Chapter 3. Experimental Procedures

The specific field protocols for collection and storage of groundwater samples for analyses of dissolved helium, radon, fluoride and precipitation of inorganic carbon for radiocarbon dating were developed and standardized as part of this work. The protocols were validated in the laboratory before field application. Purge and trap system for extracting dissolved CFCs in groundwater was also developed and tested. The existing analytical facilities at PRL were used for measuring stable isotope ratios of oxygen and hydrogen, and activities of ^{14}C and ^{222}Rn.

Groundwater samples in this study were collected from tubewells, hand pumps, dug wells and thermal springs ranging in depth from 3m to 350m. Prior to sampling, the hand pumps and tubewells were purged long enough (>3 well volumes) to flush out any stagnant water. The standard water quality parameters like temperature, pH and electrical conductivity (EC) were measured in the field during sampling using the μ-processor based water analysis kit (Brand: Century: CMK-731).

Sampling, storage and analytical techniques for some geochemical and isotopic parameters as developed as part of this work are described in the following.

3.1 Helium in Soil-air and Groundwater

3.1.1 Soil air and Groundwater Sampling

Soil air samples were collected from 1 m below ground. A 1.2-metre long copper tube (Φ = 5 mm) with perforation on 15-cm of its lower end was inserted into the soil. The ground surface near the upper end of the copper tube was then hammered and moistened to effectively seal the hole from direct contact with atmosphere. The upper end of the copper tube was connected to a hand-operated suction pump by a Tygon tube. The pump was operated sufficiently long to ensure removal of atmosphere/ soil-air mixture from the copper tube and the surrounding soil-air. The upper end of Tygon tube was then closed using a 3-way stopcock for accumulating soil-air inside the tubes. After about 12 hours, the hypodermic needle fitted to the third end of the stopcock was made to pierce the rubber stopper of a 1.2-litre pre-evacuated soda-lime glass bottle for soil-air sample collection. Withdrawal of the hypodermic needle, quickly, from rubber stopper effectively sealed the soil-air sample.

Groundwater samples were collected directly from the pump outlet using a PVC tube (Φ = 8 mm) to divert the water flow and to transfer the same to the bottom of a 1.2-litre soda-lime glass sample bottle, pre-rinsed with groundwater from the same

source being sampled. It was ensured that the tubewell was pumping at least for half an hour prior to sampling. In case of a hand pump, it was operated at least for 15 minutes before sampling.

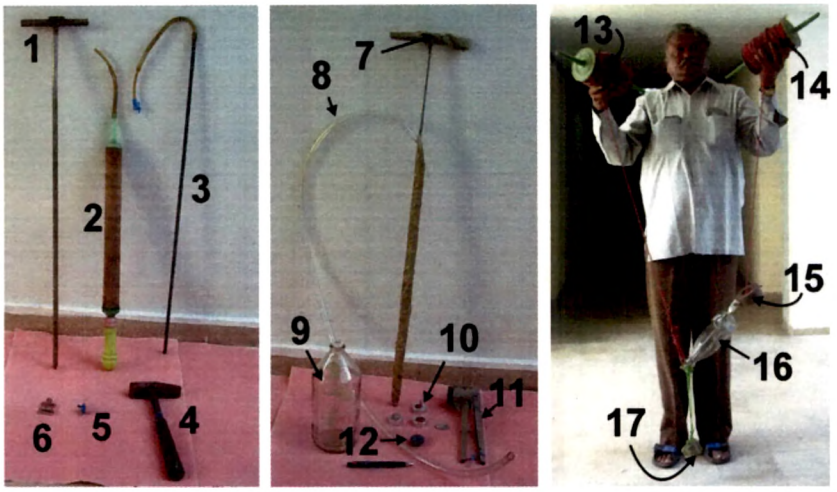

Figure 3.1 Various tools and gadgets used for sampling of groundwater and soil air. 1 – Metallic rod; 2 – Hand operated suction pump; 3 – copper tube perforated at the bottom; 4 – Hammer; 5 –Three-way valve; 6 – Pinch cock; 7 & 8 – Metallic rod with a PVC tube tied on it for diverting groundwater flow from pump outlet; 9 – 1.2-litre soda-lime glass bottle; 10 – three layers of the aluminium seal; 11 – Hand operated crimping tool for aluminium seal; 12 – Bromo-butyl synthetic rubber stopper; 13 & 14 – Nylon ropes connected to mouth and base of the collection glass bottle for extraction of water from the desired depth of the water column in dug wells, lakes and streams; 15 – Heavy weight tied to the base of the glass bottle; 16 – The water collection glass bottle ; 17 – Heavy weight tied to the mouth of the bottle. Weights (15 and 17) are meant to keep the bottle vertical while lowering or lifting and for reverting the bottle at the desired depth in the water column.

After allowing the sample bottle to overflow for a while and when no bubbles were visually seen, the PVC tube was withdrawn and the sample volume was reduced to a factory -marked position on the sampling bottle leaving 98 ml of air above water surface. The bottle was then sealed within few seconds with a rubber stopper and triple aluminium protection cap using a handheld crimping tool. Wherever pumping facility did not exist (e.g. a dug well), the sample was collected by immersing an inverted (mouth down) empty 2-litre glass bottle inside the water with the help of a rope and suitable weight attached to keep it inverted. After the bottle reached the required sampling depth, it was reverted (mouth up) for water sampling. The collected sample was then transferred to a 1.2-litre soda-lime bottle and sealed as above.

The bottles filled with water sample were stored in corrugated hardboard box with

compartments made to accommodate one bottle per compartment. The bottles were stored in inverted position to minimise any loss of helium from the stopper. The air in the bottle got equilibrated with water by movement during transportation and additionally by shaking for sometime in laboratory before analysing helium concentration by the standardised procedure described in the following (Section 3.1.3). The various field implements used for sampling helium from soil air and the groundwater are shown in Figure 3.1.

3.1.2 Sample Storage

Helium permeates readily through many materials, it is therefore important to carefully choose the containers in which the soil-air and groundwater samples intended for subsequent helium analyses are to be stored. The optimal material for such containers is oxygen free high conductivity (OFHC) copper tubing in which samples for helium analyses are sealed by crimping at both ends (Craig and Lupton, 1976; Lupton et al. 1977). Gupta et al. (1990) showed that loss of dissolved helium from thick walled soda-lime glass bottles, with conventional laboratory rubber stopper was less than 3% during a storage period of 24 h.

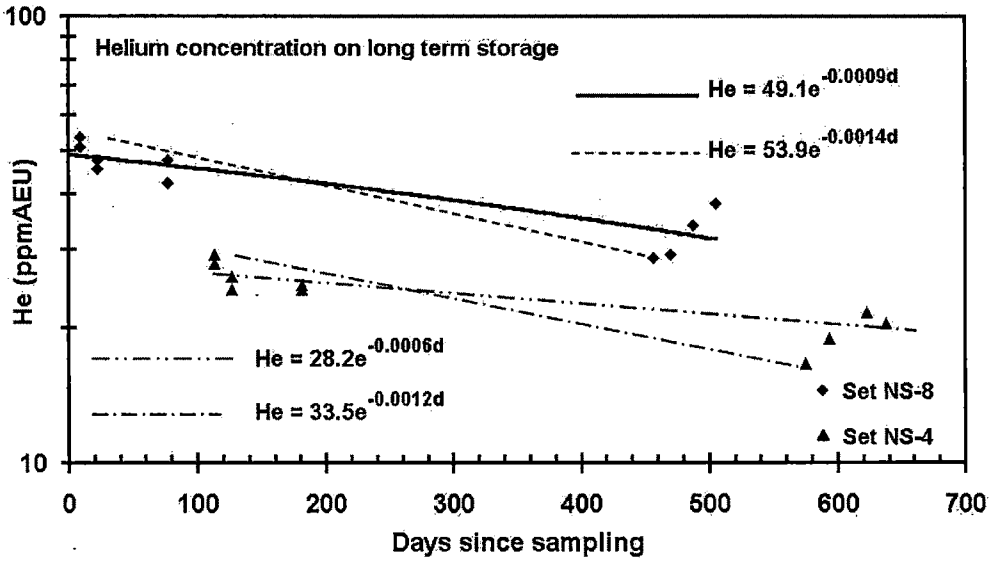

Figure 3.2 Residual helium concentrations on long term storage in soda-lime glass sampling bottles with bromobutyl rubber stopper and triple aluminium protection seal. Two separate sets of multiple samples were collected from two different sources. Individual samples were analysed subsequently at various intervals during a period of 20 months after the sample collection. The maximum observed loss of helium is given by the steepest line on this log-linear plot which corresponds to a loss of <0.15 % per day. The average loss, obtained by averaging the rates from the two best fit lines is, however, 0.075% per day.

This storage method, however, was not suited for soil-air and for equilibration measurement techniques of helium. Therefore, thick (3 mm) walled soda-lime glass bottles with bromobutyl synthetic rubber stopper manufactured according to guidelines of U.S. Pharmacopoeia standard II (USP Std-II) and secured by additional triple aluminium cap fixed by hand held crimping tool in the field were used for sample collection and storage. The synthetic rubber stopper was easily pierced by hypodermic needle and seals effectively when the needle was withdrawn. Each bottle used for sampling is pre-checked for maintenance of vacuum by evacuating the same and measuring the air pressure inside after 10 days. Bottles showing pressure > 2 torr were rejected. To test the integrity of samples against leakage and diffusion of helium, two identical sets of water samples (ten each) each were simultaneously collected from the same source following the procedure described previously. Helium concentrations in these sets of sample bottles were measured over a period of 20 months. The measured concentrations were then plotted on a log-linear plot (Figure 3.2) It was assumed that the loss during storage is a first order rate process; like radioactive decay, depending on the concentration. The slope of the steepest line through any particular set of data points corresponds to the highest loss rate and the best fit line corresponds to the average loss rate. It is seen from Figure 3.2 that the maximum loss of helium during storage was given by the line (He=53.94*exp(–0.0014d) for NS-8). Applying the standard concept of half life; a value of 495 days was obtained corresponding to 50 % helium loss using this equation. This corresponds to a loss of <0.15 % per day.

