 ? · L to C · ? H 2 O ? Air Factor C of Equation 3.12 summarizes the molecular coefficients, known from the literature, as well as the specific quantities of the instrument. For example, for C calculations you can use the values of the following parameters: Einstein coefficient for reaction Equation 3.8, A to 1.26·106 s-1 (Crosley and Lenge 1975); and kp 2.3 x 10 x 11 cm, 3 s, 1 (Kley and Stone 1978). If C is a constant, the number of fluorescence photons detected is proportional to the H2O [H2O]/[air] mix ratio for measurements in the troposphere and lower stratosphere. The water vapour mixture ratio (µ) can then be expressed (after Kley and Stone 1978) as 3.13 () µ to J · C · F - For measurements at higher altitudes, equation 3.11 should be used to obtain the correct water vapour mixture ratios. Therefore, under conditions with negligible oxygen absorption, fluorescence gives a direct measurement of the atmospheric water vapour mixing ratio in this case (Yushkov et al. 1995). Of course, we have to keep in mind that in reality, C is a function of the photo dissociation rate of reaction Equation 3.7, and therefore depends on the photon flow in the volume of fluorescence, which in turn depends on variations in the intensity of the lamp (Zoger et al. 1999). The first fluorescent hygrometers suitable for atmosphere research have been developed by Kley and Stone in 1978. However, the actual flight instrument for use in the stratosphere was described and characterized in 1979 (Kley et al. 1979). Later fluorescent hygrometers have appeared, developed in other laboratories (Goutail and Pommerau 1987; 1990, 1994; 1991; Yushkov et al. 1995; 1999). The most advanced Lyman-alpha fluorescence hygrometers have been developed in the Laboratories of the National Oceanic and Atmospheric Administration (NOAA) in Boulder, Harvard and Jülich (Germany). All existing fluorescent hygrometers are based on a similar principle, but constructively may differ essentially. Its versions are shown in Figure 3.35. Typically, the difference the design is associated with different designations of developed devices and a different approach to calibrating fluorescent-based hygrometers. For example, devices designed for aircraft applications, in devices intended for balloon measurements (Yushkov et al. 1995), are not limited in size and weight, allowing additional elements to be introduced, improving their parameters (Goutail and Pommerau 1987; 1999). Typically, these devices have additional measuring chambers and receivers to control the radiation intensity of the UV lamp (Figure 3.35). The presence of a closed measuring chamber essentially expands the opportunity to use fluorescent-based hygrometers, as it allows them to be used during the day. Figure 3.35(a) Sketch of the fluorescence cell and the main components such as Lyman-alpha radiation source, photomultiplier tube, UV vacuum detectors (VUV) and mirror unit on the hygrometer designed by Zoger et al. (1999). (b) Conceptual diagram illustrating the main mechanical and optical components of the airborne rapid stratospheric hygrometer (FISH). The cell size is 0.3 l in total. As the lamp is not monochrome, the number of background counts of the lamp should also be taken into account. Therefore, a rotating mirror is implemented between the lamp and the measuring cell. During a measurement cycle, the mirror is placed in three different positions to determine the total Ng fluorescence rate (mirror position 1), the N0 background rate (mirror position 3), and the intensity of the 10 lamp (mirror position 2). Therefore, the mirror unit allows to monitor the intensity of Lyman-alpha radiation (I0) and a determination of background rates and dark count. Ng is the number of fluorescence photons detected proportional to the water vapour mixing ratio. Therefore, calibration factors can be determined that are almost independent of changes in radiation source output. Measurements using this hygrometer can be performed with < 0.2 ppmv accuracy over an integration time of 1 s. (a) De Zoger, M. et al. J. Geophys. 104, 1807-1816, 1999. Excuse me. (b) by Meyer, et al. Atmos. Chem. It's a physics. 15, 8521–8538, 2015. Published by the European Union of Geosciences (as open access). The hygrometer shown in Figure 3.36 has no such possibility, as measurements take place in open space. This means that readings are sensitive to environmental solar radiation, which usually exceeds the fluorescence radiation to be detected. Figure 3.36(a) Optical scheme and b) Fluorescent-based compact hygrometer electronic block diagram designed by Yushkov et al. (1995) to carry out measurements of high-resolution stratospheric and stratospheric water vapour balloons at night. To increase useful signal detection efficiency and reduce device size, the radiation source and optical sensing system are placed coaxially. The lenses are made of glass The front lens has a diameter of 50 mm and is sealed to the lamp body. The focal length is 10 mm, which leads to a distance of 24 mm between the windows of the ultraviolet vacuum lamp (VUV) and the volume analyzer. Analyzed. did not use special measuring cells. Measurements are carried out in open space in the vicinity of the target. Therefore, the device does not need a suction system to take samples of the air to be analyzed. The total measurement uncertainty is less than 10% in stratospheric mixing proportions greater than 3 ppmv increasing to approximately 20% in mixing proportions less than 3 ppmv. A description of the improved version of the hygrometer that can be found in (Lykov et al. 2011, 2012). Compact and lightweight hygrometer has a mass of 0.5 kg. The absence of the receiver, controlling the radiation intensity of the lamp, the authors explain by the high