The Automatic Hydrogen Gas Measurement Apparatus Developed in Sakai Group since 1993.

(2007-10-21)

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Comments about the Measurements (KS).

Recently, many researchers start to pay much more attention to the solar energy conversion and storage which use the so-called visible light induced water splitting process. To put this into a practical use, it is still important for us chemists to study and develop efficient catalysts for lowering the activation barriers for both oxygen-evolving and hydrogen-evolving reactions in aqueous media. In order to carry out this kind of experiments, it is often important to be able to accurately measure the amount of either molecular oxygen (O_2) or molecular hydrogen (H_2) either in the gas phase above the solution or in solution. The former can be more easily carried out because a relatively excellent oxygen meter is now commercially available with a reasonably low cost. For example, we now use an oxygen meter (YSI model 5300A equipped with a 5331 oxygen probe electrode) in our recent studies attempting to develop more highly efficient oxygen-evolving ruthenium catalysts from a standpoint of coordination chemistry. This electrode determines the O_2 concentration in solution by use of electrochemical reduction of oxygen permeated through the special membrane coverd over the special electrode surface. When the amount of oxygen gas is relatively low, we suffer from the leak coming into the measurement vessel from the surrounding atmospheric air.

When we work up on the quantitative analysis of molecular hydrogen, the most standard method, which is highly sensitive at the same time, is to measure the gas above the sample solution using a gas chromatography. The commonly used column is a Molecular Sieves 5A (or 13X; a little bit more expensive but is useful when one wants to separate CO, NH_3 etc. at the same time) column. The temperature for the column is 30-40 °C, while those for the injection and the detector ports should be set at 80 °C.

The stainless steel column having a length of 2-3 m with an inner diameter of 3 mm (outer diameter is 4 mm) is used.

The detector should be a thermal conductivity detector (TCD), and the Ar carrier gas is employed at a flow rate of 50 ml/min. The flow rate should be tuned up correctly before the measurement by monitoring the flow rate using the classical soap membrane passage method (a gas burette should be connected to the vent port of each carrier line in each case). Note that the most commonly used gas chromatograph has two ports for the carrier routes, one is for the measurement and the other for the reference. Both carriers are passed through a TCD detector, in which an electrical circuit (called a Wheat stone bridge) is used to balance the so-called four resistances (R1, R2, R3, and R4). For example, one couple of resistances (R1 and R4 positioned in a diagonal position) will be used for the sample carrier and the other set (R2 and R3) is used for the standard carrier gas. The TCD works based on the concept that the resistance of metal wires (e.g., Pt) gives a response to the change of temperature. Then how the temperature is changed? It uses the difference in thermal conductivity of gas surrounding the metal wire. Suppose that the metal wire is located inside a certain cavity having a wall with controlled temperature. The sample gas should be continuously passed between the wire and the wall. If there is a sufficient difference in temperature between the wire and the wall, the thermal heat is transferred from the wire to the wall by conduction through the gas passed between them, where the wire has higher temperature and the wall has lower temperature. If the thermal conductivity of the gas is high (such as H_2 and He), the wire will quickly lose the heat to experience sharper decrease in temperature. To the contrary, if the gas passed through is either O_2, N_2 or Ar, which has a lower thermal conductivity,

the rate for the transfer of heat from the wire to the wall is relatively slow. Thus, in the measurement of H_2, it is reasonable to use either N_2 or Ar as a carrier gas. If you also want to know a factor arising from the leak of air, it is more reliable/reasonable to select Ar as a carrier in your experiments, since from the leak of N_2 you can tell about how much leak you get in each experiment. Thus, Ar, which is much more expensive compared to N_2, should be selected in the analysis of H_2. To the contrary, when Ar is used as a carrier gas, we lose the sensitivity about the measurement of O_2, since the thermal conductivities of these two gases are not largely different to each other. If you want to have a higher sensitivity for O_2, you should use He as a carrier for such a purpose. However, you should remind that you now have a much lower sensitivity for H_2 with use of He as a carrier. In case where the amount of oxygen evolved is high enough, you do not have to worry too much about this issue. In such a case, just use Ar for the simultaneous measurements monitoring both H_2 and O_2. This is the main concept of how you select the carrier gas for your experiments.

After buying and packing up your stainless steel column with Molecular Sieve 5A or 13X (MS-5A or MS-13X), you should once do the 'AGING' procedure, which is to dry up the MS-5A by complete removal of water adsorbed over the adsorption site of it. By applying this procedure, the capability of separating the gases (H_2, O_2, and N_2) is greatly improved. To the contrary, it can be said that the retention time for each gas largely depends on how much amount of water is adsorbed over the active sites. Thus it is very important to maintain the conditions for the measurements constant all the time (three sets of temperatures and the flow rate, described above). By keeping the conditions same, one can tell about degradation in the separation capability of MS-5A. It should be

also noted that the connection between the two stainless steel columns and the thermal conductivity detector must be disconnected so as to avoid the contamination of the detector with some dirty emission from the column. The contaminants which have been adsorbed will also be released during the 'AGING' procedure (200 °C, overnight).

Then, how we do the quantitative analysis to determine the amounts of H_2 and O_2 by the gas chromatographic technique? One important thing is to have an accurate standard gas sample. For such purposes, the most classical method is to have a glass flask equipped with both a septum port and a three-way stop valve (or two-way stop valve to be connected to a Ar/vacuum line). The total gas phase volume should be separately determined by filling the flask with water under the conditions same to those it is actually used for making the standard gas. From the weight of water, the total volume should be determined, first. Next, the gas phase inside the flask should be replaced with Ar at temperature same with the subsequent experimental condition. Suppose that the flask has a volume of about 300 ml now. Then by collecting and adding 0.1 ml of pure H_2, which was taken from the pure H_2 tank, to the tank, the H_2 gas can be diluted by using a gas tight syringe. A standard 300 ppm H_2 gas with Ar base is thus available for your experiment. When H_2 gas is collected, H_2 gas should be continuously flowed inside a narrow tube for which the needle of the gas tight syringe can be inserted. By exchanging the gas inside the syringe many times under the stream of pure H_2 gas, you can, in a sense, correctly prepare your standard sample. Be careful not to purge the H_2 gas too much where you do not have sufficient ventilation of air. Preferably, it must be carried out under a hum hood. Otherwise, your room should be opened and the air should be passed through the room to avoid an accidental flaming of H_2. A special care

should be paid when you work up with pure H_2 gas. When you do the manual collection and injection of gas from a sealed photolysis vial, the gas inside the vial is filled with Ar under ambient pressure (1 atm = 0.1 Mpa) and the syringe should be always filled with Ar by substituting the gas inside the syringe under the stream of Ar, as discussed above for the manual collection of H_2 by a syringe technique. Substitute the gas phase with pure Ar, perhaps more than 7 times. Use the gas tight having a total volume of 0.25 ml. The appropriate volume for collection is, say, 0.1 ml. The syringe needle is preferable to be the one which has a hole beside the needle. If the needle has a hole on top of it, like those used in hospital, the needle will be soon stacked with a piece of rubber derived from either the septum used for the photolysis solution or that used for the injection port of the gas chromatograph. So, the use of a special needle having a pin hole at the side body of the needle is highly recommended. When you collect the sample from the photolysis solution, a great care should be paid not to contaminate the gas phase inside the sample flask. In order to avoid the contamination of the gas phase inside the sample flask with the leak of air derived from the contamination of the syringe with the air, one should first clean up the syringe with pure Ar, as mentioned above, and then keep, e.g., 0.1 ml of Ar inside the syringe after the repeated substitution procedures. Then, just before you insert your needle through the rubber septum on top of the photolysis vial, you should push out all the Ar gas and the needle should be quickly inserted into the vial to collect the sample gas. Before pushing out the Ar gas, the top of the needle should be just a little bit inserted into the rubber septum but without inserting the hole on the side of the syringe so that the operator can quickly insert the needle just after the push-out

event. After inserting the needle into the sealed vial involving the photolysis solution (ca. 10 ml) together with the gas phase (ca. 20 ml, but the volume must be accurately determined prior to the photolysis for use in later calculations). The concentrations of H_2 or O_2 can be determined because you have already determined the peak area of each gas for the standard gas mixture, e.g., consisting of H_2 (ca. 500 pm), O_2 (2000 ppm), and Ar. Namely, the group of authors purchase a large tank involving the similar amount of standard gas (see Figure 4). If H_2 and O_2 are involved at higher concentrations, it may become dangerous (explosive!) (the above shown level of the contents should be no problem). Please also be careful not to keep the tank so long, since the content of H_2 will be changed after a long period. This comes from the relatively high permeability of H_2 through the metals, as many of you know. It is suggested by the people in the company selling such a standard mixing gas that it is preferable to renew the tank every year.