3.1.3 Analytical Procedure

A helium leak detector (ALCATEL Model ASM 100 HDS) comprising a tuned mass-spectrometer for helium ions (m/e = 4) was used for helium measurements by connecting an inlet port to its sniffer probe. This system was in many ways similar to the one used by Friedman and Denton (1975) and Reimer (1984). Equilibrated air samples (Figure 3.3a) were drawn from the head space of the bottles by piercing their rubber seal using a 20 ml syringe (Syringe-1). As the sample was drawn, an equal amount of air from another syringe (Syringe-2) entered the bottle and mixed with the sample gas. The test sample drawn in Syringe-1 was injected first into a pre-evacuated Syringe-3 by piercing the rubber septum on the inlet port and then allowed to be sucked into the leak detector through a moisture trap connected to the sniffer probe (Figure 3.3). The system response, directly proportional to the partial pressure of helium in the air /gas flowing through the analyser was recorded as voltage output on a data logger and chart recorder. The measured helium concentrations were corrected for (i) volume of headspace, (ii) water volume, (iii) volume of air drawn in during analysis and (iv) duration of storage. The

average loss, obtained by averaging the rates from the two best fit lines is, however, 0.075% per day as shown in Figure 3.2.

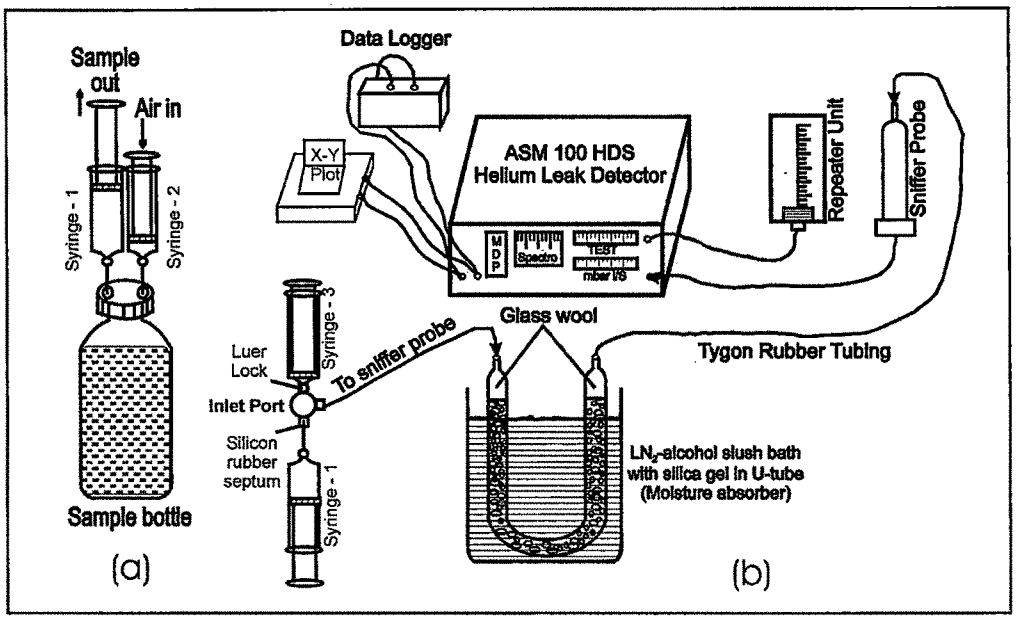

Figure 3.3 Schematic diagram showing layout of (a) drawing of equilibrated air sample and (b) helium measurement through helium leak detector for water/ air/ gas samples.

As mentioned in Section 2.6.2, helium measurements in this study are expressed in terms of Air Equilibration Units (AEU) because these were actually made on equilibrated headspace air samples.

3.1.3.1 Calibration of Helium Leak Detector

The helium leak detector was calibrated using atmospheric air with He concentration of 5.3-ppmv. The standard calibration curve for the chart recorder reading (set at 10 V range) is given by the expression:

$$He = Const_1 . \exp(Const_2 * D_s)$$

Eq. (3.1)

where, D_s is the number of chart recorder divisions at the 10 V full-scale setting and He is the concentration of helium (in ppmv).

If the chart recorder divisions are measured as deviation/ difference from the atmospheric background reading, the above equation can be rewritten as;

$$He = 5.3 \exp(Const_2 * (D_s - D_{bkg}))$$

Eq. (3.2)

where, (D_s - D_{bkg}) is the difference between the chart recorder reading of the sample and the atmospheric background.

The calibration checks carried out for this study were designed to verify the combination of factory calibration and modifications made subsequently in the input port and to verify the robustness of procedure specified in Section 3.1.3 above for helium assay in air/ gas samples. For this purpose two experiments were carried out, (i) repeated dilution of an arbitrary helium concentration sample with fixed volume of atmospheric air; and (ii) determination of Henry's law constant for helium.

3.1.3.2 Dilution by Atmospheric Air

A fixed volume (=V_A) of air is drawn from the head space (volume = V_0) of storage bottle using a hypodermic syringe. As the sample is drawn, equal volume of atmospheric air is allowed to enter the sampling bottle through another hypodermic syringe (Figure 3.3a). As a result, helium concentration in the air sample, being drawn from the head space, varies continuously in response to dilution by atmospheric air and mixing with remaining air in the bottle. If drawing of sample and resulting dilution is repeated several times, a recursive equation can be obtained as under (Gupta and Deshpande, 2003):

$$C_{Mn} = \frac{C_0 \quad e^{-(n-1)f}}{f}(1-e^{-f}) - \frac{C_A e^{-(n-1)f}}{f}(1-e^{-f}) + C_A$$

Eq. (3.3)

where, C_{Mn} = measured helium concentration after n^{th} dilution;

C_0 = original helium concentration in volume V_0;

C_A = is the helium concentration of incoming atmospheric air; and

$f = V_A/V_0$.

For $C_A << C_0$, $$C_{Mn} = \frac{C_0 \quad e^{-(n-1)f}}{f}(1-e^{-f})$$

Therefore,

$$\frac{C_{Mn}}{C_{M(n-1)}} = e^{-f}$$

Eq. (3.4)

Thus, the measured helium concentration will decrease by a factor e^{-f} after every dilution. In the standard experiments for this study, the volume of sample air drawn (V_A) was 20 ml; and volume of the head space (V_0) was 56 ml, governed by the factory made marking on the bottle.

Calibration of the instrument and the entire analytical procedure, starting with air/gas sample with any arbitrary helium concentration, can be experimentally checked using Eq. (3.4). A graph of two separate experiments showing measured and calculated helium concentration variation involving repeated dilution with atmospheric air is given in Figure 3.4a. The close agreement between the measured and calculated values not only confirms the correctness of the calibration procedure but also of the experimental procedures followed.

3.1.3.3 Estimation of Henry's Law Constant

Henry's Law states that the solubility of any sparingly soluble gas in water is proportional to the partial pressure of that gas in the air, in equilibrium with water. For n^{th} equilibration, the relation derived for determination of Henry's law constant by repeated equilibration of atmospheric air with water containing dissolved helium is (Gupta and Deshpande, 2003):

$$\log C_{Gn} = \log C_{G0} - n\log(1+FH_x) \qquad \text{Eq. (3.5)}$$

Where; C_{Gn} = Concentration of helium in gas phase after n^{th} equilibration

C_{G0} = Original concentration of helium in gas phase

$F = V_G/V_L$ = Volume of gas phase / Volume of liquid phase

H_x = Henry's law constant

Plot of 'log C_{Gn}' vs 'n' (equilibration number) would be a straight line with its intercept = $\log C_{G0}$ and slope = $-\log(1+ F H_x)$.

In these experiments, while the values of C_O were arbitrarily varied, the values of V_G and V_L were 50 ml each. Figure 3.4b shows measured helium concentration in equilibrated air against the number of equilibrations in several experiments involving different initial helium concentrations. The average estimated value of Henry's law constant for six sets of similar experiments is 98 against the reported values of 105.7 at 25°C (Weiss, 1971) and 94.5 at 25°C (Fry et al, 1995; Perry, 1984). Agreement between the values obtained in different experiments and between estimated and reported values reconfirms the validity of calibration procedure adopted in the entire experimental set up and the robustness of the procedure standardised for estimation of helium concentration in air /water sample.

Reproducibility of measured helium values was checked by repeated analyses on a set of 4 samples collected at the same time in two different bottles in the concentration range of 5.3 to 340 ppmAEU. The results of these experiments (Table 3.1) show that the analytical precision of measurement of helium concentration is better than 5%.

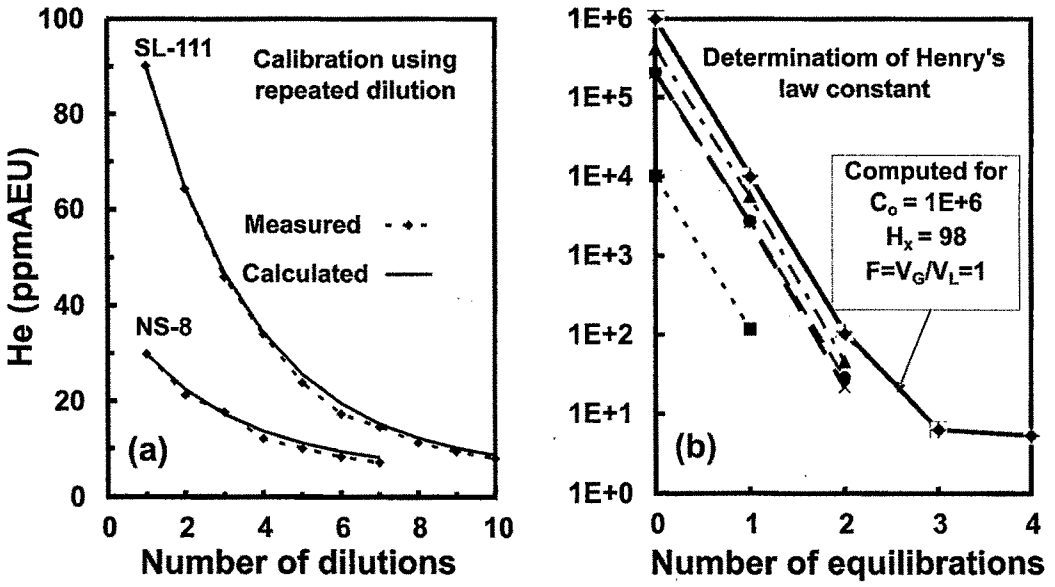

Figure 3.4 (a) Comparison of measured and calculated dilution curves; and (b) the results of a set of six experiments undertaken for estimation of Henry's law constant for water-helium system. The experimental values are similar to the known value of 105.7 at 25oC (Weiss, 1971). These experiments validate the calibration of the helium measurements and the robustness of the analytical procedure.

