CHAPTER 2

MATERIALS, INSTRUMENTATION AND EXPERIMENTAL TECHNIQUES

This chapter deals with various materials, instruments and experimental techniques used to measure natural radioactivity in air, water and soil in the studied area. For the measurement of radon/thoron and their progeny concentration in air, single entry pinhole dosimeter, direct radon/thoron progeny sensors (DRPS/DTPS) (for passive measurement) and Smart RnDuo (for active measurement) has been used. For the measurement of radon/thoron exhalation rates in soil and radon concentration in water Smart RnDuo developed by BARC, Mumbai, India and for the estimation of uranium in water LED Fluorimeter has been used. The detailed explanation about these equipment/ materials has been given below.

2.1 SINGLE ENTRY PINHOLE DOSIMETER

For assessment of radon/thoron gases in the indoor environment of dwellings, a single entry pinhole dosimeter has been deployed which is based on the radon/ thoron discrimination technique (Figure 2.1).

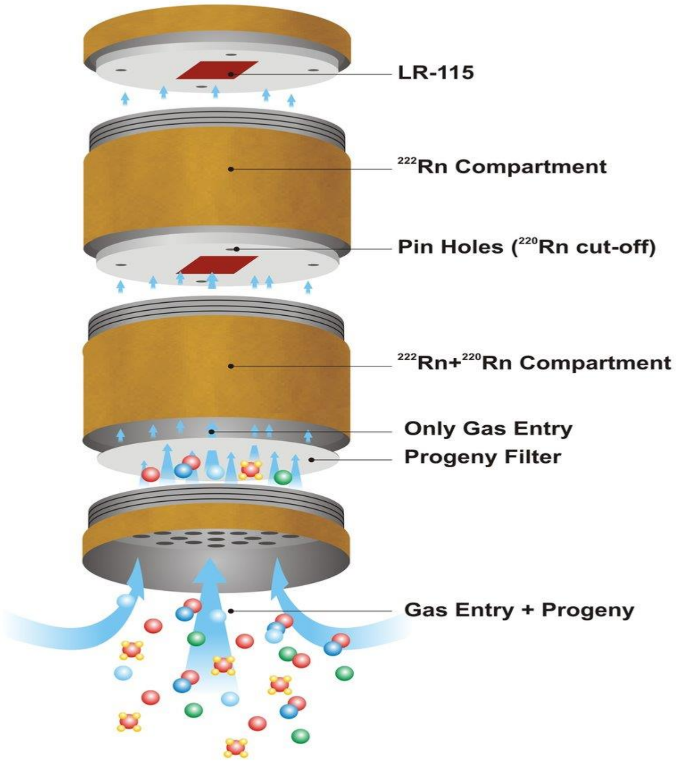

Figure 2.1: Single entry pinhole dosimeter

The dosimeter system is divided into two compartments by a central pin-hole disc made of High-Density Polyethylene (HDPE) material that acts as a thoron discriminator and has 4 pinholes with the radius of each hole is 0.5 mm (Sahoo et al., 2013). This device consists of two identical chambers of length of 4.1 cm and a radius of 3.1 cm (same dimensions as in the twin cup dosimeter developed by Eappen and Mayya, 2004). The first compartment “radon + thoron chamber”, takes a sample of ambient air, which is then filtered to remove particles (Sapra et al., 2016). Both chambers are internally coated with metallic powder (nickel) to have neutral electric field inside the chamber volume, so that the deposition of progenies from gases will be uniform throughout the volume. The minimum detection limit for radon is 4 Bqm^{-3} and for thoron is 6 Bqm^{-3}, considering 4 tracks.cm^{-2} as background tracks in LR-115 (Sahoo et al., 2013).

The instrument has been calibrated at Bhabha Atomic Research Centre, Mumbai following standard protocol. The calibration factor is basically converts the observed track densities to the activity concentration of radon and thoron in the dwellings. If T is the background corrected track density observed on LR-115 type-II films due to exposure in a given mode to a concentration C of a given species for a time t, then:

T = k.C.t

Where, C is the concentration in Bqm^{-3}

k is the calibration factor (tr.cm^{-2}d^{-1}/Bqm^{-3}))

t is the time in days

T is the track density in tracks cm^{-2}

The calibration factors for radon and thoron for the single entry pinhole dosimeter may be obtained using following equation (Sahoo et al., 2013):

$$K_{R,1} = \frac{T_{R,1}-B}{tC_R} \quad (1)$$

$$K_{R,2} = \frac{T_{R,2}-B}{tC_R} \quad (2)$$

$$K_{T,1} = \frac{T_{T,1}-B}{tC_T} \quad (3)$$

$$K_{T,2} = \frac{T_{T,2}-B}{tC_T} \quad (4)$$

where $k_{R,1}$, $k_{R,2}$, $k_{T,1}$, $k_{T,2}$ are the calibration factors (tr.cm^{-2}d^{-1}(Bqm^{-3})) of radon and thoron in 'radon + thoron' and 'radon' chamber respectively,

$T_{R,1}$, $T_{R,2}$, $T_{T,1}$, $T_{T,2}$ are the total track densities (tr.cm^{-2}) in LR-115 detectors for 'radon + thoron' and 'radon' chambers for radon and thoron exposure respectively.

B is the background track density in unexposed LR-115 detector measured as 4±2 tr.cm^{-2}.