Next, it should be discussed why the automatic measurement system is so good. Why they are so important? There were two major reasons when KS decided to develop such an automated system in 1993. One comes from our tough efforts in keep watching the photolysis solution and keep collecting and injecting the sample gas onto a gas chromatograph every 5 min?, 10 min?, 30 min?, 60 min, or 3 h? It is often very time consuming and we need to have a tough mind to keep doing the same thing, which is in a sense very stressful! When KS was an undergraduate student, he did not go home for a just ridiculously long days (During one month in January, he only went home two days per week. It continued four weeks! At the final stage of these sets of experiments, he was always sleeping in a chair but was always waking up every an hour to collect and

do the injection event for each 14-h of measurement). Some of his students after moving to Seikei University, Mr. Takeshita (1991) and Mr. Goshima (1992), also devoted their enthusiastic efforts to do the similarly tough photolysis experiments. Next year, in 1993, KS and Mr. Ue started to develop the automated system as follows.

First, we attempted to monitor the the output signal from the TCD dectector, which comes out just as a change in voltage. The full scale for the output signal for the Shimadzu GC-14A is 10 mV (GC = Gas Chromatograph). Many other Shimadzu GC systems provide the similar signal output. First, we decided to use an interface board commercially available for the NEC PC-9801 model series of personal computer. At that time, many scientists were quite familiar with data analysis using such PCs using the N88-Basic programs made by themselves. So the initial version of our automated system was also developed based on such an N88-Basic program. To monitor the output signal from a GC, we first attempted to use the so-called AD converter (AD = Analog-to-Digital). However, we next encountered the fact that the standard input level for the commercially available AD boards are usually in the order of 1 or 10 V in their full scale for the input. One the other hand, the AD boards generally assign their bits to the full scale. For example, if the board has a resolution of 14 bits, the full scale will be divided by 2^{14} (16384 data points). If one uses the board as is, the GC output signal only has a data points of ca. 164 if the AD has a full scale of 1 V. If the board has a full scale of 10 V, your GC data will be assigned to one of the 16 points, which means that your GC data have fairly broad information and are useless for calibrating the amount of each gas with accuracy. Thus, we had to turn our attention to amplifying the output signal

from a GC, at least, by a factor of two orders of magnitude. In order to achieve such an amplifier, op-amps (operation amplifiers) are available with reasonably low costs. So, we endeavored to make our own hand-made op-amps, by referring some books of electrical circuits. We actually could make an appropriate circuit but suffered a lot from a huge noise preventing us to conduct appropriate measurements. The answer was that such op-amps not only amplify the signal level but also the noise level. Since the signal was in the level of μV, the noise derived from the surrounding (noise from a power supplier etc.) had the same order of magnitude. We finally gave up using an AD converter for our use in monitoring the signal output from a GC.

The equipment we then decided to use, which we still use now (the same one!), is a digital multimeter (DigiMul) from Advantest (model TR6846) equipped with a GPIB interface board. Currently, the program (coded by Pascal using Delphi5) runs on a Dos/V machine operating uner the Windows XP, where a GPIB board from Interface (model PC-4301) is used for the GPIB talking. Data collecting interval is manually set at the DigiMul as 3 data points per second (3 data/s). The data is free of the noise because of the quite excellent noise filtering systems already installed in the DigiMul. Such noise filtering systems are rather common in such DigiMuls.

Under the above GC conditions, H_2, O_2, and N_2 give their retention time, e.g., at *ca.* 0.8 min, *ca.* 1.6 min, and *ca.* 3.4 min, respectively. Therefore, The minimum interval time for the measurement may set as 5 min. The automated H_2 measurement should be initiated by a thread routine programmed in a Delphi5 package. The switching of gas values can be made by using a switching board supplied from Interface (PCI-2503).

As shown in Figure 1, 2, and 8, the automatic injection of an accurate volume of the sample gas can be carried out by using the so-called 6-way valve. Two positions can be set with regard to the connecting manner for the 6 gas lines (SUS pipe with an outer diameter of 2 mm). Two are connected to the sample gas flow line, two for the sample gas storing loop (SUS; ca. 1.8 m x 1 mm I.D.; 2 mm for O.D.), and two for the GC analysis line (I.D. = Inner Diameter; O.D. = Outer Diameter). The 6-way valve is supplied from Gasukuro Kogyo Co. Ltd. (model AU-SF-6). The switching should be made by applying 100 V (AC) with a short time (within a second). There are two ports for applying 100 V (AC) so that the port position can be switched back and forth. Be careful not to supply the current for a longer time so as not to burn out the solenoid coil with heat (KS broke it right after he received the first one in 1993, and it cost some amount of money to renew the coils). Some additional electrical-circuit chips should be added to the circuit of this 100-V supplier but was not so difficult to treat with (it was just to follow the suggestions given by the company supplied the 6-way valve). During the waiting time, the sampling loop is connected to the vent from the gas above the photolysis solution and is connected to the GC analysis line during the analysis stage, which last about 3.5 min. Typically, the flow rate for the bubbling of a photolysis solution was set as 10 ml/min. This was classically tuned up by use of a needle valve using the soap membrane flow meter until 5 years ago, but is now more accurately controlled by use of a mass flow controller supplied from STEC (E40MK3 + PAC-D2). The STEC E40MK3/PAC-D2 apparatus has a well-controlled constant flow rate (10.00 ml/min), and is supplied for the use only for a single type of gas (e.g., Ar) (if you want

to have the mass flow controller for N_2, you should request it to the company). When you start using this system, it is preferable that you check the flow rate using the the soap membrane flow meter, for it might have a wrong value in its flow rate. The pressure of the gas input port for the mass flow controller must be set at 0.2 MPa (2 atm, or 2 kgf/cm^2). If this pressure is too low, the flow rate may lose the accuracy or the fluctuation may arise. The SUS tube for the Ar carrier for the sampling line is then reduced into a thinner tube having an outer dimeter of 1/16 inch (0.8 mm I.D.). As shown in some photos below, this sampling flow line is then connected to a teflon tube (2.0 mm O.D. x 0.5 mm I.D.; ca.1.8 m in length until it reaches the photolysis solution). The connection between the stainless steel tube from the mass flow controller and the teflon tube can be fit using a piece of silicon tube having an I.D. of 1.0 mm (3.0 mm O.D.). The silicon tube fitting is used here because of its rubber like material character, and therefore it can fit slightly a larger size of tubes owing to its appropriate flexibility. In this case, 1.6-2.0 mm of tubes are fit into a silicon tube having an inner diameter of 1.0 mm, where the length of the silicon tube is ca. 2 cm.

As for the photolysis vessel, we previously developed drum-shaped photolysis cells equipped with a glass tube (14 mm O.D.) and a transparent glass joint (greaseless type). However, they were an order-made and a bit expensive cells and there was a difficulty in washing inside the vessels. In some cases, metals (such as Pt black) deposited over the surface inside the cell had to be dissolved by pouring aqua resia or a $K_2Cr_2O_7/H_2SO_4$ solution and the cells had to be left overnight. It was so time consuming and, in a sense, waste of energy (including the cost for running such experiments). From such reasons,

we decided, in 2003, not to use such cells and to use very common glass vials having an inner volume of ca. 20 ml. The first equipment was designed and developed with Mr. Osada (Undergrad, Tokyo University of Science, 2003). Dr. Ozawa (Grad. Studnt; now PD in Koji Tanaka's group, IMS) also helped designing the new system at that time. For this purpose, we selected screw vials from Maruemu Co. Ltd. (screw vials, model No. 5 (code: 010107), http://www.maruemu.com/pdf/cord01/01.pdf). The cap is made of P.P. (polypropylene, which is harder than P.E.). The inner packing must be just taken away. A large circular hole (I.D. ???? mm) was made by drilling to fit a teflon-made flow connection unit as shown in Figure 10. A Viton packing is used to tightly fit the teflon unit to the glass vial. The teflon-made option was originally designed to accommodate two screw-type attachment units. The brown tubes (called PEEK tubes) in Figure 10 are those used in the standard HPLC instruments, and thereby the screw type also follows the type available for use in HPCL. The connection of the teflon and the PEEK tube is again achieved using the same silicon tube described above. Inside the photolysis cell, a short teflon tube is again connected using a piece of silicon tube to the port where the Ar sampling gas is introduced into the cell. This is to bubble the photolysis solution, and to be able to renew the tube to eliminate the factor arising from the small amount of contaminants adsorbed on the surface of the tube because of the previous experiments. The use of such cheap vial enables us to be able to frequently renew the vial to eliminate again the factors, e.g., arising from the metal or solid samples deposited over the surface of the glassware. Inside the vial, a teflon covered magnetic stirrer chip (1 cm in length) is added and the solution is always stirred at a constant rate.