Table 3.1 Reproducibility of measured helium concentration in groundwater samples.

Sample location	Helium Concentration (ppmAEU)		Variability (%)
	Sample-1	Sample-2	
Ranip	6.17	6.20	1
Bagodra	339.7	339.7	0
Roika	24.3	24.8	2
Tilaknagar	5.3	5.3	0

3.2 Radon in Groundwater

For ^{222}Rn measurements, groundwater from pump outlet was piped directly into 630-ml PVC bottles (Brand: Tarson) by a PVC tube and allowed to overflow for >> 3 bottle volumes to minimise atmospheric contamination during sampling. The bottles were completely filled up to the brim and capped immediately and sealed with parafilm (Brand: AMERICAN Can Company) to prevent escape of dissolved gases.

^{222}Rn was measured, within 5 days of sample collection, by counting 609 keV gamma rays produced by the decay of its short-lived daughter ^{214}Bi using a high purity germanium (HPGe) gamma ray spectrometer. The background in the ^{214}Bi peak was

0.062 ± 0.001 cpm. The counting efficiency of ^{214}Bi, determined using a ^{226}Ra source of known activity (107.4 ± 0.4 dpm) in the same configuration as the sample bottle, was 0.31 ± 0.01%. Repeated counting for some samples after a period of more than three weeks confirmed that ^{222}Rn was unsupported by the decay of ^{226}Ra present in the groundwater. Values of ^{222}Rn activity were decay corrected to the time of collection, with errors quoted as one standard deviation based on counting statistics. Total uncertainty of ^{222}Rn measurements, based on repeat analyses and counting statistics, is <10%. The radon measurements were made by Dr. Meetu Agarwal (see Agarwal et al, 2006).

3.3 Fluoride in Groundwater

The groundwater samples for analyses of dissolved fluoride were collected in 1.2 litre soda-lime glass bottles after thoroughly rinsing with the sample water. All the procedures and precautions for sampling remain the same as mentioned in case of helium (Section 3.1.1). To ensure the integrity of stored water for fluoride contamination from the sampling bottles, de-ionised water was stored in several sample bottles over a period of one year. No measurable fluoride was detected in the stored water.

The fluoride concentrations were measured in the laboratory by colorimetry within a few days of the sample collection, using 580 nm tuned colorimeter (Model: Hach) using the SPADNS reagent method. The Hach colorimeter used for this study is a high quality filter photometer designed for single parameter colorimetry. The instrument was calibrated to measure fluoride in water samples ranging in concentration from 0 to 2.0 mg/l using borosilicate vials with high degree of transparency and optical uniformity. The borosilicate vials and other glassware were first cleaned with 1:1 HNO_3 and followed by thoroughly rinsing with deionised water. The identified borosilicate vials and other glassware were used exclusively for fluoride analyses to avoid contamination and to maintain identical transparency and optical uniformity between set of samples analysed at different times.

The instrument was recalibrated before analysing every set of 10 samples, using two-point calibration facility provided in the instrument. For any fluoride measurement, including that for calibration, 10 ml of liquid to be analysed (sample water, deionised water or standard solution) was poured into the borosilicate vials using high precision volumetric dispenser. Thereafter, 2 ml of SPADNS Reagent was dispensed into the same vial. The vial was tightly capped and swirled thoroughly for homogenisation. The fluoride ions in the liquid reacted with SPADNS Reagent which is a red zirconium-dye solution. The fluoride ion combines with part of the zirconium ion to form a colourless complex, thus bleaching (discolouring) the red colour of the solution in proportion to the

fluoride concentration. This reaction is generally completed within a minute; therefore, the vials were left aside for a few minutes after adding SPADNS Reagent and swirling thoroughly. The degree of discolouration of the solution is directly proportional to the fluoride concentration of the sample.

The vial was then placed in the cell holder of the instrument with a light emitting diode (wavelength 580 nm) on one side and a silicon detector cell (filter bandwidth 15nm; absorbance range 0-1Å) on the other. The liquid crystal display of the instrument provided a direct readout of fluoride concentration (in mg/l). The precision of fluoride measurements was better than 0.1 ppm.

There are various ions and compounds (e.g. chloride, ferric iron, ortho-phosphates, sulphates, aluminium and alkalinity as $CaCO_3$, etc.) that can interfere with fluoride in the colorimetric analyses of water samples. Any natural water sample can have variety of such elements which can interfere with fluoride and result in systematic error in the estimated concentration of fluoride. The error introduced due to interference by various ions and compounds in the colorimetric analyses of fluoride as provided by the Hach Company is given in Table 3.2.

Table 3.2 Colorimetric interference of selected ions and compounds

Ion/Compound	Concentration (mg/l)	Error introduced (± mg/l F^-)
Alkalinity (as CaCO3)	5000	–0.1
Aluminium	.01	–0.1
Chloride	7000	+0.1
Ferric Iron	10	–0.1
Ortho-phosphate	16	+0.1
Sodium Hexametaphosphate	1.0	+0.1
Sulphate	200	+0.1

It is seen from the Table 3.2 that at a precision level better than 0.1ppm, very high concentrations of interfering ions are required to affect the measurements. Such high values of alkalinity, chloride and sulphates were not found (at 27 locations where these parameters were measured as part of sampling protocol for radiocarbon dating; Table 4.6). Also the unpublished data of routine surveys, conducted by Gujarat Water Resources Development Corporation Ltd. (GWRDC), did not report high values of these parameters. In view of this, any error in fluoride measurements due to the interfering ions and compounds was ignored.

Figure 3.5 (a) Picture showing a specially designed foldable stand with conical aluminium base which holds the high density PVC bag filled with 100 litre of water sample. The supernatant water is decanted by piercing the bag after the carbonate precipitates settle in the conical base of the bag; (b) Carbonate precipitates are transferred from PVC bag into 1.2-litre soda-lime glass bottle without exposure to atmosphere.

3.4 Groundwater Radiocarbon Dating

For ^{14}C dating, about 100 litre of groundwater is piped directly into a collapsible high density PVC bag through a narrow opening. The PVC bag is kept in the folded condition in a stand designed specifically for this purpose and assembled from its prefabricated parts at the site (Figure 3.5a). The PVC bag unfolds only when the groundwater gets filled into it. Before piping in the groundwater, a few pellets of NaOH (~10g) were added to the PVC bag to raise the solution pH to >10 for immobilising the dissolved CO_2 in the form of CO_3^{2-} and its eventual precipitation as barium carbonate. At pH greater than 10.3 most of the dissolved CO_2 is in the form of CO_3^{2-} since at this pH, activity of HCO_3^- drops and activity of CO_3^{2-} rises rapidly (Drever, 1997).

Depending upon the alkalinity and sulphate concentration of groundwater samples (measured in the field), a pre-determined amount of barium chloride ($BaCl_2$) was then added to the 'groundwater-NaOH' solution to ensure complete precipitation of dissolved carbonates (Clark and Fritz, 1997). Following vigorous stirring, the mixture was left undisturbed for precipitates to settle in the conical base of the PVC bag (Figure 3.5a).

It usually takes 4-5 hours for the precipitates to settle. After decanting the supernatant liquid, precipitates were transferred to glass bottles (Figure 3.5b) and sealed by capping the bottle with a bromobutyl synthetic rubber stopper and triple aluminium protective cover on it using a hand held crimping tool. Care was taken to prevent/minimise sample exchange with atmospheric CO_2 during the entire field procedure.

On reaction with orthophosphoric acid, barium carbonate precipitates liberate CO_2. The liberated CO_2 was first converted to acetylene and then trimerised into benzene (C_6H_6) and the ^{14}C activity in the benzene counted by liquid scintillation spectroscopy (Gupta and Polach, 1985). A small aliquot of the sample CO_2 was sealed in glass ampoules for $\delta^{13}C$ measurement using SIRM (PDZ Europa Model GEO 20-20). The processing and analyses of the CO_2 liberated from the groundwater samples was done by Dr. M.G. Yadava in the ^{14}C laboratory of PRL.

3.5 Chlorofluorocarbons (CFCs) in Groundwater

3.5.1 Sample Collection and Storage

Sample collection and storage of groundwater for CFC analyses is the most critical aspect of employing CFCs as hydrological tracer. This is because: (i) inadvertent introduction of as little as 0.01 cc of modern air can be detected in the highly sensitive chromatographic analyses and can introduce significant error in estimating the groundwater recharge age, particularly of old ground waters; and (ii) there are severe restrictions on availability of suitable material for storing the water sample. All the conventionally used containers like glass bottles with rubber stopper, high density plastic-rubber-polymer bottles, glass flasks with stopcock, glass syringes with luer locks, polypropylenes syringes with luer locks, syringes with neoprene or Teflon plungers, tubes made up of stainless steel, copper or aluminium etc, are not really suitable for sample collection and storage for CFC analyses. Most of the materials used in construction of these conventional containers either absorb the CFCs from atmosphere/ water or leach/ release significant amounts of CFCs or other chlorinated compounds. In addition, CFCs can diffuse from the air through the polymers into the sample (Reynolds et al, 1990; Bullister, 1984). Significant uptake of halocarbons by aluminium and stainless steel occurs within an hour and a week respectively. However, all these materials and methods have been used earlier by various researchers with known limitations of the respective method (Thompson et al, 1974; Schultz, 1976; Warner and Weiss, 1985; Bullister and Weiss, 1988; Bu and Warner, 1995; Jean-Baptiste et al, 1994; Wilkowske and Solomon, 1997; Hofer and Imboden, 1998). No uptake of halocarbons, however, was observed even after 5 weeks of storage in borosilicate vials (Reynolds et

al, 1990). Busenberg and Plummer (1992) designed an involved procedure for collection and storage of water samples in the field.