stability of the radiation intensity of the lamps used in the hygrometer. (Idea of Yushkov, V. et al., SPIE Proc., 2506, 783-794, 1995.) In this sense, the current device can only be used at night. However, devices with an open structure have another significant advantage. They prevent H2O desorption contamination from walls, which is very important when measuring in the atmosphere with a very low concentration of water vapour. For fluorescence excitation, the UV hydrogen vacuum or krypton lamps described above can be used (Varier 1967; Buck 1976b; 1999). As mentioned above, the radiation from the hydrogen lamp contains a Lyman line (121.6 nm). A spectral oxygen window in this line provides the most effective generation of excited hydroxyl radicals within the volume where fluorescence is being recorded. The radiation from krypton's vacuum UV lamp does not possess this property. UV hydrogen vacuum lamps may have a different design, which is associated with the use of various hydrogen sources. The most common sources of hydrogen are uranium hydride and a mixture of hydrogen and helium. According to Varier (1967) and Buck (1976b), the intensity of a 121.6 nm line in brightness discharge lamps using a mixture of 2%–25% hydrogen and helium or argon grows through decreased recombination of hydrogen atoms on the walls of the bulb. These lamps are easier to manufacture and are more environmentally safe compared to those containing uranium and uranium hydride (Hutchenson 1972; 2002). It was established that uranium hydride could be replaced by ZrCo zirconocarbide, which has the same thermodynamic properties (Lykov et al. 2012). This replacement eliminates thermostatic control of the lamp, which helps reduce the size and weight of the hygrometer. But, it was established that in the spectra of hydrogen UV lamps within the range of 200–360 nm is present an intensive hydrogen continuum, which overrides the hydroxyl fluorescence spectrum and can cause considerable noise during laboratory calibration of hygrometers in a chamber Therefore, in optical fluorescence hygrometers, which use a hydrogen discharge lamp, a radiation of 270–320 nm should be rejected with a special window filter. For this type of filter, mgF2 is generally used, spectral spectral characteristics Figure 3.37. Figure 3.37 Typical spectra of the transmittance of the monocrystalline magnesium fluoride window of the hydrogen lamp without filter (1) and with filter (2) for selective absorption at 300 nm. (Data extracted from Yushkov, V. et al., SPIE Proc., 2506, 783-794, 1995). To improve sensitivity, an interference filter centered at 318 nm is also desirable. Selects the spectral region, matching the emission of the upper rotational levels of oh*s A - X system band (0 - 0). With regard to the measurement of sensitivity of photofragm fluorescence, it is usually carried out by sun blind photomultiplier (PM). A HAMAMATSU R647-P photomultiplier is generally used for these purposes. In some devices, in addition to the elements indicated above, one (Goutail and Pommerau 1987) or two (Zoger et al. 1999) may also be present. They are applied to control the intensity of radiation, used for fluorescence excitation. Usually these detectors are the no-no-ionization chamber detectors. The energy required to ionize does NOT correspond to a threshold wavelength of 134 nm. Therefore, ionization cells filled with NO are a highly selective radiation sensor for the VACUUM UV spectral region (VUV) (Samson 1967). An iodine ionization cell that is sensitive from 115 to 135 nm (Kelly et al. 1989) can also be used. The electronic system used in hygrometer designed for lamp modulation and synchronous demodulation of the received signal. This technique improves the noise-to-signal ratio by more than 100 times. Studies have shown that fluorescent-based hygrometers have high sensitivity. In addition, they are compact enough for balloon and aircraft measurements (Table 3.13). Rocket-transmitted measurements have also been reported in the mesosphere using this technique (Khaplanov et al. 1996). In addition, the Lyman-alpha fluorescence technique can achieve a wide dynamic range for measurements from the middle troposphere and greater than approximately 1000 ppmv in the dry stratosphere with only 2.5 ppmv, where changes in the order of 0.1 ppmv can be detected with a relatively uncertain ±5%. At that high response rate, when the integration time is in the order of 1 sec, it allows the measurement of small-scale characteristics in the atmosphere. However, the H2O measuring range of these devices is limited to pressures below 300 hPa due to strong Lyman-alpha absorption in the lower troposphere. Other disadvantages of these hygrometers are the instability of the emission hydrogen UV lamp, a relatively short lifespan, and the lack of commercially produced samples with reproducible parameters. Numerous studies have confirmed that optical hygrometers have several important advantages, which found in other hygrometers. At first, the measurement of water vapour using this optical (or spectroscopic) technique has received a very favorable response from the industry because these devices employ a contactless sensor for the detection of water vapour in various environments, including natural gas: the sample never comes into direct contact with the sensor element. This non-contact approach significantly reduces instrument maintenance requirements and reduces overall equipment maintenance costs. In addition, in principle, optical methods for moisture measurement can be used in extreme environmental conditions (high pressure, high temperature, aggressive gases, etc.) and lack of measurement delay. The response speed is limited only by the speed of the indicator or recorder. The time