It is preferable that the vial is immersed in a water bath thermostatted at 20 ℃. The major purpose is to control the reaction temperature. Another purpose is to eliminate the IR radiation. It is also convenient if you have some appropriate ports for locating band path filters or neutral density filters (5 x 5 cm^2 in size) to control the type of lights you use in the photoirradiation. However, it is also preferable that these filters are soaked in the same water bath, since they will gradually degrade if they are just used without cooling. Since the photoirradiation will be done by use of a relatively high power light source (300 – 350 W Xe in our cases), anything can be degraded if it is continuously irradiated without any cooling facility.

As for the use of a Xe short arc lamp, the use of an ozoneless type of lamp is highly recommended, since no ventilator is required to set up your lamp (e.g., Ushio UXL-500D-O, see http://www.ushio.com/products/scientificmedical/xenonshortarc-uxl.htm, where the last –O corresponds to the lamp which does not emit ozone gas when it is operated). Ozone is generated by the illumination of strong ultraviolet lights to air, so the ozoneless type means that the ultraviolet lights are considerably eliminated in the "–O" type of lamps. We use a power supplier for a Ushio 500 W Xe lamp system but usually operate it at a current of 17.5 A at 20 V, providing a power of 350 W (the 500 W Xe lamp can be operated at 500 W by applying a current of 25 A at 20 V). The hand-made lamp house used in our group was developed in 1991 when KS moved from Waseda University to Seikei University as a research associate in the group of Prof. Taro Tsubomura. He kindly gave us the instruction to develop such a hand-made housing for the Xe lamp. We only bought a power supplier and a Xe lamp, together with

some parts (fan, brass boards, mirror, lens, xy stage, z rod stage, etc.). The the brass boards for the main body of the lamp house was processed at a small company, which was owned by the father of a student who was involved in this research activity as an undergrad. student (Mr. Yamada). It is amazing because it is still good enough for our use in our research.

Finally, KS would like to give some important message, which he thinks to be very important for carrying out the gas analysis. Although we cannot directly see the gases with our naked eyes, researchers can gain some important skills in handling them in experiments. If one does not suffer from the leak of air coming into the sample flask or vial, one must have an improved sense of technique in working with such gas analysis. Even if the flask is opened, it will not suffer from the leak of air from the outside while the pressure inside is higher than that outside. If a balloon connected to a flask is large enough to keep the pressure inside higher than that in the outside, air has little chances to get into the flask. It is just based on a very simple law. However, an operator who does not have a sufficient skill will suffer a lot with contamination of the flask with air. Think about an experiment in which one attempts to do the reduction of water into molecular hydrogen. If one is not aware of the leak of air, reduction of molecular oxygen rather than the reduction of water may preferentially occur merely because the operator has poor skill in avoiding the introduction of molecular oxygen into the reaction vessel. If this is the case, the operator will lose the reality.

In the following slides, some experimental procedures are summarized together with the photographs of the experimental setups in our group. That's all for this occasion. In the future, we will try adding some instructions about the programming in Delphi.   KS

Photolysis Experiments.

Photochemical hydrogen production from water was analyzed by using an automatic H_2 monitoring system developed in our group. In this system, continuous flow of Ar (10.0 ml/min, controlled by a STEC SEC-E40/PAC-D2 digital mass flow controller) was bubbled through a photolysis solution (10 ml) containing contained in a Pyrex vial (ca. 20 ml). The vent gas from the vial was introduced into a 6-way valve which allowed the automatic injection of the sample gas onto a gas chromatograph (Shimadzu GC-14A equipped with a Molecular Sieve 5A column of 2 m x 3 mm I.D., and thermostated at 30 ºC). The injection of the sample gas and the output signal from the thermal conductivity detector of the gas chromatograph were both controlled by the a control software operating on a Windows system. Photolysis solutions were stirred continuously and irradiated after deaerateding with Ar for at least 30 min prior to the photolysis. The standard gas (500 ppm H_2 / Ar) used was purchased from Tomoe Shokai. The photoirradiation was carried out by an Ushio xenon short arc lamp UXL500D-O (operated at 350 W). Photolysis vial was immersed in a water bath thermostated at 20 ºC to remove IR radiation and to eliminate the temperature effect., where the optical path between the photolysis solution and the Xe lamp were always given by either water or Pyrex glass. In order to illuminate visible-light, usingIn some experiments, an UV cut-off filter (HOYA L39 filter; transmittance at 390 nm is 50 %) was used to examine the effect of UV irradiation.
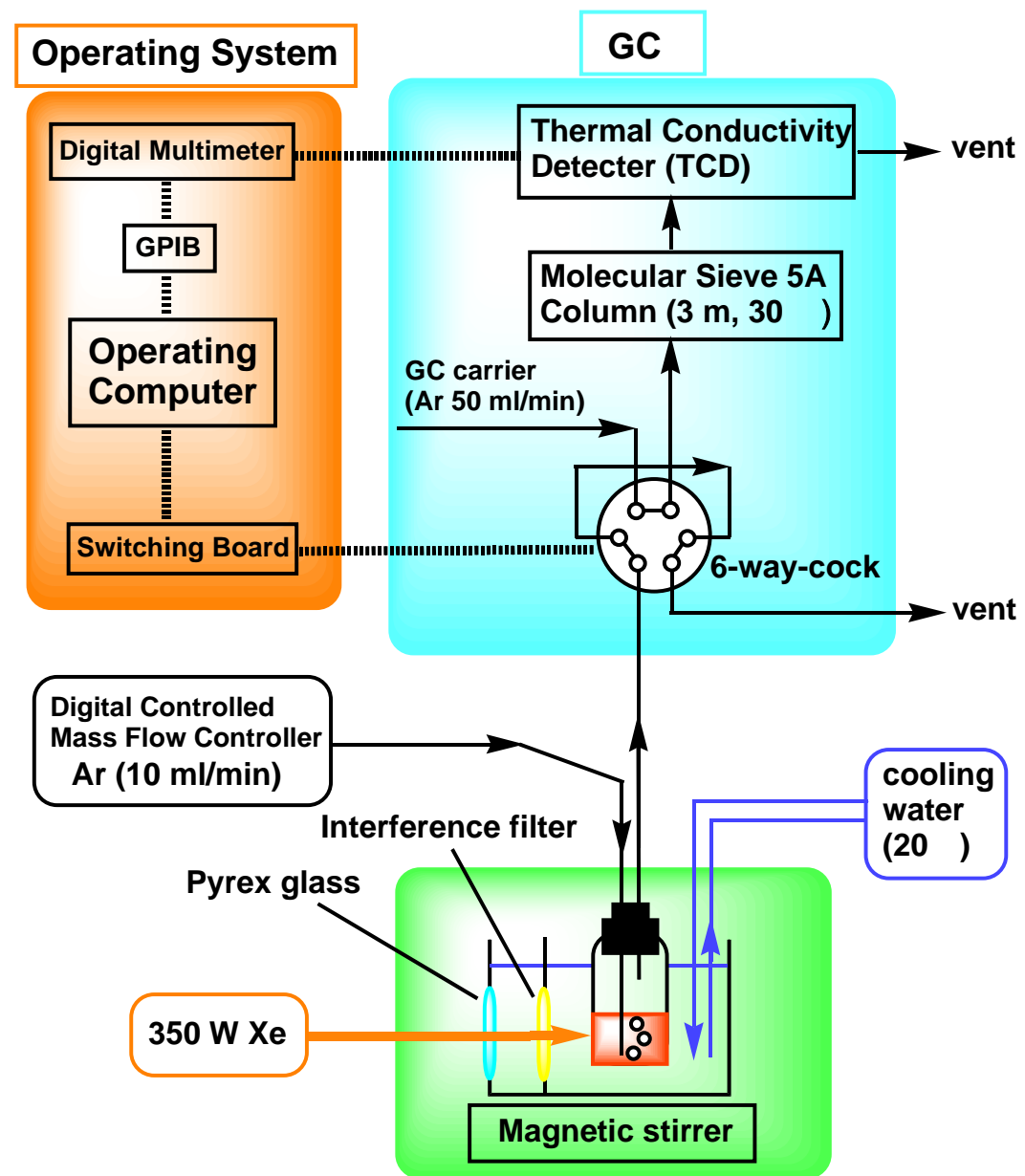
Operating System

Digital Multimeter

GPIB

Operating Computer

Switching Board

GC

Thermal Conductivity Detecter (TCD) → vent

Molecular Sieve 5A Column (3 m, 30　)

GC carrier (Ar 50 ml/min)

6-way-cock

→ vent

Digital Controlled Mass Flow Controller Ar (10 ml/min)

Interference filter

Pyrex glass

350 W Xe

cooling water (20　)

Magnetic stirrer

Figure 1.