C_R and C_T are the average concentrations (Bqm^{-3}) of radon and thoron at the entry face respectively, and t is the exposure period.

The gas enters into the ‘radon + thoron chamber’ through a glass fibre filter paper which is placed at the entry face. The air from this compartment, which contains both radon and thoron, diffuses to the second compartment "radon chamber" through pinholes that act as diffusion barriers, preventing thoron from entering this chamber due to shorter half life (55.6 s) in comparison to radon (3.82 days). Therefore, only radon gas reaches the second compartment. LR-115 Type-II films (manufactured by Kodak Pathe, France) of size 3×3 cm^2, placed in first and second compartment registered tracks formed due to alpha particles produced from the decay of radon and thoron respectively (Eppan et al., 2007).

2.2 DIRECT RADON/THORON PROGENY SENSORS (DRPS/DTPS)

Direct progeny measurement by passive energy discrimination techniques employing suitable absorbers began by Fleischer (1984) and manifested by Nikezic and Baixeras (1996) and Da Saliva and Yoshimura (2005). For the measurement of progenies of radon and thoron, deposition-based progeny sensors (DRPS/DTPS) have been used (Figure 2.2). These progeny sensors work on the principle that the LR-115 Type-II detector having a detection limit of 3 - 4 MeV (Ceser and Geraldo, 1981) mounted with absorbers (aluminized mylar) of appropriate thickness to detects the alpha particles having different energies emitted from the deposited progeny atoms (Mishra and Mayya, 2008). The minimum detection limit of DTPS is 0.1 Bqm^{-3} and for DRPS detection limit is 1 Bqm^{-3}.

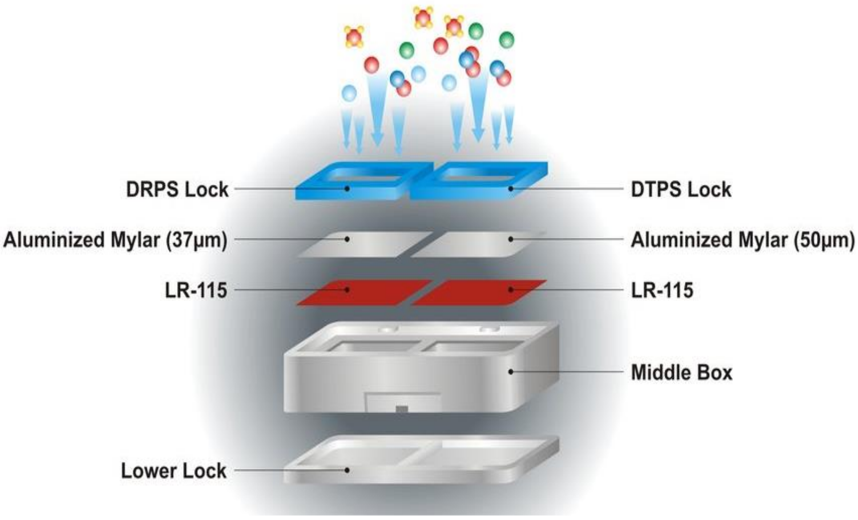

Figure 2.2: Deposition based radon/thoron progeny sensors (DRPS/DTPS)

DTPS has LR-115 Type-II films (2.5×2.5 cm^2) mounted with 50 μm aluminized mylar as an absorber to selectively detects only 8.78 MeV alpha particles which are emitted from Po-212 (progeny of thoron). While detecting predominantly 7.69 MeV alpha particles released from Po-214 (radon progeny), DRPS is used using a combination of 25 μm aluminized mylar and 12 μm cellulose nitrate with an effective thickness of 37 μm as an absorber (Mishra and Mayya, 2009). The advantage of this sensor is that there is no interference from gas and thus it gives a direct estimation of the airborne concentration of the alpha- emitter progeny. The airborne concentrations are estimated from the deposited activity via effective deposition velocity. These sensors have been calibrated in laboratory controlled conditions and in the indoor environment. From the tracks formed on the exposed films, equilibrium equivalent progeny concentration (EERC/EETC) has been calculated.

2.3 CELLULOSE NITRATE (LR-115 TYPE-II) FILMS (SSNTD)

The field of solid state nuclear track detector (SSNTD) had been started in the year of 1958 by D.A. Young at AERE Haewell (1958). SSNTDs are insulating solids both man-madeand naturally occurring (Fleischer et al., 1975; Iyer et al., 1972). Different types of SSNTDs detectors are available which include plastics, inorganic crystals and glasses. The various plastics track detectors such as allyl diglycol carbonate (CR-39), bisphenol-A polycarbonate (Lexan, Makrofol) and cellulose nitrate (CN 85, LR-115) are available to record the tracks of only those alpha particles whose energy lie in the particular range. The SSNTDs are used in various scientific fields such as Nuclear Physics (for the measurement of uranium in soil by fission track method, search for super heavy elements), element content and their distribution, in radon/thoron dosimeter (for measuring the radon/thoron concentration) and in biological applications (for measuring the alpha activity content in blood and lead content in teeth and bones) (Bhagwat, 1993). SSNTDs are less sensitive if used for short duration and hence, in this study these have been used for long period of four months at one place.