constant of an optical hygrometer is usually a few milliseconds. Therefore, these instruments are very useful for tracking rapid humidity fluctuations, as the method does not require the detector to achieve steam-pressure balance with the sample. This makes the method ideal for use in measuring the humidity of an aircraft or under any circumstances where rapid moisture changes can occur. In addition, the optical method has a specific sampling; it is possible to take samples instantly of any desired atmospheric route length of a few millimeters to thousands of meters (Figure 3.38), and by doing so reaching an integrated value of absolute humidity on the road in question. This is called open path measurement. If the length of the path is appreciable, the value obtained is more representative than that obtained by point sampling (Foskett et al. 1953). Of course, extractive or cell-based IR measurements, commonly used in previously considered optical hygrometers, have the obvious advantage over the open path configuration that the physical conditions (concentration, pressure, temperature, absorber path length, etc.) of the measurement can be easily controlled or changed at will (Table 3.14). This provides better conditions for long-term measurements when high determination accuracy is needed, for example, for fundamental studies in gas spectroscopy or the development of analytical methods. Open trajectory measurements, on the other hand, are more prone to technical difficulties related to changing atmospheric (meteorological) conditions that lead to uncertainties, but the on-site nature of these studies also offers distinctive advantages. Figure 3.38 Experimental configuration for remote monitoring of the atmosphere with retroreflector by open path measurement. (From Korotcenkov, G. (Ed.), Electrochemical and Optical Sensors, Momentum Press, New York, 311–476. Excuse me.) Advantages of extractive open path (closed cell) Adjustable path length, regardless of plume size Simplicity, repeatability Lower detection Limits stable conditions, longer measurement times quantitative and background spectra more easily collected In situ measurement, non-invasive sampling Detection of very polar, reactive and labile compounds Integrated in-line measurements (average) pollution area sources can be examined: pollution area sources can be examined: pollution contamination area sources can be examined at dangerous sites Disadvantages Time delay between sampling and measuring Very polar, reactive compounds difficult to sample (may lead to errors in analysis) Memory effects, Losses on the cell wall Path length limited by the size of the pen field adjustment required at each site Time dependence No temperature control and pressure Decrease of S/N for longer paths Calibration spectra on the same path as the sample cannot be collected Experiments are difficult to repeat The advantages of optical hygrometer can also include its ability to maintain high sensitivity capillary hygrometer, electric hygrometer and even the dew point apparatus become less sensitive. In addition, the optical hygrometer will work well below and above the freezing point. In addition, this instrument has a negligible drift and can generally operate in a wide range of humidity. Optical hygrometers can be used for high humidity measurement as well as for very low concentrations in the ppmv range. Finally, the method does not in any way alter the concentration of the sample by adding or subtracting water or changing the state of any part of the sample as in dew point or psychrometric methods. We should keep in mind that all the devices mentioned above have advantages and also deficiencies. Optical techniques often require high effort in equipment and analysis. These aren't tiny. The size of the measuring cell with the required optical path length is a limiting factor in the development of IR hygrometers. Attempts to reduce the size of IR hygrometers are accompanied by a measurement range restriction and decreased sensitivity. Miniaturization of UV hygrometers is impossible due to the size of existing UV light sources and radiation detectors in this area. In addition, optical hygrometers are expensive compared to other devices. They may also suffer from contamination. In addition, regular calibration is required for many traditional instruments, which is inconvenient and costly. Other hygrometers such as dew hygrometers or frost point are generally used for this purpose. Therefore, according to WMO reports (1992, 2011), optical hygrometers are more suitable for measuring changes in vapour concentration rather than absolute levels. While has the desire to learn more about optical sensors and optical spectroscopy may refer to revisions and books published in this field (Wolffbein 1991, 1992, 2006; Ligler and Rowe Taitt 2002; Narayanaswamy and Wolffbein 2004; Orellana and Moreno-Bondi 2005; Orellana and Moreno-Bondi 2005; Ktachenko 2006; 2008; 2011, and many others), Allen M.G. 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Page 2 Print publications date: January February April May May June August August August December 2019 2018 2017 2016 2015 2014 2013 20 12 2011 2010 2009 2008 2007 2006 2005 2004 2003 2002 2001 2000 2002 2001 Prev 2001 Dates of online publication of : January February March April May June August August September December 2019 2018 2017 2016 2015 2014 2013 2012 2011 20102009 2008 2007 2006 2005 2004 2003 2002 2001 2000 Before 2001 to: January March March April June July August December December 2020 2019 2018 2017 2016 2015 2014 2013 2012 2011 2010 2009 2008 2007 2006 2005 2004 2003 2002 2001 2000 2002 2001 2012 2011 2010 2009 2008 2007 2006 2005 2004 2003 2002 2001 Prev 2001 Page 3 Humidity indicators are not sensors. However