The analysis lines used in our automatic hydrogen measurement apparatus.
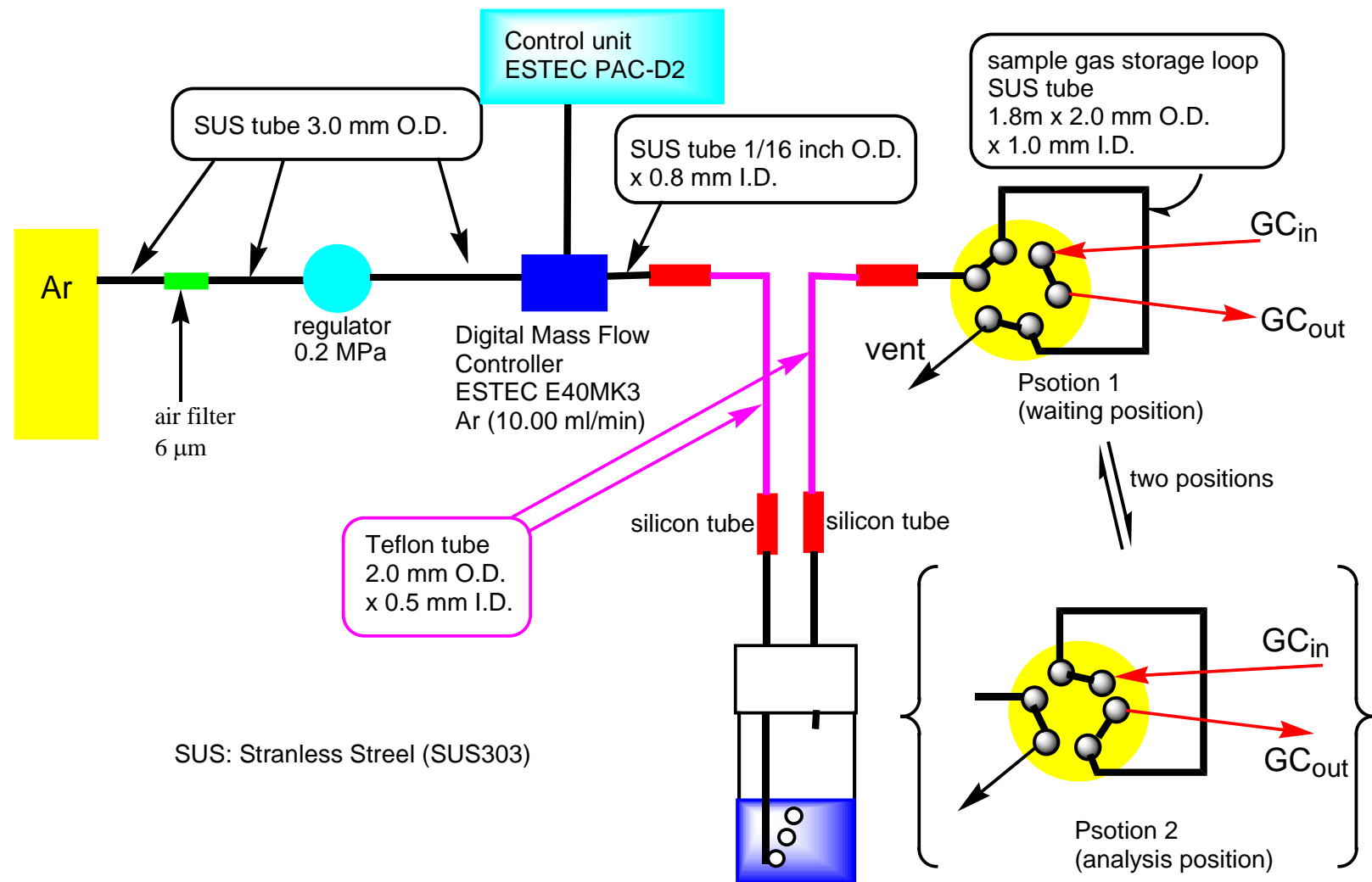
Figure 2. Types and names for the equipments used in our continuous flow measurement lines. The two positions used to switch the measurement lines are also shown.
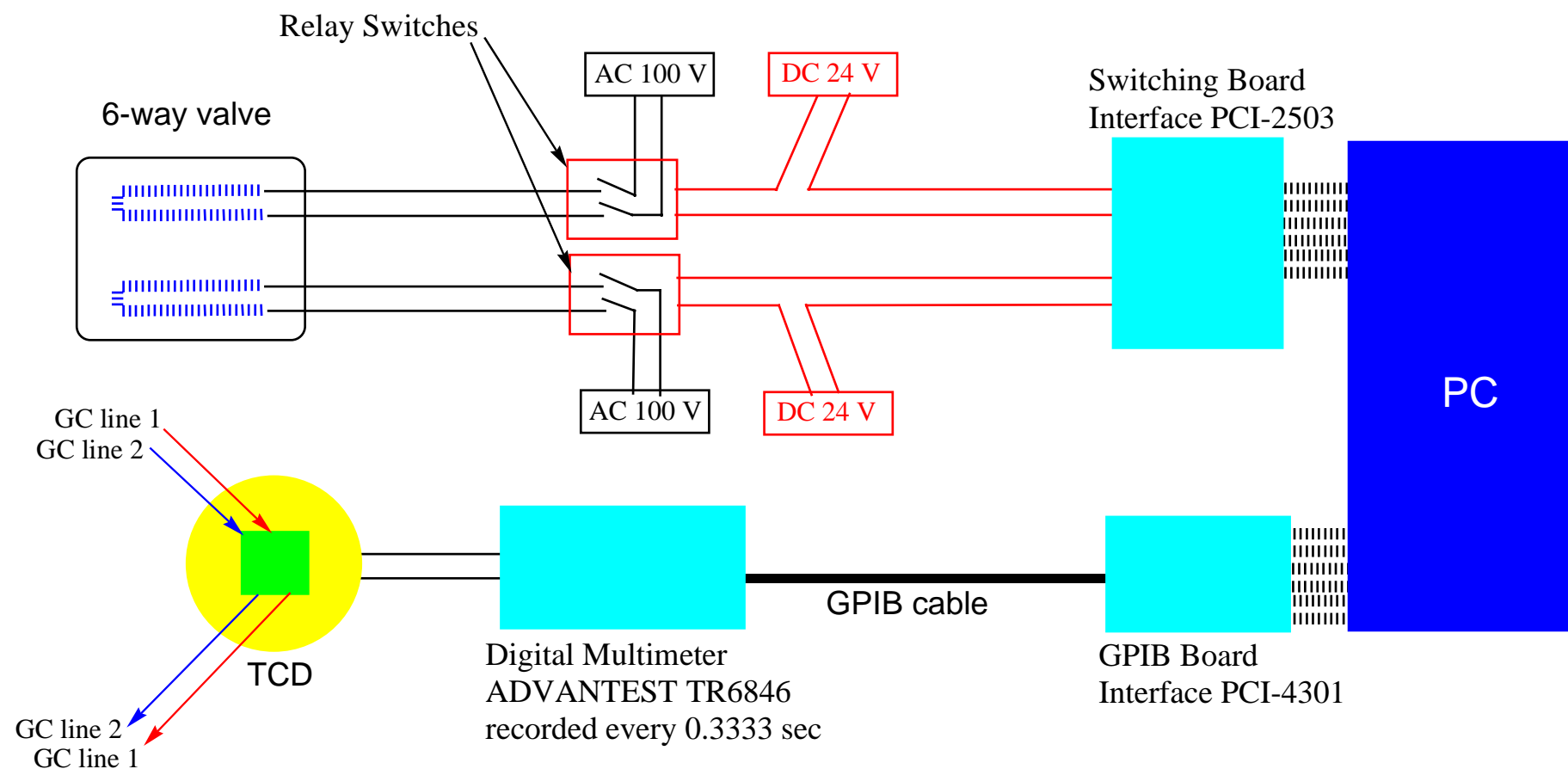
Figure 3. The detailed switching circuits and the connections around the PC, interface boards, switching relays, 6-way valves equipped with solenoid coils, TCD output, etc., are illustrated. Some condensers or diodes should be added to the parts where 100 V (AC) is applied to each solenoid coils for the 6-way valves.

Standard gas made up of (Ar base, 500 ppm H_2, 2000 ppm O_2).

Ar tank

Figure 4.
The right tank is used for the GC line (50 ml/min) together with the sampling line introduced at a flow rate of 10 ml/min for the photolysis solution. The tank is also used for the substitution task for the syringe. It is preferable that the air filter removing dusts is inserted into these lines right after their output ports from the tanks, since the stop valves will suffer from the stack of dusts to have trouble with leaks through the valves.