LR-115 type-II detector also known as cellulose nitrate plastic track detector, manufactured by Kodak, France has been used for the detection and measurement of alpha radiations. The chemical formula of LR-115 type-II film is $C_6H_8O_9N_2$ (Figure 2.3). It consists of active red layer or cellulose nitrate layer having thickness 11.5 to 12.0 µm which is coated on 100 µm clear polyester base (PET). The general structure of cellulose nitrate plastic track detector (LR-115 type-II) is shown in Figure 2.3.

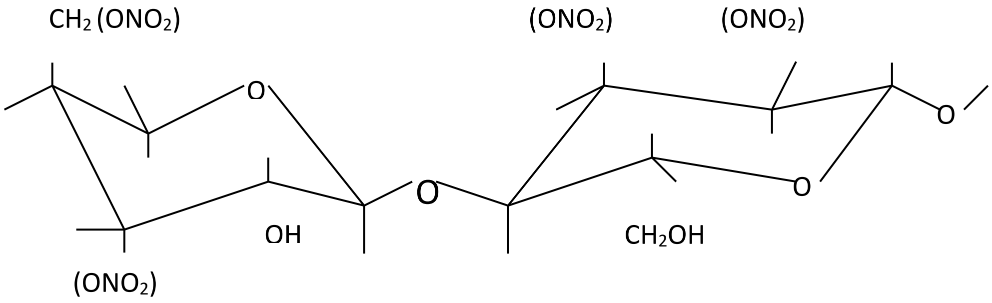

Figure 2.3: The structural formula of cellulose nitrate (LR-115) plastic track detector

LR-115 type-II solid state nuclear track detector is sensitive to only alpha particles having energy range from 1.7 to 4.8 Mev (Abu-Jarad et al., 1980; Jonsson, 1981). Therefore, it does not detect the alpha particles emitted from radon/thoron progenies because of their high energies(6.0 MeV from Po-218 and 7.68 MeV from Po-214) even more than upper threshold energy. LR-115 type-II detectors are usually unaffected by light, moderate heating, temperature and humidity (Durrani et al., 1997) and also insensitive to β, γ, X rays, infrared and ultraviolet rays. In the present study, the indoor radon/thoron and their progeny concentrations were measured using these alpha track detectors.

Fleischer and his collaborators (UNSCEAR, 1982) has explained mechanism of track formation using ion explosion spike model. According to this model, when a positive charged particle passes through the insulating detector, it stripped out the orbital electrons of the atom and leaves a narrow trail damage on the surface of this film having diameter varies from 1 µm to 15 µm. These narrow trail damages are called "latent tracks" (Figure 2.4). These tracks cannot be seen by naked eye. But after the etching of these detectors, the tracks can be counted with the help of spark counter.

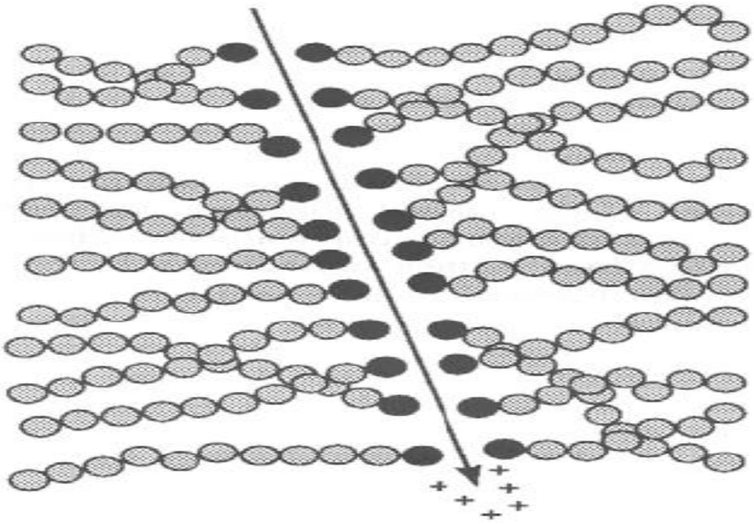

Figure 2.4: Tracks formed in polymers caused by the passage of heavily charged particles (Fleischer et al., 1975)

2.4 CONSTANT TEMPERATURE BATH UNIT FOR ETCHING

The tracks formed on the detectors known as latent tracks, were typically invisible to the naked eye. These latent tracks were enlarged/developed by chemical etching so that they could be examined under spark counter. Several chemical etchants like NaOH, KOH are used depending on the etching conditions for different detectors, particle sensitivity and the critical angle of etching.

In present study, a constant temperature bath unit (Figure 2.5) has been used to etch the retrieved LR-115 films from the dosimeters to enlarge the tracks of alpha particles. This instrument is double walled, insulated with glass wool for inner vessel. The bath tub is divided into mainly two parts: circulating pump and water tank with electrical heater. The water tank is sub-divided into three compartments for etching vessels of dimensions (16.5 cm × 5 cm × 7.5 cm) with lids. Each etching vessel supports a rod to accommodate ten SSNTD cartridges for etching, making a total of thirty LR-115 films processed simultaneously. 16 cm long brass etching rods are available. A resistive heater heats the water inside the bath to a predetermined temperature of 60°C, and then a circulating pump moves the heated water throughout the tank to ensure uniform heating. With a digital display setup and an auto-cut mechanism, a solid state time proportional controller keeps the water at the predetermined temperature.