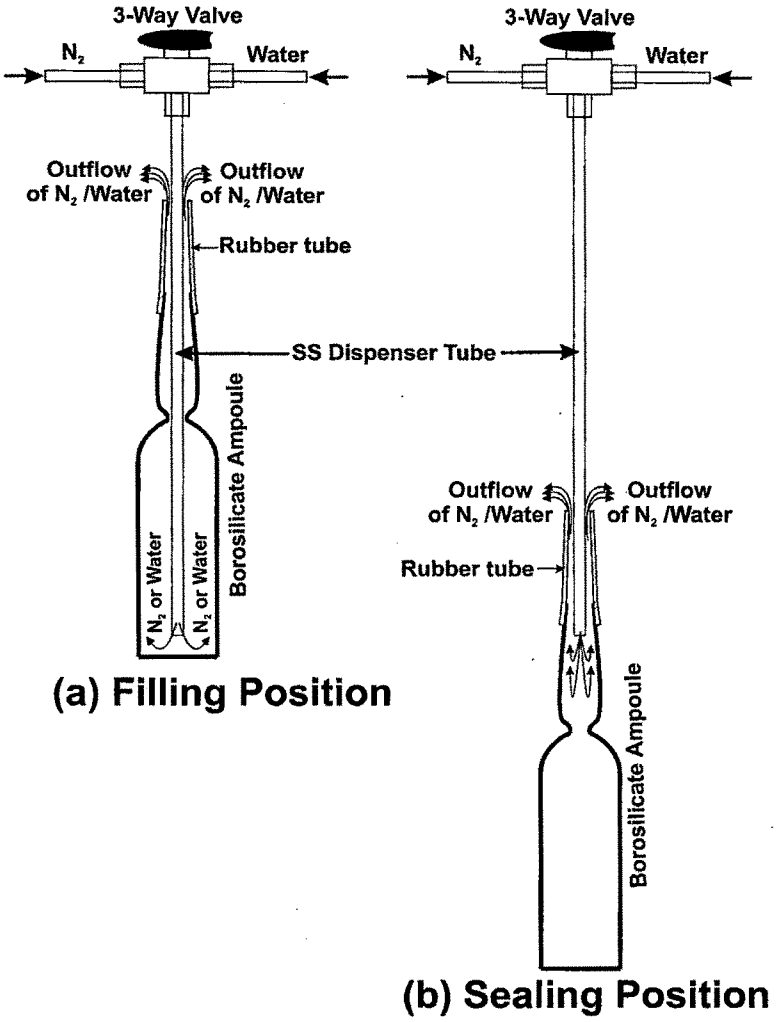

Figure 3.6 The groundwater sampling system for CFC analyses. (a) Relative position of 3-way valve and ampoule for flushing the ampoule with ultrapure nitrogen and filling with groundwater sample. (b) Relative position of 3-way valve and ampoule for evacuating the neck of ampoule and sealing it. (see the text for details)

As part of this work, a specific field procedure of water sample collection for CFC analyses was developed and tested for its integrity. The groundwater samples were collected in specially designed 60-ml borosilicate glass ampoules with constriction at the top and a tubular mouth (Figure 3.6). The sampling system comprises a 3-way valve (OD – 3.2 mm/ 1/8"), a borosilicate ampoule and a metallic stand that can hold these two at

variable heights. Figure 3.6 depicts how water sample was collected in the borosilicate ampoules.

As seen in Figure 3.6(a), one port of a 3-way Swagelok valve is supplied with ultrapure nitrogen and the second port of the valve is supplied with groundwater from the pump outlet. A 60-cm long SS tube (OD – 3.2 mm/ 1/8") is connected to the third port of the 3-way valve that acts as a dispenser of ultrapure nitrogen gas or water as required. The 3-way valve and the borosilicate ampoule (with a 30-cm long rubber tube tightly fixed on its tubular neck) are firmly held in the metallic stand such that the SS dispenser passes through the rubber tube and reaches the bottom of the ampoule. Since even a minute amount of atmospheric air can contaminate the water sample, the ampoule is thoroughly flushed with ultrapure nitrogen for 5 minutes at a flow rate of ~300 ml/ min. The water sample is then introduced into the ampoule by turning the 3-way valve towards water port. After the vial is completely filled with water, sufficient volume (~1 litre) of water is allowed to overflow from the rubber tube leaving no trace of atmospheric air inside the ampoule and the rubber tube. While water is overflowing, the ampoule along with the attached rubber tube is slowly pulled down to the level at which the lower end of SS dispenser tube reaches just above the tubular mouth of the ampoule (Figure 3.6b). The nitrogen flow is then restarted in this position (Figure 3.6b) by turning the 3-way valve towards gas port. The stream of nitrogen immediately starts displacing the water from the tubular mouth of the ampoule via rubber tube. When the water is completely displaced from the tubular part of the ampoule, it is wiped from outside with a tissue paper and the tubular mouth of ampoule is then fused with sharp, violet flame of LPG-Oxygen mixture. After ampoule is cooled to room temperature, it is checked for perfection in sealing. This is done by trying to see if any water droplets come out of ampoule by jerking. If water droplets come out of ampoule due to jerking, the ampoule is rejected. As a matter of abundant precaution for any inadvertent loss of sample during transportation or analyses, it is advisable to collect at least three ampoules of each groundwater sample.

3.5.2 Purge and Trap System for Extraction of CFCs

Since water samples can not be directly injected and vaporised into the injection port of Gas Chromatograph, the dissolved CFCs from these are extracted in a separate Purge and Trap system and injected into analytical column for subsequent Gas Chromatographic analyses. A new purge and trap system was designed and built following Busenberg and Plummer (1982). The photograph of the complete CFC analytical system including newly built purge and trap system is shown in Figure 3.7 and Figure 3.8. The line drawing of the entire analytical set up is given in Figure 3.9. The

purge and trap system is used not only for extraction and injection of the CFCs from water sample but also for injecting the standard gas mixture or any other gas injected from pressurised cylinder or large volume syringes.

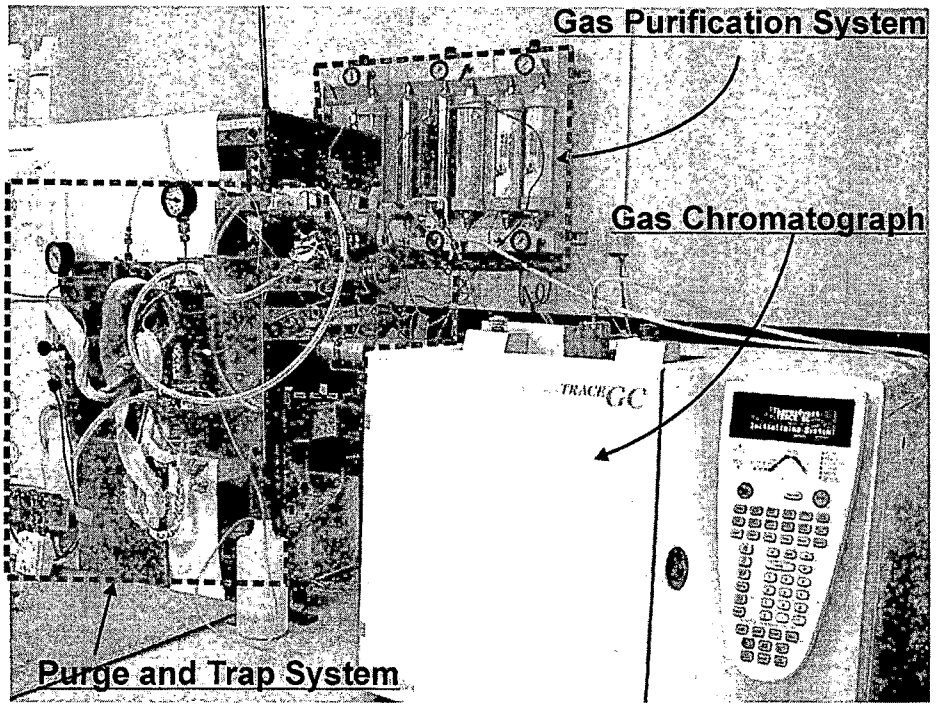

Figure 3.7 A gas purification subsystem, purge and trap subsystem and the gas chromotograph are the major components of the Groundwater CFC Laboratory. A blow up of the purge and trap system is shown in Figure 3.8. Complete line drawing of the CFC analytical set up is shown in Figure 3.9.

As seen in Figure 3.8 and Figure 3.9, the CFC analytical system is a complex network comprising various valves, gauges, purge tower, purge housing etc. The valves V-2, V-3, V-4, and V-6 are 6-port Valco Rotary Valves and V-7 is a 4-port Valco Rotary Valve. The Valco valves can be electrically actuated either through remote switches operated manually or by programmable computer command during gas chromatographic run. The valves V-1 and V-5 are manually operated 5-port Swagelok valves. The valves V-8, V-9, V-10, V-11 and V-12 are manually operated 3-port Swagelok valves. The direction of gas flow through various parts of the CFC analytical system is indicated by the arrows. With the help of these valves various sections of the analytical system can either be isolated or connected and the desired stream of gas can be made to flow through.

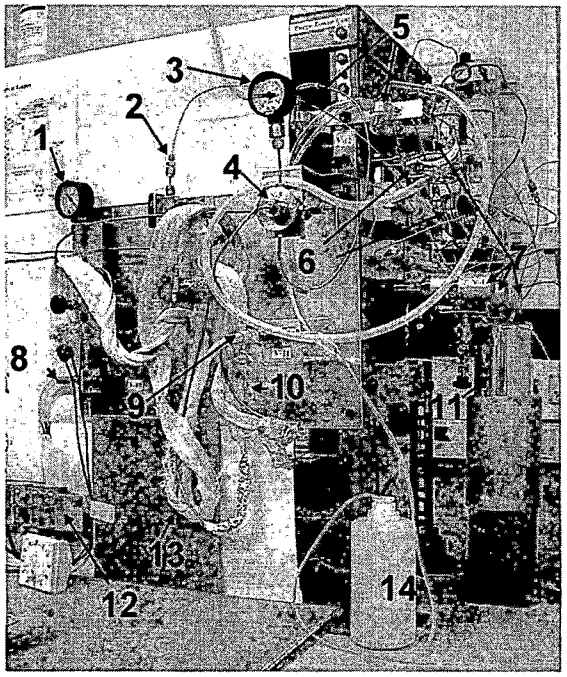

Figure 3.8 Blow up of the Purge and Trap System showing its constituents. 1 – Vacuum gauge; 2 – Carrier gas injection port; 3 – Pressure gauge; 4 – Multi-port valve; 5 – Bubblers; 6 – Gas sampling loops; 7- Valco valves; 8 – Suction port; 9 – Water inlet port; 10 – Purge tower; 11 – CFC trap in Dewar flask; 12 – Switch for Valco valves; 13- heating tape; 14 – Drain collector.