Figure 5.
An electrical power supplier for the 300-500 W Xe lamp. Be careful when you start up the Xe lamp, since an extremely high voltage will be generated when it is started. With this high voltage, a very strong shot noise generated will affect the computer system located near the starter to freeze the PC system. So, you have to be careful not to locate your PC close to the Xe lamp set. The variable switch at the left bottom of the front panel should be tuned up using a minus driver to set the current applied.
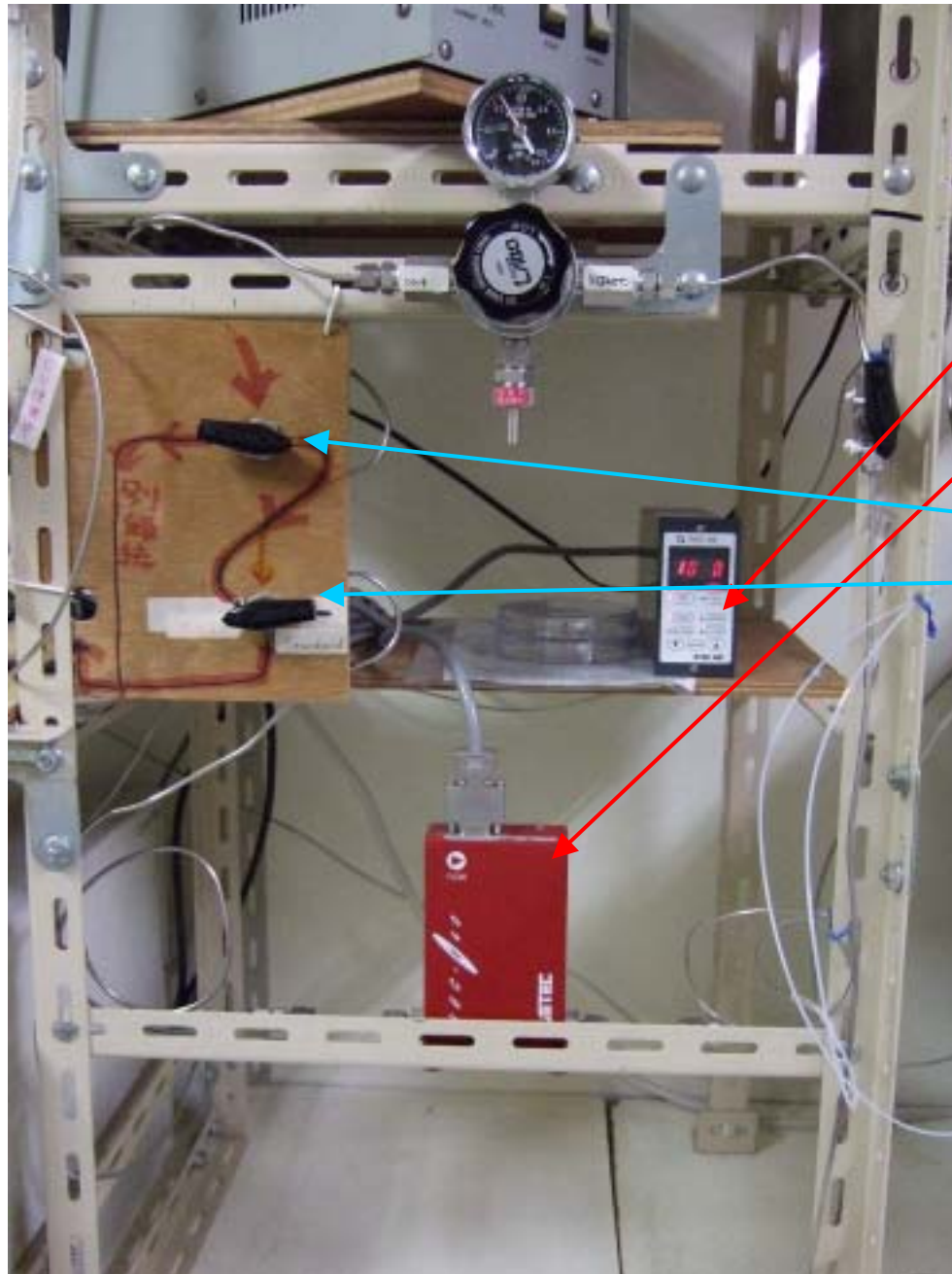
Control unit
Estec PAC-D2

Digital Controlled
Mass Flow Controller
ESTEC E40MK3
Ar (10.00 ml/min).

Three-way valve for
selecting the line.

Figure 6.
There are two three-way cocks on the wooden panel. These are used to select the line for introducing into the mass flow controller, and also to select the pure Ar line for the use in the manual method (for substitution of a syringe).
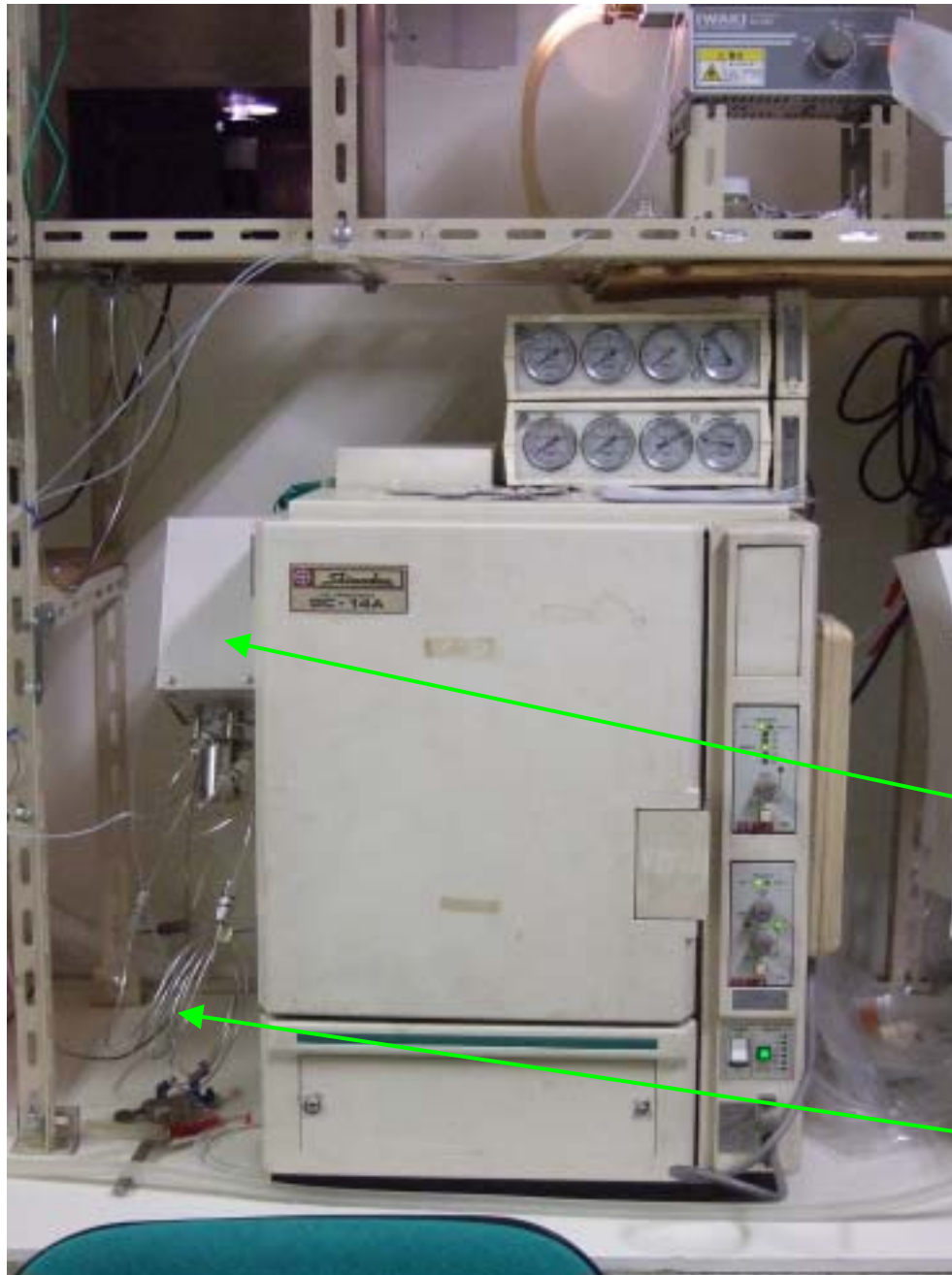
Figure 7.
Shimadzu GC-14A, equipped with a Molecular Sieve 5A column (2.0 m x 3 mm I.D. (4 mm O.D.), which is further equipped with a guard column (0.5 m x 3 mm I.D.; 4 mm O.D.; Molecular Sieve 5A). The instrument is operated under the conditions as follows: column oven 30 ºC, injection port 80 ºC, detector port 80 ºC, flow rate of the Ar carrier 50 ml/min.

A 6-way value which can e switched by applying 100 V (AC) at two ports: GL Science Inc. AU-SF-6.