Before the etching of retrieved films, the bulk etch rate of the etching bath was standardized using unused films. The optimum etching process removes 4 μm thick film leaving a residual detector thickness of 8 μm. The track development in LR-115 type-II films is determined by bulk etch rate (V_B). Before processing actual samples, a trial run is conducted with a small number of unused LR-115 Type-II films using NaOH (chemical etchant) at 60˚C for 90 minutes to set the bulk etch rate at 4 - 4.5 $\mu m h^{-1}$. The LR-115 films' weight is measured both before and after etching using weighing balance, and bulk etch rate (V_B) is calculated by following equation:

$$\text{Bulk etch rate } (V_B) = \frac{W_i - W_f}{A \times \rho \times t} \tag{5}$$

Where, W_i and W_f are weight of detector before and after etching respectively,
A is the area of detector,
ρ is the density of detector (1.5 gcm^{-3})
and t is the time of etching (90 minutes).

Once the bulk etch rate is stable, 2.5 N of NaOH solutions have been prepared at room temperature and exposed films were loaded in the etching bath unit using cartridges and films were etched at 60°C for 90 minutes (Eppan and Mayya, 2004). After etching the films were cleaned using distilled water for few minutes to remove etching residue from etch pits and then left to dry.

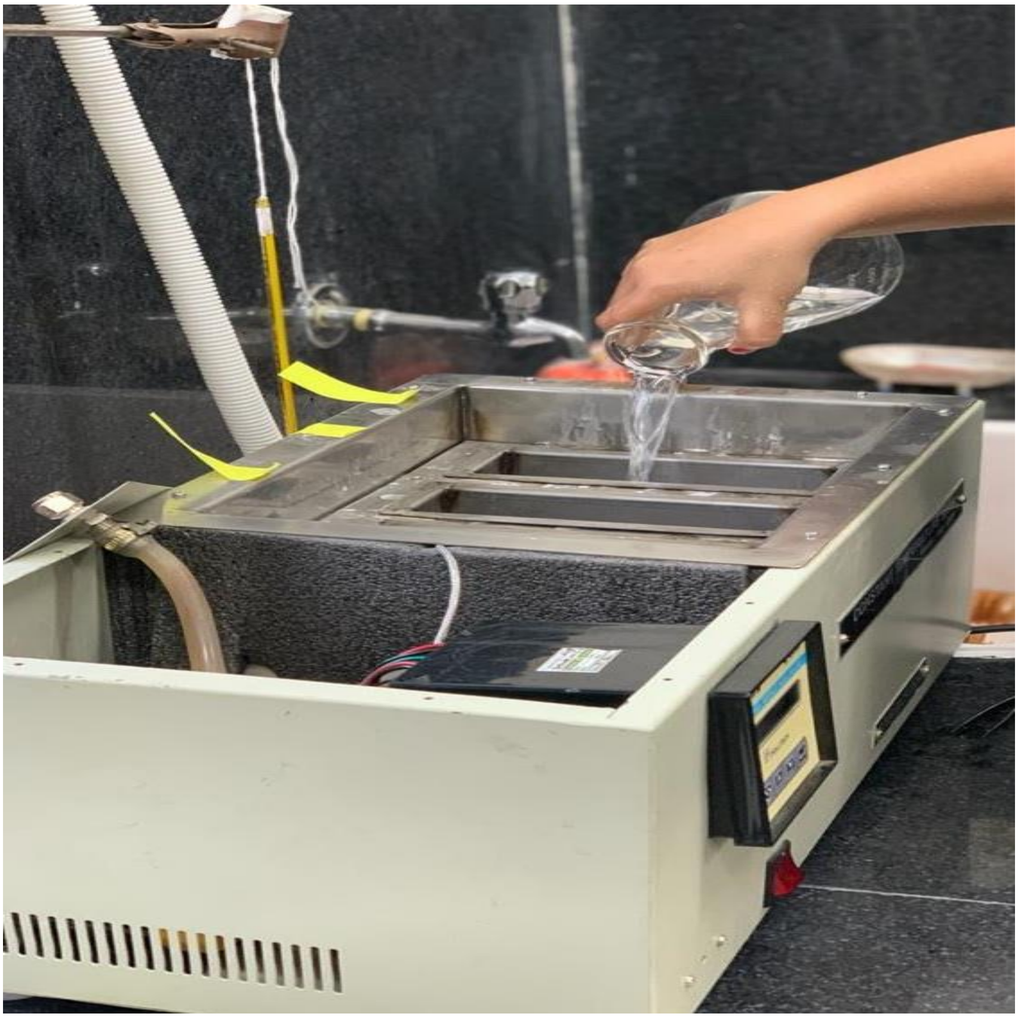

Figure 2.5: Constant temperature bath unit

(Radiation Physics Lab, Department of Physics, MRSPTU, Bathinda)

2.5 SPARK COUNTER

The etched alpha tracks on detectors were counted using a spark counter (Model PSI–SC 1) manufactured by Polltech Instruments Pvt. Ltd., Mumbai, India has been used, which is a simple, accurate and inexpensive equipment (Figure 2.6). It automatically counts the number of holes developed on the LR-115 Type-II film. Spark counter was first invented by Tommasino and Cross (1970) and has been the most successful device ever since. The spark counting technique, which is appropriate for plastic detectors, is a fast method for registering low and medium track densities. In comparison to optical counting, the efficiency of spark counter is ~95% ± 5% (Sahu et al., 2014).