For extraction of dissolved CFCs from water, the borosilicate ampoule with water sample is connected to water sample port of V-11 with a Tygon tube (Figure 3.8). The purge tower and the Tygon tube connecting to ampoule are evacuated through suction port (V-10) using the rotary vacuum pump. After the desired level of vacuum is generated in the purge tower, it is isolated from the vacuum pump. On breaking the flame fused tip of the ampoule, the water sample is sucked into the purge tower. When 30 ml of water enters the purge tower (with pre-scored volume marks), the inflow is stopped by the valve V-11. The stream of purging gas (Ar/CH_4) is started by switching V-4 and the purging is done for 4 minutes. During the four minutes of purging, the dissolved CFCs and other gases purged from the water sample, together with moisture, are carried by purging gas. The moisture is trapped in two Magnesium Perchlorate [$Mg(ClO_4)_2$] moisture traps. The CFC-11, CFC-12 and CFC-113 are trapped on the CFC-trap (Figure 3.9) held at –40 °C. Other unimportant dissolved species (of no interest) are carried out of the system by the purging gas. The trapped CFCs are released by heating the trap with boiling water bath. A stream of carrier gas (Ar/CH_4) flowing into detector is then diverted through the CFC-trap for 30 seconds by programmed PC commands which operate the V-4 valve. Within 30 seconds, the gases released from CFC-trap are

transported into the analytical column through the pre-column. The purpose of the pre-column is to prevent the late eluting compounds from entering the analytical column. Such compounds are trapped on the pre-column and flushed out of the system by a stream of Ar/CH_4 in the opposite direction. Detailed specifications of the CFC-trap, analytical column and pre-column are given in Table 3.3.

Table 3.3 Technical specifications of various packed columns

Sr. No.	Column Type	Purpose	Technical Specification
1	CFC Trap Column	To trap the three CFC Species (F-11, F-12 and F-113) simultaneously on a single column	▪ Packed column ▪ (200 mm) 8" long, (3.2 mm)1/8" OD, (2.2 mm) 0.085" ID, SS - 304 type stainless steel tube ▪ Glass wool plug and 1 inch length of glass beads on either end. ▪ Packed with equal length of Porapak-T (80/100 mesh) and Porous-Sil C (80/100 mesh) separated by small amount of glass beads.
2	Pre-column	To prevent the late eluting compounds entering the analytical column	▪ (150 mm) 6" long, (3.2 mm)1/8" OD, (2.2 mm) 0.085" ID, SS - 304 type stainless steel tube ▪ Packed with Porous-Sil C (80/100 mesh), with a small glass wool plug at each end.
3	Analytical column	For chromatographic separation of three CFC Species (F-11, F-12 and F-113) simultaneously using a single column	▪ (3.05 m) 10' long, (3.2 mm)1/8" OD, (2.2 mm) 0.085" ID, SS - 304 type stainless steel tube ▪ Packed with Porous-Sil C (80/100 mesh), with a small glass wool plug at each end

The procedure for analysing CFCs in stripping gas (for background), standard gas mixture, atmospheric air as well as water samples involve a sequence of about 30 operations like evacuation of purge tower, cooling or heating of traps, switching of valves for diverting the stream of gas or isolating a particular portion of the analytical system etc. Each step is equally important for a reproducible analysis. The sequence of operations involved in analysing CFCs in stripping gas (for background), CFC standard, atmospheric air, and water sample are given respectively in Table 3.4, Table 3.5, Table 3.6 and Table 3.7.

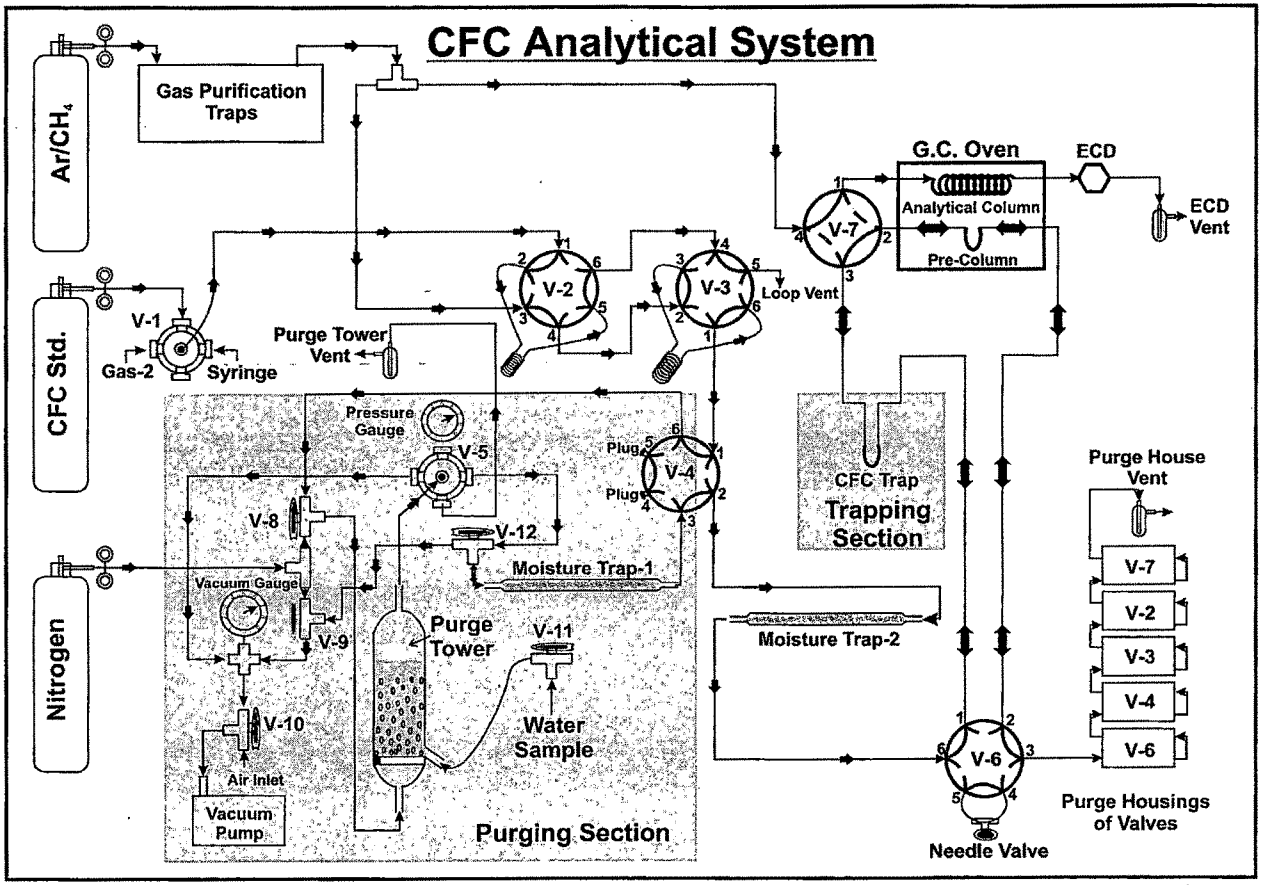

Figure 3.9 Line drawing of the complete CFC analytical system.

Table 3.4 Sequence of operations for analysing Ar/CH_4 stripper gas as background.

STEP	SEQUENCE OF ACTIONS
1.	Prepare the -40^0C slush (LN_2 + alcohol) and Set the valves as follows: V-1 → DOWN (Blind); V-2, V-3, V-4, and V-6 → LOAD; V-5 → RIGHT (Towards V-12) V-7 → INJECT; V-8 → UP (Stripper Gas side); V-12 → RIGHT (Towards V-5)
2.	Ensure the Stripper Gas flow rate of ~100 cc/min at Purge Housing vent
3.	V-4 → INJECT (Purging section is isolated from the rest of the stripping flow line)
4.	Switch on the Vacuum pump and set the valves as follows: V-10 → UP (Towards Vacuum Gauge); V-9 → DOWN (Towards Vacuum Gauge) V-5 → LEFT (Connecting purge tower to Suction line) V-12 → LEFT (Connecting Moisture Trap-1 to Suction line)
5.	Wait till Vacuum Gauge shows –29.5 (In Hg , black scale)
6.	V-5 → UP (Secondary evacuation of Pressure Gauge by Purge Tower)
7.	V-5 → LEFT (Connecting purge tower to Suction line)
8.	V-5 → RIGHT (Secondary evacuation up to V-12 by Purge Tower)
9.	V-5 → LEFT (Connecting purge tower to Suction line)
10.	Wait till Vacuum Gauge shows –29.5 (In Hg, black scale).
11.	V-5 → UP (Purge Tower connected to Pressure Gauge)
12.	V-6 → INJECT (CFC Trap and Pre-column isolated)
13.	Needle Valve at V-6 → CLOSE (system isolated from atmosphere at V-6)
14.	V-4 → LOAD (Stripper gas starts filling the Purge Tower; Moisture Trap-2 connected to suction line through Moisture Trap-1)
15.	Evacuate purge tower (by switching V5 → left) 3 times at 1 atmosphere. Wait till pressure gauge shows 2 kg/cm^2
16.	V-12 → RIGHT (Moisture Trap-1 connected to V-5)
17.	V-5 → RIGHT (Stripping gas from pressurised Purge Tower flows into Moisture Traps)
18.	Wait for 15 seconds for stripping gas to fill the evacuated moisture traps
19.	V-6 → LOAD (stripping gas flows out at purge housing vent through CFC Trap and Pre-column)
20.	Needle Valve at V-6 → OPEN 2 turns; Wait till flow through purge house vent is stabilised
21.	V-6 → INJECT (CFC Trap and Pre-column isolated)
22.	Immerse the CFC Trap in slush at -40^0C and Start the stopwatch. (Pre-cooling for 1 min.)
23.	At 1 min. V-6 → LOAD
24.	Switch on the Kettle and keep the boiling water ready.
25.	At 5 min. in stopcock, V-6 → INJECT
26.	Immerse the CFC Trap in boiling water bath and start stopwatch. Complete the next two steps in less than a min.
27.	Open the "View sample being acquired" window, set the scale of 0-3 mV
28.	Start Auto-zero function and register the output and offset in logbook
29.	At 1.5 min. Press "PREP RUN" button. When in "READY TO INJECT" state, Press "START"
30.	At start of the run V-7 automatically switches to LOAD and returns to INJECT after 30 sec.
31.	When V-7 returns to INJECT position: V-6 → LOAD (stripping gas starts back flushing the Pre-column)
32.	Switch off the Vacuum pump and V-10 → DOWN (Air inlet)
33.	When the run ends, the indicator returns to "STANDBY/PREP RUN" mode. Evaluate the Chromatogram, adjust the scale of view and take printout

Table 3.5 Sequence of operations for analysing CFC Standard.