Gas loop for the temporatl storage of the sampling gas all the time when the instrument is in the ready position.
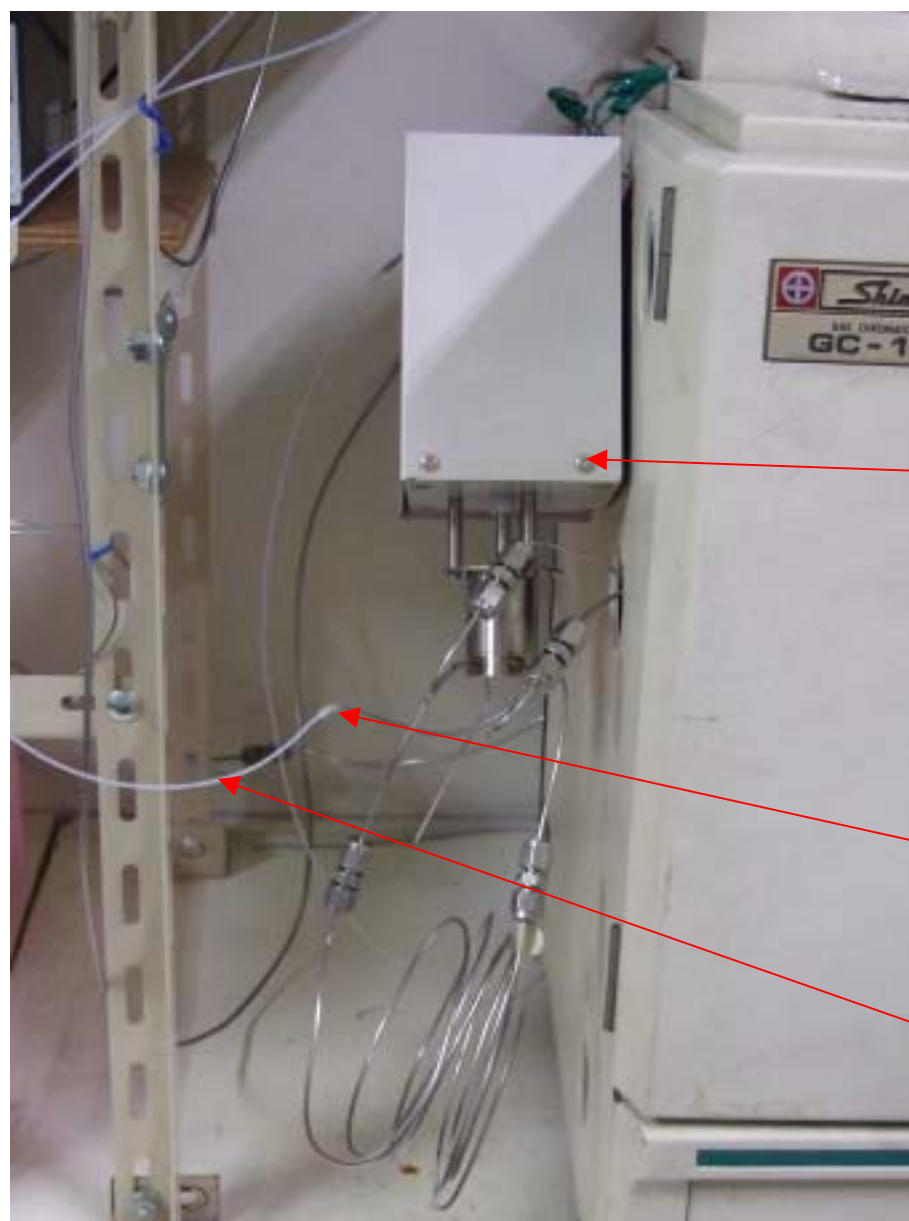
Figure 8.
A 6-way value which can e switched by applying 100 V (AC) at two ports: GL Science Inc. AU-SF-6.

A silicon tube connecting a teflon tube and a stainless steel tube.
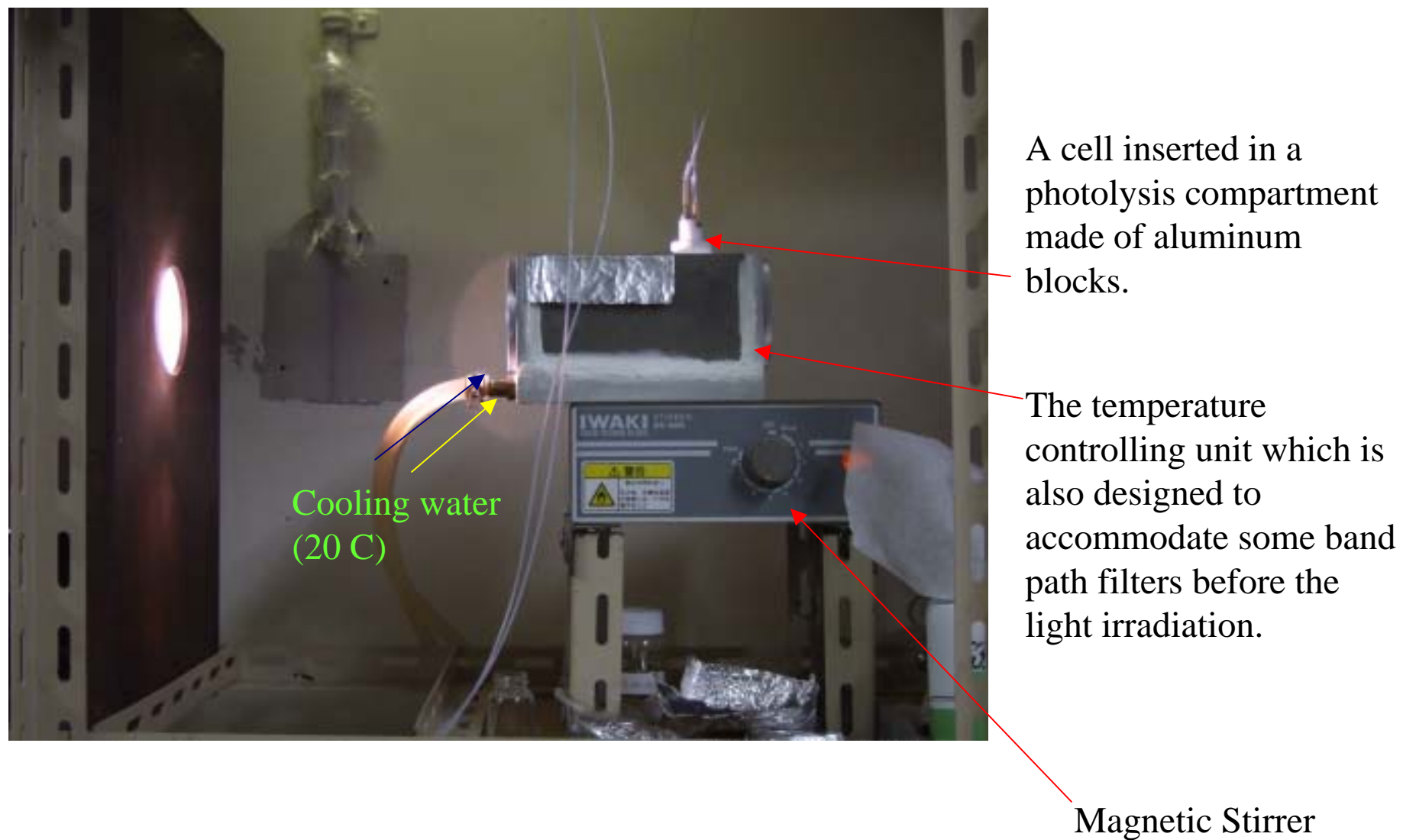
A teflon tube.

A cell inserted in a photolysis compartment made of aluminum blocks.

The temperature controlling unit which is also designed to accommodate some band path filters before the light irradiation.

Cooling water (20 C)