Figure 2.6: Spark counter

(Radiation Physics Lab, Department of Physics, MRSPTU, Bathinda)

The spark counter is enclosure having dimensions (25cm × 20cm × 20cm) and comprises of following units: Electronics comprises of a primary micro-controller card with the necessary circuits for setting a programmable high voltage module to set the high voltage, a counting circuit to count sparks, and various interface circuits for the key and LCD module. A highly regulated device called the High Voltage Module may produce high voltage ranging from 100 to 999V. Through the keys, the voltage for counting and sparking both can be programmed. During RUN mode, the spark detector is powered by a relay with a high dielectric constant. The acrylic detector base and stainless steel counterweight are the two components of a spark detector. A fixed stainless steel disc having an area of 1 cm^2 and a spring-loaded stainless steel contact are both featured on the acrylic detector base.

To determine the ideal operating voltage for a spark counter, calibration is performed. For the same, the pre-spark voltage is set at 900V, the gate duration is set at 6s, and the count voltage is set at 300V. The metal surface of an aluminized mylar should be facing the etched LR-115 film and touching an electrode pin. The counter is operated at variable voltage in 20V steps ranging from 300 to 900V, and subsequent track counts are shown against sparking voltage. For 420 to 560V, a plateau curve is found. The central region of the plateau indicates the optimum counting voltage which means that even with a small change in the applied voltage the number of tracks counted by the counter remains constant. In our study, the operating voltage is set at 450 V and used for analysis of etched films.

A thin plastic track detector (Kodak LR-115) that has been exposed to alpha particles and etched is sandwiched between two electrodes in a spark counter to simulate a capacitor. Through holes are created in the detector following the particle paths during chemical etching. The detector is covered with aluminized mylar and placed on top of thick conductive electrode. The plastic foil's aluminized side is towards the detector. The contact between detector and electrodes is further strengthened by a relatively heavy weight on top of the foil. Figure 2.7 shows the spark counter's circuit diagram. A track-hole allows for an electrical discharge or spark to occur when a high voltage is put across the capacitor. The voltage pulse produced across a load resistor is counted electronically by the counter.

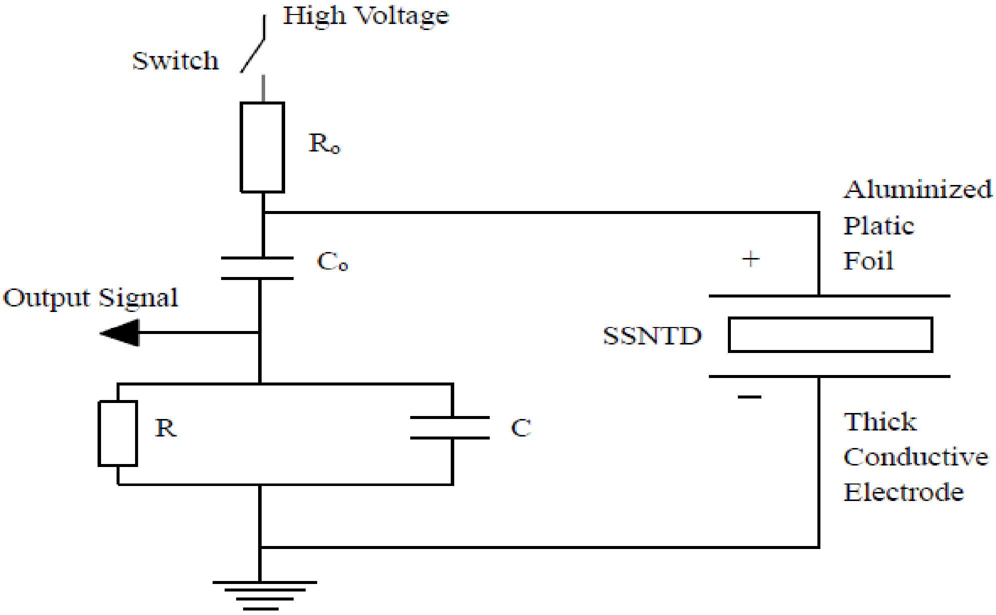

Figure 2.7: Circuit diagram of spark counter

The small layer of aluminium coating (less than 1 μm thick) is vaporized by the spark travelling through a track hole, and the spark also creates a considerably larger circular spot on the track before it is stopped by a short-circuit. The capacitor is re-charged, but due to aluminium evaporation on the electrode, a second spark cannot occur in the same track hole. Thus, until every track hole has been counted, the spark jumps arbitrarily from one to the next. The counted sparks on the exposed detector has been used for further calculations.

2.6 SMART RnDuo: A SCINTILLATION BASED DETECTOR

Smart RnDuo is a technologically advanced portable continuous radon/thoron monitor, designed for multiple applications in radon and thoron studies. In this present study, scintillation-based radon monitor, Smart RnDuo developed by Radiation Protection & Advisory Division (RP&AD) at Bhabha Atomic Research Centre (BARC), Mumbai, India has been used for the measurement of radon/thoron in air, water and soil. It is based on the principle of detection of alpha particles which strike the detector and produces scintillations with ZnS:Ag coating inside the cell. These scintillations are counted by Photo Multiplier Tube combined and converted to radon/thoron activity using inbuilt algorithm (Figure 2.8). The instrument is calibrated against standard radon-thoron sources (Model RN-1025 & TH-1025) received from Pylon Electronics Inc., Ottawa, Canada in a 0.5 m^3 calibration chamber available at Bhabha Atomic Research Centre (BARC), Mumbai, India. This calibration has arrangement of controlling the relative humidity from 10% to 99% and temperature from 20°C to 50°C (Jobbagy et al., 2017). The advantage of portable monitor is that there is no effect of humidity and traces of various gases present in samples. The instrument has radon/thoron sensitivity of 1.2 CPH$(Bqm^{-3})^{-1}$ and 0.8 CPH$(Bqm^{-3})^{-1}$, respectively with alpha detection proficiency of the scintillation cell is near about 75% (Gaware et al., 2011).