STEP	SEQUENCE OF ACTIONS
1.	Prepare the -40^0C slush (LN_2 + alcohol) and Set the valves as follows: V-1 → DOWN (Blind); V-2, V-3, V-4, and V-6 → LOAD; V-5 → RIGHT (Towards V-12) V-7 → INJECT; V-8 → UP (Stripper Gas side); V-12 → RIGHT (Towards V-5)
2.	Ensure the Stripper Gas flow rate of ~100 cc/min at Purge Housing vent
3.	V-4 → INJECT (Purging section is isolated from the rest of the stripping flow line)
4.	Switch on the Vacuum pump and set the valves as follows: V-10 → UP (Towards Vacuum Gauge); V-9 → DOWN (Towards Vacuum Gauge) V-5 → LEFT (Connecting purge tower to Suction line) V-12 → LEFT (Connecting Moisture Trap-1 to Suction line)
5.	Wait till Vacuum Gauge shows –29.5 (In Hg, black scale)
6.	V-5 → UP (Secondary evacuation of Pressure Gauge by Purge Tower)
7.	V-5 → LEFT (Connecting purge tower to Suction line)
8.	V-5 → RIGHT (Secondary evacuation up to V-12 by Purge Tower)
9.	V-5 → LEFT (Connecting purge tower to Suction line)
10.	Wait till Vacuum Gauge shows –29.5 (In Hg, black scale)
11.	V-6 → INJECT (CFC Trap and Pre-column isolated)
12.	Needle Valve at V-6 → CLOSE (system isolated from atmosphere at V-6)
13.	V-4 → LOAD (Stripper gas starts filling the Purge Tower; Moisture Trap-2 connected to suction line through Moisture Trap-1)
14.	Remove the Glass plug at the loop-vent and connect it to bubbler
15.	Open Primary knob of CFC Cylinder
16.	V-1 → CFC Std input side (Let CFC std flow out from Loop Vent for 2 minutes)
17.	V-3 (2 ml) or V-2 (10 ml) → INJECT (stripping gas by-passes the loop and CFC std flows through sample loop)
18.	Flush the purge tower (by switching V5 → UP and LEFT) with stripping gas 3 times at 1 atmosphere. Wait till pressure gauge shows 2 kg/cm^2.
19.	V-12 → RIGHT (Moisture Trap-1 connected to V-5)
20.	V-5 → RIGHT (Stripping gas from pressurised Purge Tower flows into Moisture Traps)
21.	Wait for 15 seconds for stripping gas to fill the evacuated moisture traps
22.	V-6 → LOAD (stripping gas flows out at purge housing vent through CFC Trap and Pre-column)
23.	Needle Valve at V-6 → OPEN 2 turns; Wait till flow through purge house vent is stabilised
24.	V-6 → INJECT (CFC Trap and Pre-column isolated)
25.	Immerse the CFC Trap in slush at -40^0C and start stopwatch. (Pre-cooling for 1 min.)
26.	At 1 min. V-1 → DOWN (blind). Close Primary knob of CFC Cylinder.
27.	When the bubbling stops at the loop-vent: V-6 → LOAD; V-3 (2cc) or V-2 (10cc) → LOAD (Stripper flows through the respective loop and carries the CFC std from the loop). Start stopwatch.
28.	Switch on the Kettle and keep the boiling water ready.
29.	At 4 min.: V-6 → INJECT
30.	Immerse the CFC Trap in boiling water bath and start stopwatch. Complete the next two steps in less than a min.
31.	Open the "View sample being acquired" window, set the scale of 0-3 mv.
32.	Start Auto-zero function and register the output, offset and sample number in logbook
33.	At 1.5 min. Press "PREP RUN" button. When in "READY TO INJECT" state, Press "START"
34.	At start of the run V-7 automatically switches to LOAD and returns to INJECT after 30 sec.
35.	When V-7 returns to INJECT position: V-6 → LOAD (stripping gas starts back flushing the Pre-column)
36.	Switch off the Vacuum pump and V-10 → DOWN (Air inlet)
37.	When the run ends, the indicator returns to "STANDBY/PREP RUN" mode. Evaluate the Chromatogram, adjust the scale of view and take printout

Table 3.6 Sequence of operations for analysing atmospheric air.

STEP	SEQUENCE OF ACTIONS
1.	Prepare the -40^0C slush (LN_2 + alcohol) and Set the valves as follows: V-1 → DOWN (Blind); V-2, V-3, V-4, and V-6 → LOAD; V-5 → RIGHT (Towards V-12) V-7 → INJECT; V-8 → UP (Stripper Gas side); V-12 → RIGHT (Towards V-5)
2.	Ensure the Stripper Gas flow rate of ~100 cc/min at Purge Housing vent
3.	V-4 → INJECT (Purging section is isolated from the rest of the stripping flow line)
4.	Switch on the Vacuum pump and set the valves as follows: V-10 → UP (Towards Vacuum Gauge); V-9 → DOWN (Towards Vacuum Gauge) V-5 → LEFT (Connecting purge tower to Suction line) V-12 → LEFT (Connecting Moisture Trap-1 to Suction line)
5.	Wait till Vacuum Gauge shows –29.5 (In Hg, black scale)
6.	V-5 → UP (Secondary evacuation of Pressure Gauge by Purge Tower)
7.	V-5 → LEFT (Connecting purge tower to Suction line)
8.	V-5 → RIGHT (Secondary evacuation up to V-12 by Purge Tower)
9.	V-5 → LEFT (Connecting purge tower to Suction line)
10.	Wait till Vacuum Gauge shows –29.5 (In Hg, black scale)
11.	V-6 → INJECT (CFC Trap and Pre-column isolated)
12.	Needle Valve at V-6 → CLOSE (system isolated from atmosphere at V-6)
13.	V-4 → LOAD (Stripper gas starts filling the Purge Tower; Moisture Trap-2 connected to suction line through Moisture Trap-1)
14.	Connect the rubber tube from loop-vent to Air-inlet port of V-10
15.	V-1 → UP (Atmosphere inlet side)
16.	V-3 (2 ml) or V-2 (10 ml) → INJECT (stripping gas by-passes the loop and atmospheric air fills the loop)
17.	V-10 → DOWN (Atmospheric air sucked in through loop-vent); V-10 → UP
18.	Disconnect the rubber tube from V-10 and connect it to bubbler.
19.	Flush the purge tower (by switching V5 → UP and LEFT) with stripping gas 3 times at 1 atmosphere. Wait till pressure gauge shows 2 kg/cm^2.
20.	V-12 → RIGHT (Moisture Trap-1 connected to V-5)
21.	V-5 → RIGHT (Stripping gas from pressurised Purge Tower flows into Moisture Traps)
22.	Wait for 15 seconds for stripping gas to fill the evacuated moisture traps
23.	V-6 → LOAD (stripping gas flows out at purge housing vent)
24.	Needle Valve at V-6 → OPEN 2 turns; Wait till flow through purge house vent is stabilised
25.	V-6 → INJECT (CFC Trap and Pre-column isolated)
26.	Immerse the CFC Trap in slush at -40^0C and start stopwatch. (Pre-cooling for 1 min.)
27.	At 1 min. V-1 → DOWN (blind).
28.	V-6 → LOAD; V-3 (2cc) or V-2 (10cc) → LOAD (Stripper flows through the respective loop and carries the atmospheric air from the loop). Start stopwatch.
29.	Switch on the Kettle and keep the boiling water ready.
30.	At 4 min.: V-6 → INJECT
31.	Immerse the CFC Trap in boiling water bath and start stopwatch.
32.	Open the "View sample being acquired" window set the scale of 0-3 mv.
33.	Start Auto-zero function and register the output, offset and sample number in logbook
34.	At 1.5 min. Press "PREP RUN" button. When in "READY TO INJECT" state, Press "START"
35.	At start of the run V-7 automatically switches to LOAD and returns to INJECT after 30 sec.
36.	When V-7 returns to INJECT position: V-6 → LOAD (back flushing of Pre-column)
37.	Switch off the Vacuum pump and V-10 → DOWN (Air inlet)
38.	When the indicator returns to "STANDBY/PREP RUN" mode. Evaluate the Chromatogram, adjust the scale of view and take printout

Table 3.7 Sequence of operations for analysing Water Sample.