Magnetic Stirrer

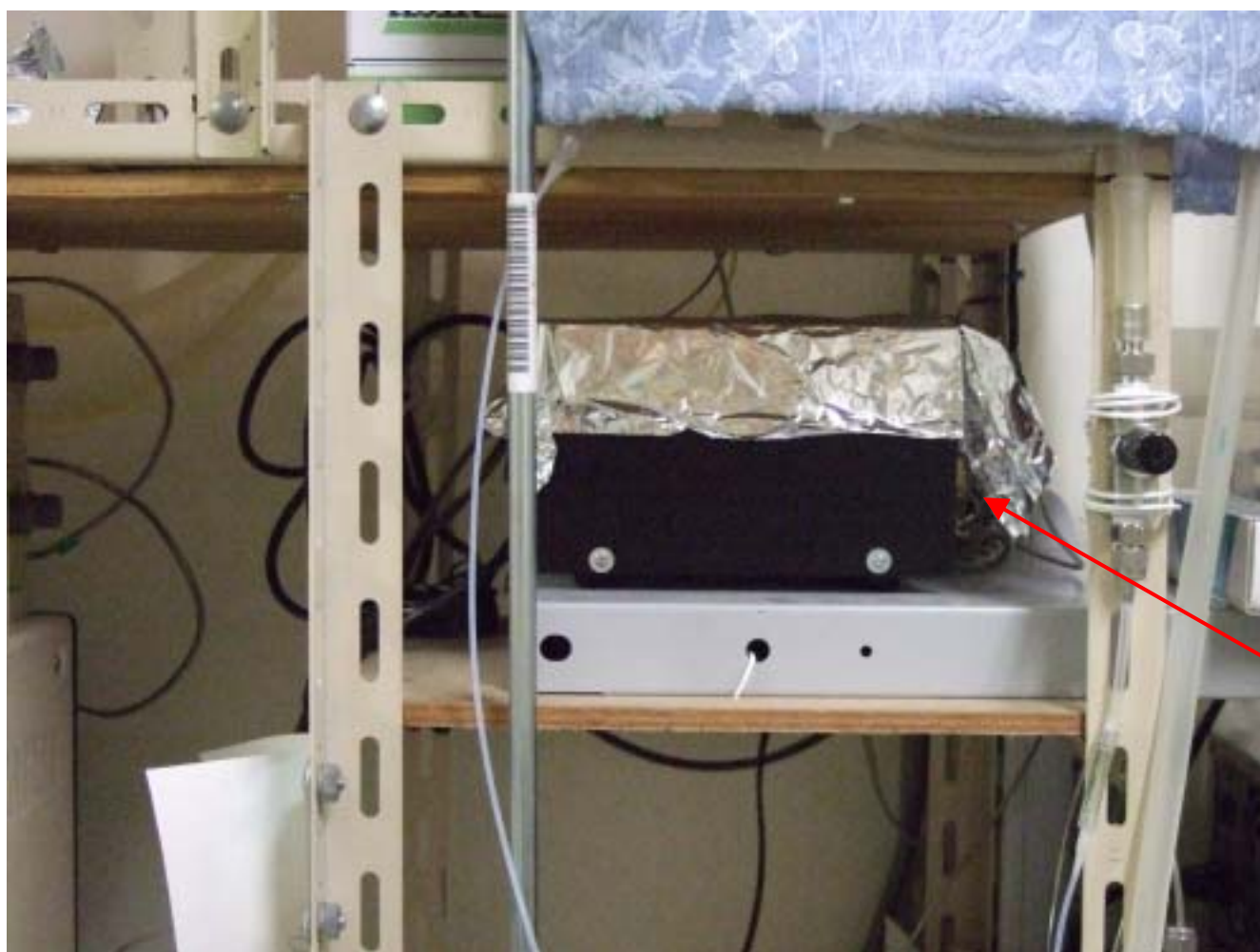**Figure 9.** A view showing the manner how the photolysis experiments are conducted.
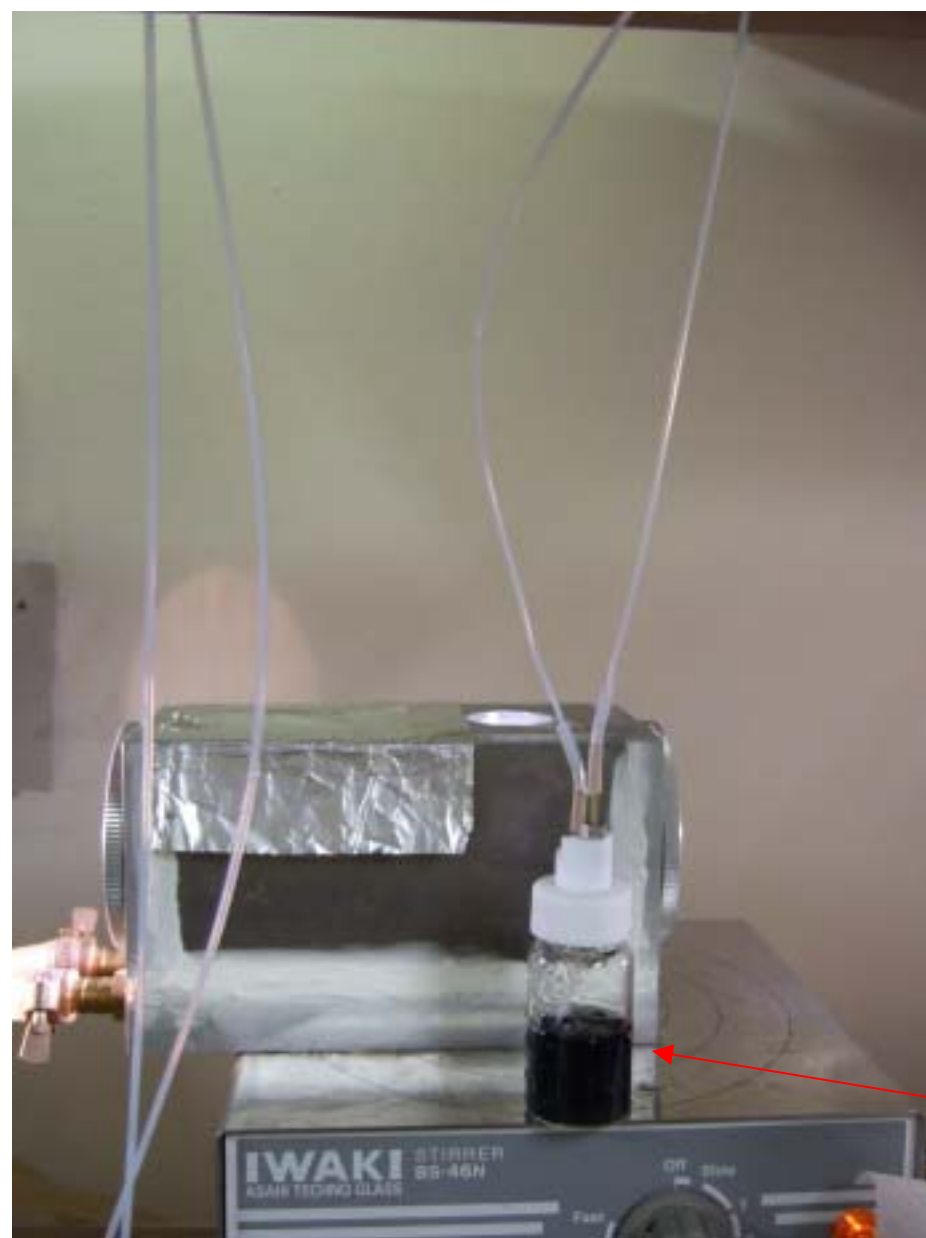
Figure 10.
The view for the cell compartment, together with the that for a photolysis vessel equipped with the teflon tube fitting parts.

Reaction solution
(10 ml)

Figure 11. Another view during the photolysis.

Figure 12. The black box contains the electrical circuits for the relays which can be switched by the PC program based on switching the board (Interface PCI 2503) installed behind the PC. The relays are switched by applying two ports of 24-V DC adaptors. The box also contains some additional electrical circuits (condensers, diodes, etc.) for they are required for the use of solenoid cock from GL Science Inc. (model AU-SF-6).

An Advantest Digital Multimeter TR6846
recorded every 0.3333 sec, controlled by the GPIB talking.

Figure 13. A controller PC operating under the Windows XP system. The program has been developed by the Delphi 5 package. Some concepts about the coding will be explained elsewhere.