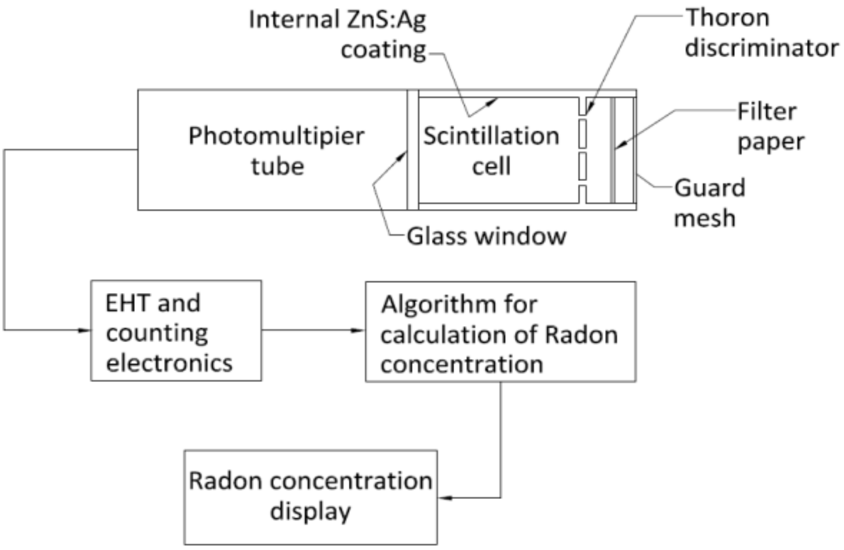

Figure 2.8: Schematic diagram of Smart RnDuo

2.6.1 Standard Protocol for Radon/Thoron Measurement

As per the procedure mentioned in the radon handbook by BARC, Mumbai (Sapra et al., 2016) for the indoor radon measurements were made in closed-building environment. The closed-building conditions were made in such a way that internal-external air exchange systems, windows, and fans were not operated at least for 12 hours before measurements so as to record the maximum build-up of radon. Positions were selected in such a way that the detector was not disturbed during the measurement period and there is adequate room for the device. Locations near excessive heat, such as stoves, and areas of high humidity were avoided. Radon gas has been sampled in RnDuo using flow mode of sampling for measurement duration of 24 hrs having cycle period of one hour. Thoron gas has been sampled in RnDuo using flow mode of sampling for measurement duration of one hour having a cycle period of 15 minutes.

2.6.2 Standard Protocol for Radon Mass Exhalation Rate in Soil

Radon mass exhalation rate is defined as activity concentration of radon per unit time from per unit mass of soil matrix and is one straight forward way for measuring the flux density of radon. Smart RnDuo is set in diffusion mode for the estimation of radon mass exhalation. Each of the soil sample was filled in accumulation chamber which is attached with detector as shown in Figure 2.9. For the measurement of radon, the gas was collected from the sample into the scintillation chamber (153 cc) which passes through a “progeny filter” and “thoron discriminator” to banish radon/thoron progeny and thoron. The “diffusion time delay” of thoron discriminator does not permit the thoron to pass into detector. Radon activity was measured from the alpha particles emitted from accumulated radon and its progeny inside the detector. As per the protocol the sample was analysed continuously for 12 hours with each cycle of 60 minutes. The build-up data was recovered from the detector for further calculations of radon mass exhalation rate of sample using standard formulae.