STEP	SEQUENCE OF ACTIONS
1.	Prepare the –40^{0}C slush (LN_2 + alcohol) and Set the valves as follows: V-1 → DOWN (Blind); V-2, V-3, V-4, and V-6 → LOAD; V-5 → RIGHT (Towards V-12) V-7 → INJECT; V-8 → UP (Stripper Gas side); V-12 → RIGHT (Towards V-5)
2.	Ensure the Stripper Gas flow rate of ~100 cc/min at Purge Housing vent
3.	Ensure that the wire-mesh is placed at the end of rubber tube connected to V-11
4.	Fix the inverted sample ampoule in the stand and connect it to V-11 through rubber tube
5.	V-4 → INJECT (Purging section is isolated from the rest of the stripping flow line)
6.	Switch on the Vacuum pump and set the valves as follows: V-10 → UP (Towards Vacuum Gauge); V-9 → DOWN (Towards Vacuum Gauge) V-5 → LEFT (Connecting purge tower to Suction line) V-12 → LEFT (Connecting Moisture Trap-1 to Suction line) V-11 → LEFT (Connecting rubber tube to purge tower)
7.	Wait till Vacuum Gauge shows –29.5 (In Hg , black scale)
8.	Check for leakage or moisture by closing V-10. If pressure increases rectify the rubber tube connection or remove the moisture by heating.
9.	V-5 → UP (Secondary evacuation of Pressure Gauge by Purge Tower)
10.	V-5 → LEFT (Connecting purge tower to Suction line)
11.	V-5 → RIGHT (Secondary evacuation up to V-12 by Purge Tower)
12.	V-5 → LEFT (Connecting purge tower to Suction line)
13.	Wait till Vacuum Gauge shows –29.5 (In Hg, black scale).
14.	V-5 → UP (Purge Tower connected to Pressure Gauge)
15.	V-6 → INJECT (CFC Trap and Pre-column isolated)
16.	Needle Valve at V-6 → CLOSE (system isolated from atmosphere at V-6)
17.	V-4 → LOAD (Stripper gas starts filling the Purge Tower; Moisture Trap-2 connected to suction line through Moisture Trap-1)
18.	Flush purge tower (by switching V5 → left) 3 times at 1 atmosphere. Wait till pressure gauge shows 1 kg/cm^2
19.	V-12 → RIGHT (Moisture Trap-1 connected to V-5)
20.	V-5 → RIGHT (Stripping gas from pressurised Purge Tower flows into Moisture Traps)
21.	After 15 Seconds V-6 → LOAD (stripping gas flows out at purge housing vent through CFC Trap and pre-column)
22.	Needle Valve at V-6 → OPEN 2 turns
23.	V-12 → CENTRE; V-8 → CENTRE; V-4 → INJECT; V-6 → INJECT
24.	Immerse the CFC Trap in slush at –40^{0}C for pre-cooling of the CFC-trap
25.	Evacuate Purge Tower and rubber tube connected to ampoule by switching V-5 → LEFT
26.	Secondary evacuation of pressure gauge and tube up to V-12 (step 9 to 12)
27.	V-5 → RIGHT
28.	Crush the tip of the Ampoule and introduce the water in purge tower. When 30 ml of water is introduced: V-11 → RIGHT
29.	Needle Valve at V-6 → CLOSE (system isolated from atmosphere at V-6)
30.	V-4 → LOAD; V-8 → UP (Bubbling starts in the purge tower); V-12 → RIGHT After 15 Seconds V-6 → LOAD and start stopwatch. ((Stripping gas flows out at purge housing vent through pre-cooled CFC trap and pre-column)
31.	Needle Valve at V-6 → OPEN 2 turns
32.	Switch on the Kettle and keep the boiling water ready.

Table continues on next page

Table continues from previous page

33. At 4 min., V-6 → INJECT
34. Immerse the CFC Trap in boiling water bath and start stopwatch. Finish next two steps in less than 1 min.
35. Open the "View sample being acquired" window, set the scale of 0-3 mV
36. Start Auto-zero function and register the output and offset in logbook
37. At 1.5 min. Press "PREP RUN" button.
    When in "READY TO INJECT" state, Press "START"
38. At start of the run V-7 automatically switches to LOAD and returns to INJECT after 30 sec.
39. After V-7 returns to INJECT
    V-4 → INJECT; V-6 → LOAD; V-5 → UP; V-8 → CENTRE; V-12 → LEFT
40. Remove the ampoule from rubber tube at V-11 and drain the water out of Purge Tower by switching V-11 → LEFT
41. Open the Nitrogen cylinder (< 2 atm. Pressure); V-8 → DOWN; Start the Nitrogen gas flow in Purge Tower and let it flow out through V-11 until no bubbling is visible from the frit of the Purge Tower.
42. V-5 → LEFT; V-11 → RIGHT
43. Start the heating coil and use the hot air blower to remove the moisture.
44. When no water drop is visible in Purge Tower stop the nitrogen gas flow.
45. When the run ends, the indicator returns to "PREP RUN" mode. Evaluate the Chromatogram, adjust the scale of view and take printout
46. Switch off the Vacuum pump and V-10 → DOWN (Air inlet)

3.5.3 Analytical Technique for Measurement of CFCs

The CFCs from water sample, stripper gas, CFC standard or atmospheric air trapped on the CFC trap by purge and trap system are injected into the analytical column of a Gas Chromatograph (GC) and analysed by an Electron Capture Detector (ECD).

An analytical method for simultaneous chromatographic separation of F-11, F-12 and F-113 was developed. The oven temperature, inlet port temperature, carrier gas flow rate and back flushing time are critical parameters in developing the analytical method for CFCs. The optimum values of these parameters established after several hundred experimental analytical runs are given in Table 3.8.

Table 3.8 Optimised analytical method for chromatographic separation of CFCs.

GC Parameter	Values
Oven	70 ^{0}C
Packed Inlet Port	65 ^{0}C
Carrier Gas	Ar (95%)/CH_4(5%)
Carrier Gas Flow rate	25 cc/min
Detector Base body	250 ^{0}C
ECD	270 ^{0}C
Runtime	10 minutes
Heating Steps	Isothermal

With a view to ensure the identical injection and back flushing time in each analysis, the operation of valves responsible for injection and back-flushing, is automated with the help of external event control facility in the GC. As shown in Figure 3.9, when position of valve V-7 is changed (from Inject to Load), the carrier gas passes through heated CFC trap and transports the trapped gases into GC. Thus, loading of V-7 at a fixed time in every analytical run ensures reproducible retention time. After the analysis has started, when position of valve V-7 is changed (from Load to Inject), the carrier gas passes directly into GC without carrying any more residues from CFC traps or pre-column. Thus, injecting of carrier gas from V-7 at a fixed time in every analytical run prevents late eluting compounds from entering into the analytical column. Therefore, these two operations of V-7 were automated.

Different injection volumes of stripper gas, CFC standard gas mixture and atmospheric air have been analysed by the above method. Some representative chromatograms for 2 ml, 5 ml and 10 ml injections of CFC standard gas mixture are shown respectively in Figure 3.10, Figure 3.11 and Figure 3.12. It is seen that all the three CFC species of interest can be identified in the injected gases based on their sequence of elution and characteristic retention time (RT). The values of peak area and retention time along with the relevant statistics for these representative chromatograms are given in Table 3.9.

The retention time and elution sequence are governed by different factors. The retention time of a compound on the column is governed by several factors such as: (i) length of column; (ii) chemical composition of the material packed in the column; (iii) the oven temperature and (iv) the carrier flow rate. In a particular system the adjustable parameters are optimised to achieve good separation of the peaks of interest within the reasonable run time. The system specifications and the optimised analytic method have been given in Table 3.3 and Table 3.8 respectively. The gases with progressively higher molecular weight (MW) elute progressively slower, therefore, the heavier gases elute later in the sequence of elution. Thus, sequence of elution is governed by molecular weighs of constituent gases in a mixture. In the present study, the observed elution sequence is: N_2O (MW = 44 $g.mol^{-1}$; RT = ~1.6 min), F-12 (MW = 121$g.mol^{-1}$; RT = ~2.27 min), (MW = 137.5 $g.mol^{-1}$; RT = ~3.8 min) and lastly F-113 (MW = 187.5 $g.mol^{-1}$; RT = ~6.1 min).

Because the parameter governing the elution sequence and RT remain constant (except when deliberately varied), the RT was found to be reproducible within ±0.1 minutes during large number of repeated analyses. Due to dependence of peak area on factors that vary unintentionally between different experiments, namely, (i) detector

sensitivity (indicated by value of baseline output voltage); (ii) quality of carrier gas (that can change when new cylinder is installed); (iii) bleeding of analytical column; and (iv) efficiency of moisture trap, considerable variation (up to 15%) in the this was observed between similar experiments carried out at different times. To achieve better reproducibility, it is therefore necessary to further automate and effectively control the unintentional variables. Peak Area calibration curve for estimating concentrations of various CFC species in unknown samples is shown in Figure 3.13.

Table 3.9 Values of peak area and retention time along with the relevant statistics for the chromatograms shown in Figure 3.10, Figure 3.11 and Figure 3.12.

RT: Retention Time; PA: Peak Area; Avg: Average; SD: Standard Deviation; %RSD = Percentage Relative Standard Deviation = SD*100/Avg

2 ml Injection of CFC Standard Mixture (See chromatograms in Figure 3.10)

Sample No.	N_2O		F-12		F-11		F-113	
	RT (minute)	PA (μv*min)	RT (minute)	PA (μv*min)	RT (minute)	PA (μv*min)	RT (minute)	PA (μv*min)
PRL-623	1.617	146214	2.267	14583	3.770	117668	6.065	11142
PRL-625	1.600	150418	2.267	12141	3.783	109864	6.100	11621
PRL-627	1.617	154807	2.267	15369	3.783	110161	6.083	12424
Avg	1.611	150480	2.267	14031.0	3.779	112564	6.083	11729
SD	0.010	4297	0.000	1683.3	0.008	4422	0.018	648
% RSD	0.609	2.9	0.000	12.0	0.199	3.9	0.288	5.5

5 ml Injection of CFC Standard Mixture (See chromatograms in Figure 3.11)

Sample No.	N_2O		F-12		F-11		F-113	
	RT (minute)	PA (μv*min)	RT (minute)	PA (μv*min)	RT (minute)	PA (μv*min)	RT (minute)	PA (μv*min)
PRL-615	1.610	272911	2.275	29779	3.803	285776	6.183	14170
PRL-617	1.610	263789	2.275	32565	3.803	273242	6.148	10454
PRL-619	1.617	279123	2.283	29743	3.817	276283	6.167	12092
Avg	1.612	271941	2.278	30696	3.808	278434	6.166	12239
SD	0.004	7713	0.005	1619	0.008	6538	0.018	1862
% RSD	0.251	2.8	0.203	5.3	0.212	2.3	0.284	15.2

10 ml Injection of CFC Standard Mixture (See chromatograms in Figure 3.12)

Sample No.	N_2O		F-12		F-11		F-113	
	RT (minute)	PA (μv*min)	RT (minute)	PA (μv*min)	RT (minute)	PA (μv*min)	RT (minute)	PA (μv*min)
PRL-634	1.600	846732	2.280	60682	3.813	687932	6.173	48771
PRL-636	1.600	941932	2.280	61745	3.813	698601	6.160	51241
PRL-638	1.583	971362	2.280	66645	3.813	738038	6.160	49461
Avg	1.594	920009	2.280	63024	3.813	708190	6.164	49824
SD	0.010	65143	0.000	3181	0.000	26394	0.008	1274
% RSD	0.616	7.1	0.000	5.0	0.000	3.7	0.122	2.6