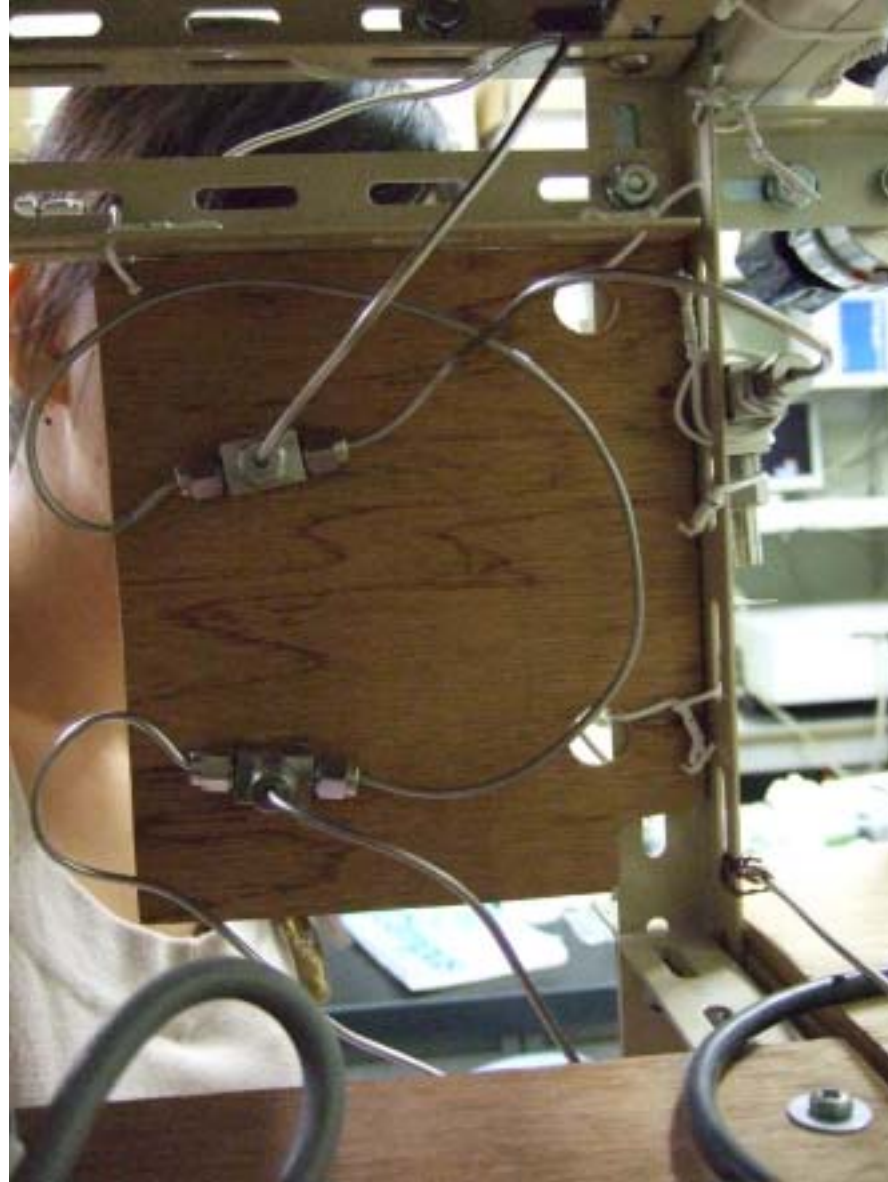**Figure 14.** The overall view for the automatic H_2 measurement system.

Figure 15.
The connections located behind the wooden board. These are to select one line for three choices: (1) Standard line for the sampling line; (2) Pure Ar line for the sampling line; (3) Pure Ar line for manual use (substitution of a syringe with Ar).

Appendix: Measurements using a sealed vial, with a manual injection procedures using a gas tight syringe (0.10 ml of injection in measurement).

When the amount of hydrogen gas is relatively small, the continuous bubbling method is not applicable due to the fact that the signal levels below the detection limit. In such a case, photolysis experiments are carried out for a 10-mL solution sealed in a vial having a total volume of ca. 30 mL. Part of the gas above the solution (0.1 mL for each measurement) was manually collected by a gas-tight syringe and was injected onto a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector and a Molecular Sieve 5A column (3 mm × 2.5 m; Ar as a carrier). Each solution was bubbled with Ar for at least 30 min prior to the photolysis. The solution was sealed in a vial with Ar gas at ambient pressure. The gas above the solution was ca. 20 mL, the exact volume for which was determined prior to the measurements. The photoirradiation was carried out by a ILC Technology CERMAX LX-300 Xe lamp equipped with a CM-2 cold mirror (240 < < 550 nm), operated at 300 W. The solution was immersed in a water bath thermostated at 20 ° C to remove IR radiation and to eliminate the temperature effect. A combination of filters L39 + SV490 (380 < < 490 nm) was employed to select the wavelength region for the photolysis.3

Figure 16. A Shimadzu GC-8AIT, which is used for the manual method. It gives a slightly different response upon the change in pressure when a relatively large volume of gas was injected. In case of GC-14A used in the automatic measurement system, a large shift is given with regard to the base line so that the calibration of the peak area has some difficulties in the case of our previous GC-14A system. We are now planning to adopt this GC for developing our new automatic hydrogen measuring system in the near future.

Figure 17. The special screw vial possesses a teflon gas collection unit, equipped with a teflon valve which can be manually opened or closed for the gas collection using a gas tight syringe. For the complete substitution of the gas inside the vial, we use a plastic bag in which the vial involving solution and a stirring chip, together with a cap equipped with the septum unit, is sealed located inside the bag, and the solution was bubble with Ar for at least 30 min, during which the gas phase inside the bag is also purged and substituted well with Ar. Finally, the cap of the vial was closed inside the sufficient flow of Ar without having the leak of air into the vial.

Figure 18. This is a standard integration apparatus supplied from Shimadzu (C-R8A). It is not only useful for the manual injection routines but also useful for the automatic measurement routines, since it can run under a Basic program, which can be used for starting or stopping the analysis by the talking through a serial port. The results of data can also be transferred from the C-R8A to the PC by the talk through the serial port. KS is now planning to adapt this integrator for the new automatic system under construction.

Figure 19. The electrical power supplier for the new Xe lamp: a ILC Technology CERMAX LX-300 Xe lamp equipped with a CM-2 cold mirror (240 < < 550 nm), operated at 300 W. This is a very good Xe lamp whose cost is also reasonable.
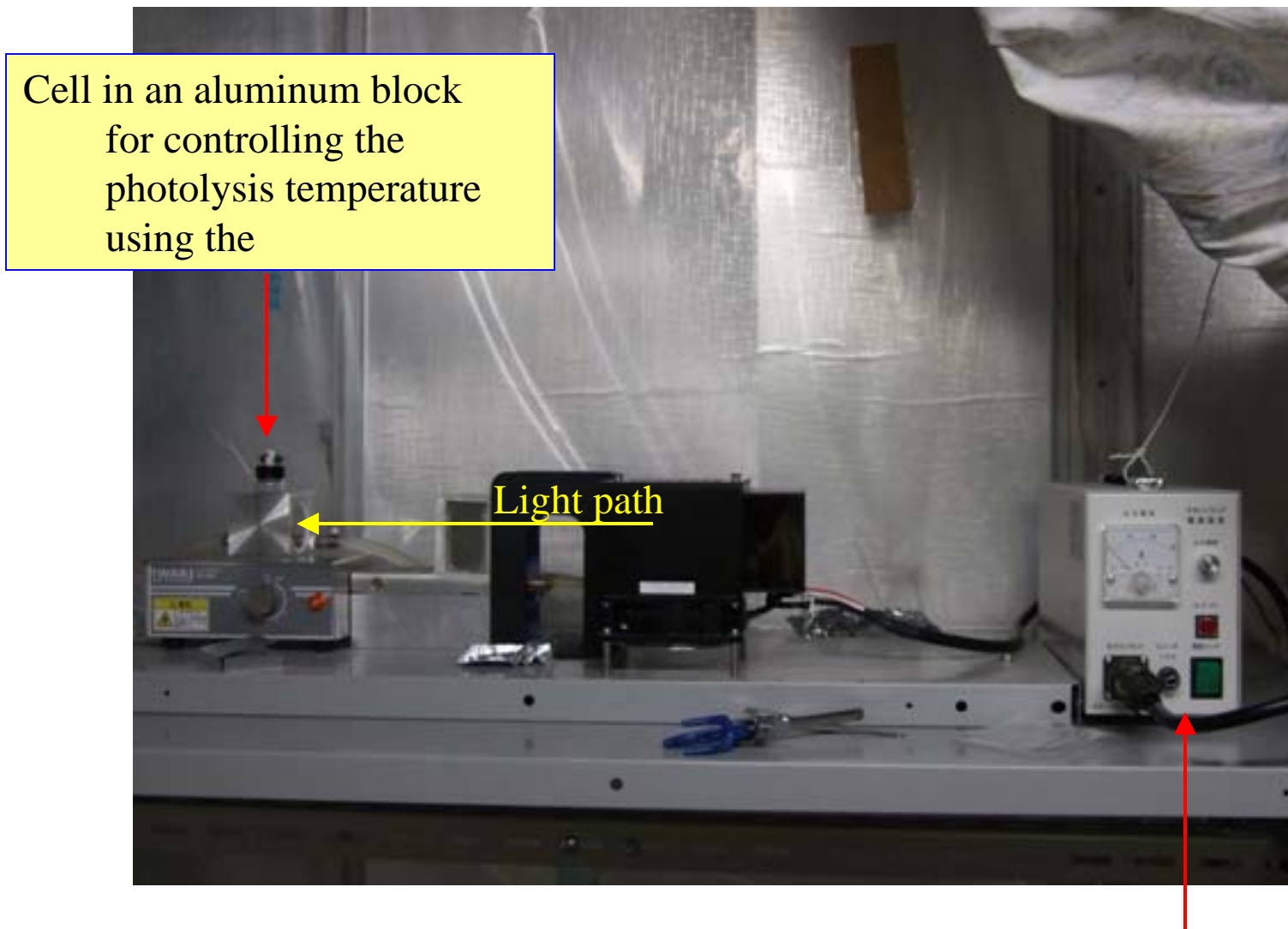
Figure 20. An overview for the setup used for the manual injection routines.

Figure 21. This shows the view for the manual injection apparatus, in which the Xe lamp is turned on and the measurement is under way as shown above.

Figure 22. A view for the photolysis cell inserted into an aluminum block sample holder.