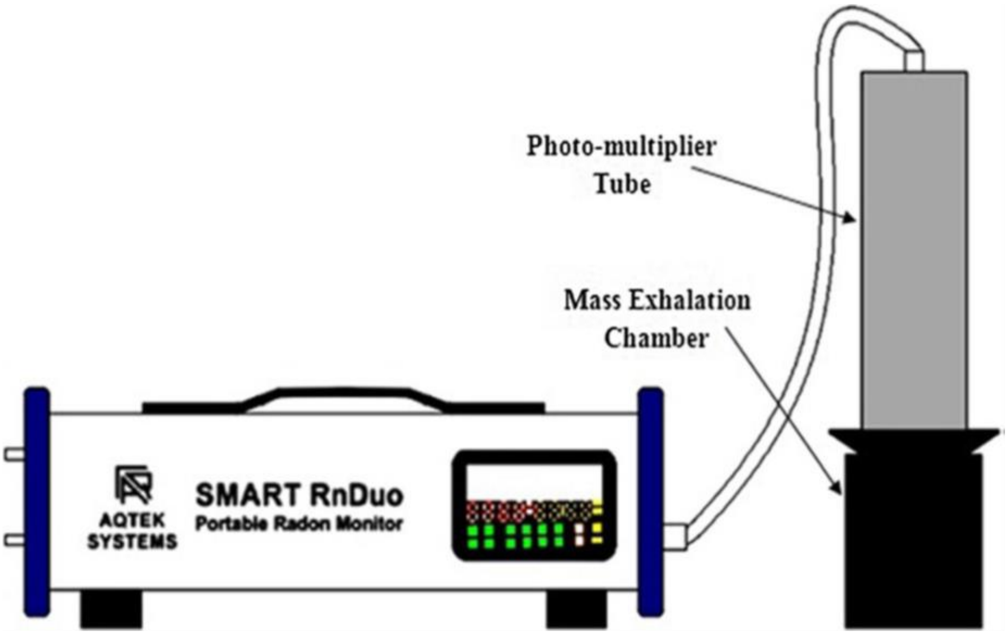

Figure 2.9: Set up for measurement of radon mass exhalation rates using Smart RnDuo (diffusion mode)

2.6.3 Standard Protocol for Thoron Surface Exhalation Rate in Soil

Due to small diffusion length of thoron in atmosphere, it is not uniformly distributed in the accumulator. Therefore, for estimation of thoron surface exhalation rate in soil samples, the detector was used in "flow mode" using inbuilt pump having flow capacity of 0.7 Lmin^{-1} (Figure 2.10). Inbuilt pump circulates the air containing thoron gas (in chamber) into lucas cell in closed loop which initially passes through a "progeny filter". Thoron activity was measured from the alpha particles emitted from accumulated thoron and its progeny inside the detector. To measure the equilibrium value of thoron concentration (C_t) in accumulation chamber, the measurement has been carried out for 1 hour with four cycles of 15 minutes each. In a 15 minute cycle of thoron mode, sampling pump is kept ON for initial 5 minutes which gives a measure of thoron and background, followed by a delay of 5 min which ensures decay of thoron and then last 5 min counting gives the measure of background counts for that cycle. The measured value of C_t has been then used to calculate the thoron surface exhalation rates.

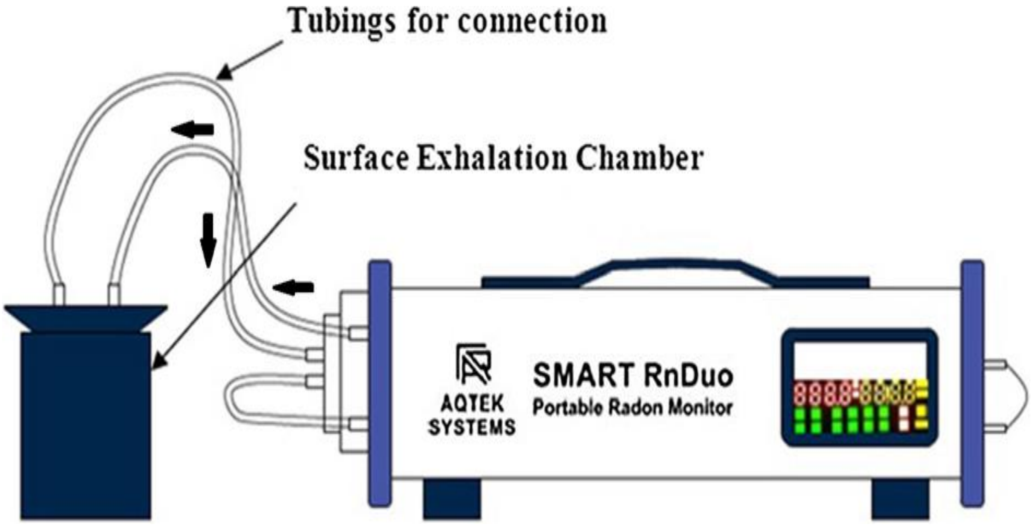

Figure 2.10: Set up for measurement of thoron surface exhalation rates using Smart RnDuo (flow mode)

2.6.4 Standard Protocol for Radon in Water

On the spot measurement has been done using Smart RnDuo for calculating the activity concentration of radon in water samples. All samples has been collected from various sources of water like canal water, handpumps, borewell, water works etc.

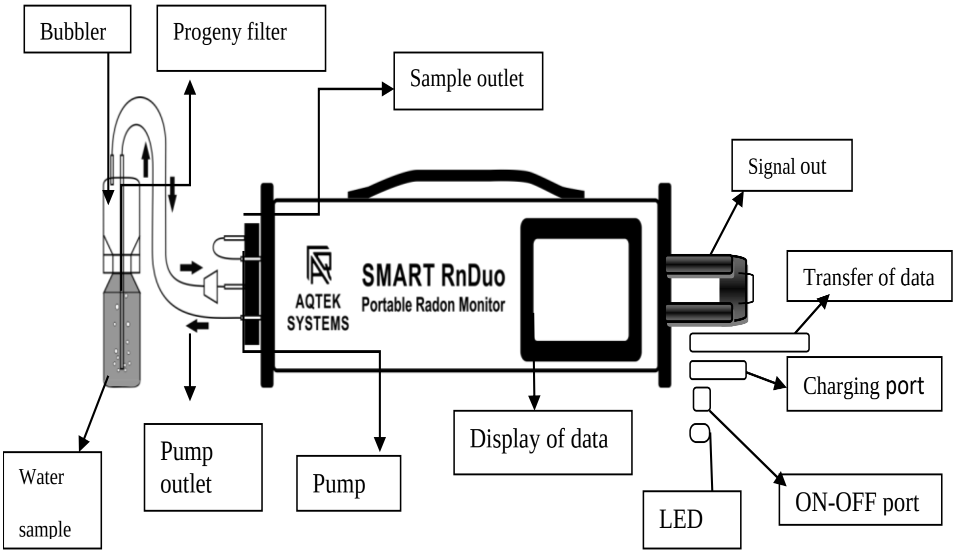

Figure 2.11: A setup for measurement of radon concentration in water samples

Complete set up for radon monitoring is shown in Figure 2.11. Prior to radon estimation, the inbuilt pump was turned on for 5 minutes to flush the air inside the detector in an open loop and afterwards sample bottle was connected with bubbler using rubber tubing. The pump was turned on in the closed loop for 5 minutes for extraction of radon from water. It has been done with the help of bubbler which is fixed on the top of sampling bottle. One end of the tube is connected with air inside the detector and other end is put inside water bottle through the bubbler in such a way that when pump is in “ON” mode then air moves from detector to the water sample and bubbles are produced in it. The pump was turned off after 5 min and was given 5 minutes delay for thoron decay and to avoid the impact of the thoron on the radon estimation. The extracted radon (C_{air}) further flows towards detector volume and gathered in scintillation cell by passing through “progeny filters” and “thoron discriminator” eliminating radon/thoron progenies and thoron. The radon measurements in Smart RnDuo are based on the detection of alpha particles emitted from radon and its decay products formed inside a cell volume which are continuously counted by the PMT and the associated counting electronics. The alpha counts obtained are processed by a microprocessor unit as per the developed algorithm which displays the concentration of radon. The sample was analysed in continuous mode for 1 hour of 15 minute cycle each at constant temperature. Smart RnDuo attains an efficiency of 95% for radon within running time of 15 minutes.

2.7 LED FLUORIMETER

In present study, LED Fluorimeter LF/2a Analyzer developed by R&D Quantalase has been used for measurement of uranium in drinking water samples (Figure 2.12). LED Fluorimeter is based on the principle of detection of fluorescence of uranium complexes in samples. When the incident UV radiation is not energetic enough to knock out electrons from the atoms, then the electrons go to higher electronic states. As excited states have a shorter lifetime, the electrons return to ground state, emitting light energy. This is known as “fluorescence” when light is instantly re-emitted at typically longer wavelengths.

Figure 2.12: LED Fluorimeter along with accessories

(Department of Environmental Science and Technology Lab, Central University of Punjab, Bathinda)

Uranium complexes emit green fluorescence under UV excitations which are detected with the help of sensitive photomultiplier tube. The fluorescence yield is proportional to the intensity of excitation source and concentration of uranium in sample. Measurement of fluorescence gives the information about the concentration of uranium in water samples. The excitation spectrum of uranium shows three broad peaks at 250nm, 330nm and 405nm.The wavelength of UV LEDs (405nm) falls within the third absorption band and hence, itis used in this instrument.

The LED source is Quantalase LED Fluorimeter which emits UV light and cause excitation in fluorescence of uranium present in water sample along with a sample compartment and photo multiplier tube as a radiation transducer. UV LEDs are used in an equipment with a 400 nm excitation wavelength to excite uranyl ions in a groundwater sample. When ions return to their ground state, green fluorescence is emitted, which may be detected using a photomultiplier tube. To prevent organic matter fluorescence from falling on the photomultiplier tube (PMT), suitable filters are placed between the LEDs and the PMT. Furthermore, suitable PMT time gating is used to prevent the fluorescence from organic materials, which has a short lifetime of around 100 ns compared to the fluorescence from uranyl ion, which has a lifetime of about 200 µs. All this process is controlled by digital form. The lower detection limit of instrument is 0.1 ± 10% µgl^{-1}.

The buffer solution was prepared using sodium pyrophosphate ($Na_4P_2O_7.10H_2O$) solution (5%) in distilled water and a pH value of 7.0 was adjusted by adding dilute (10% vol/vol) phosphoric acid solution drop wise (Rathore et al., 2004). LED Fluorimeter was calibrated with standard samples containing 10, 50 and 100 μgl^{-1} of uranium against observed values of fluorescence. After calibration, the cuvette was rinsed with distilled water before filling the new sample of water. Cuvette was filled with 6 ml of water sample with 10% of fluren added in it with the help of pippete. Then cuvette was inserted in the cuvette chamber in the LED fluorimeter and then the value of uranium concentration is obtained on the screen.

Before uranium quantification in water samples, the equipment was calibrated with recognised standards supplied by Quantalase Enterprises Pvt. Ltd., Indore, India. Concentration of uranium has been calculated by using following formula:

$$\text{Calibration Factor (CF)} = \frac{Concentration\ of\ uranium\ in\ standard\ solution}{Fluoroscence\ of\ standard - Fluoroscence\ of\ water}$$

2.8 pH AND TDS/EC METER

The physico-chemical water quality parameters like pH, electrical conductivity (EC) and total dissolved solids (TDS) in drinking water samples were measured with the help of Amphereus pH and TDS/EC meter (Figure 2.13 a & b). All the measurements were carried out at room temperature (25°C) (Taras et al., 1971).

a) b)

Figure 2.13: (a) pH meter (b) TDS/EC meter