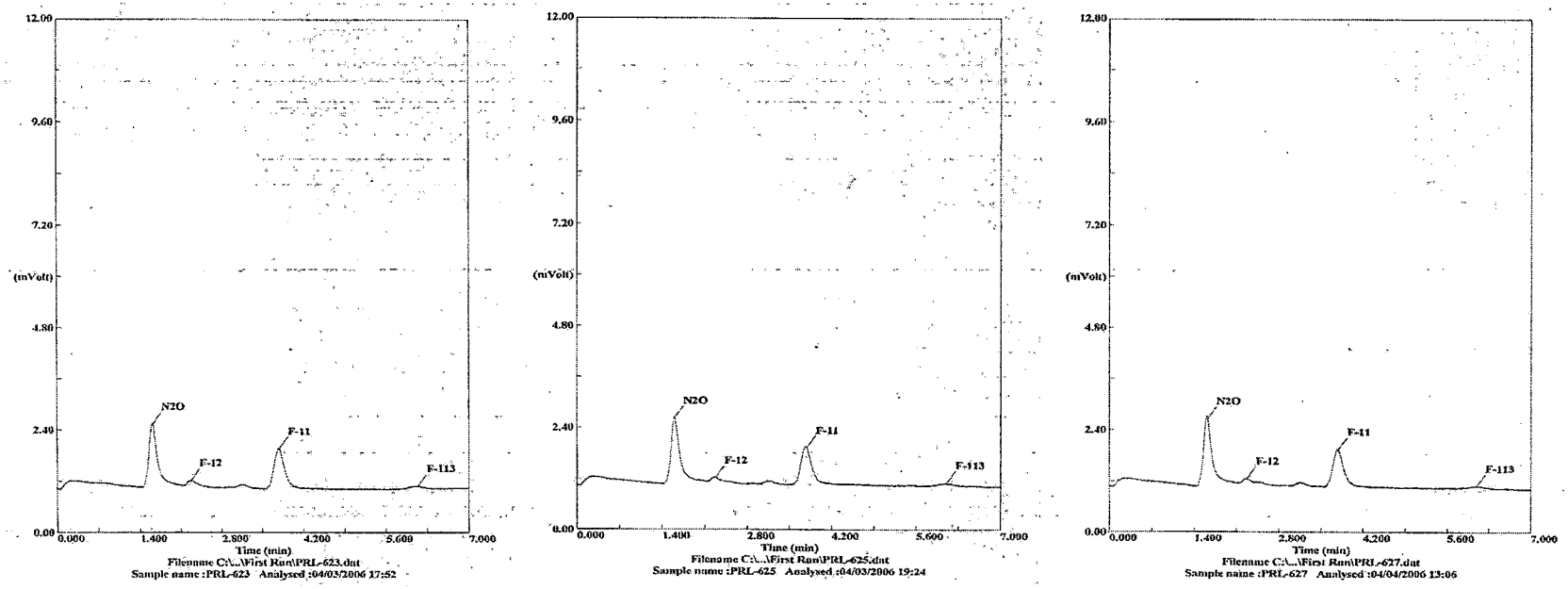

Figure 3.10 Three different chromatograms for 2 ml injection of CFC standard. Two CFC species of interest (F-12 and F-11) are identifiable from known elution time but F-113 peak is barely visible though it also can be identified from its known retention time.

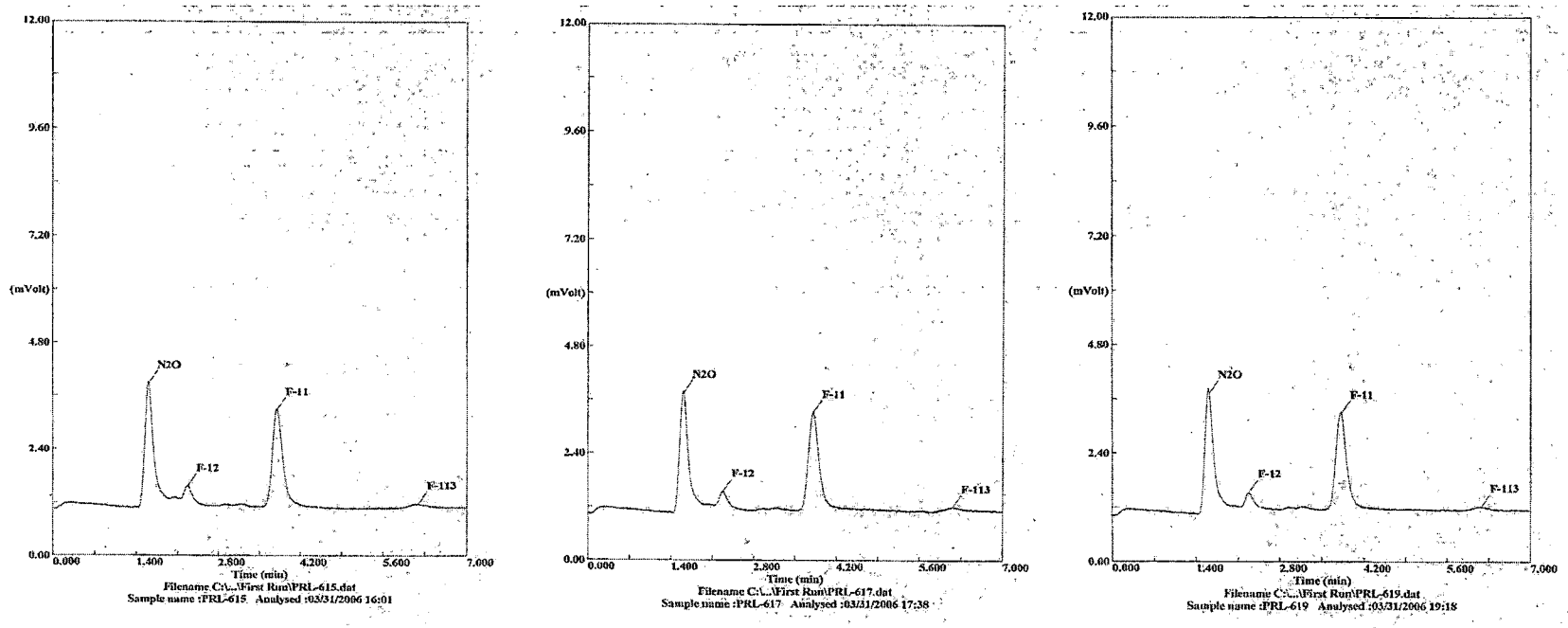

Figure 3.11 Three different chromatograms for 5 ml injection of CFC standard. Three CFC species of interest (F-12, F-11 and F-113) can be identified from their known retention time. Though identifiable, F-113 peak is small.

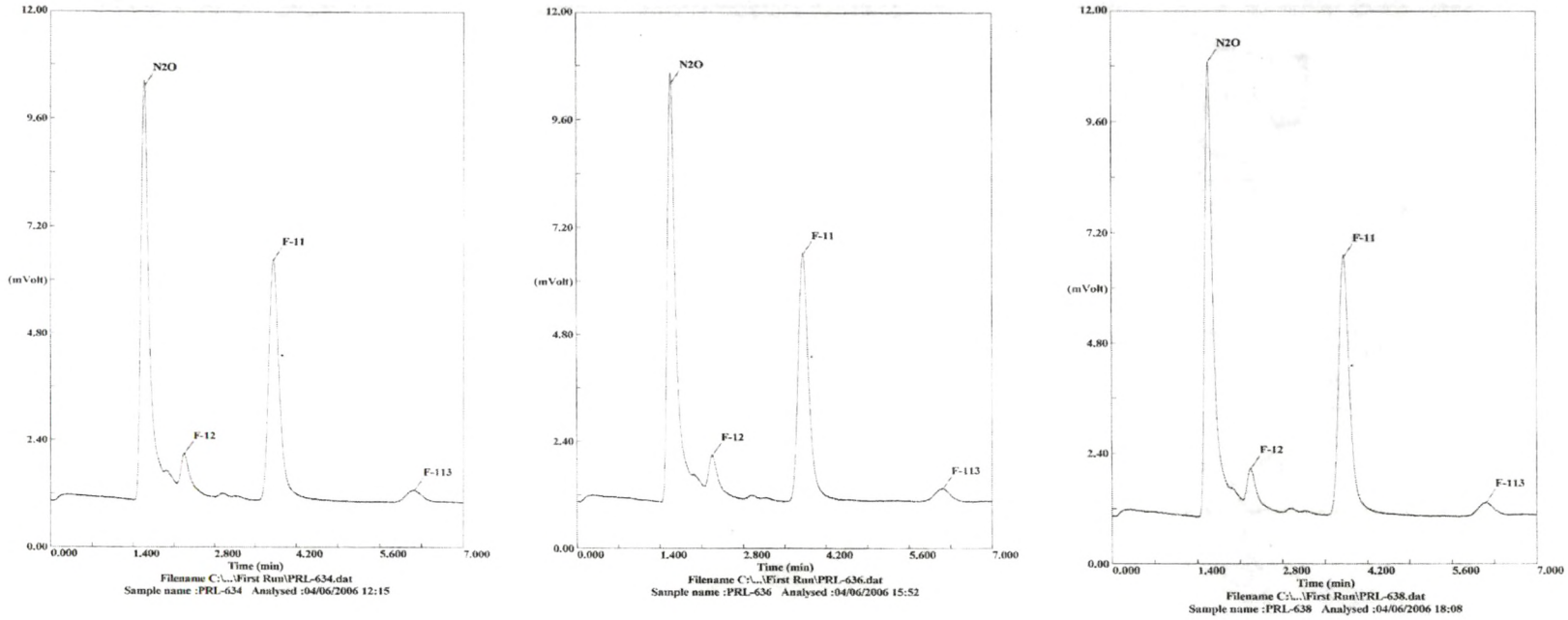

Figure 3.12 Three different chromatograms for 10 ml injection of CFC standard. All the three CFC species of interest (F-12, F-11 and F-113) can be identified from their known retention times.

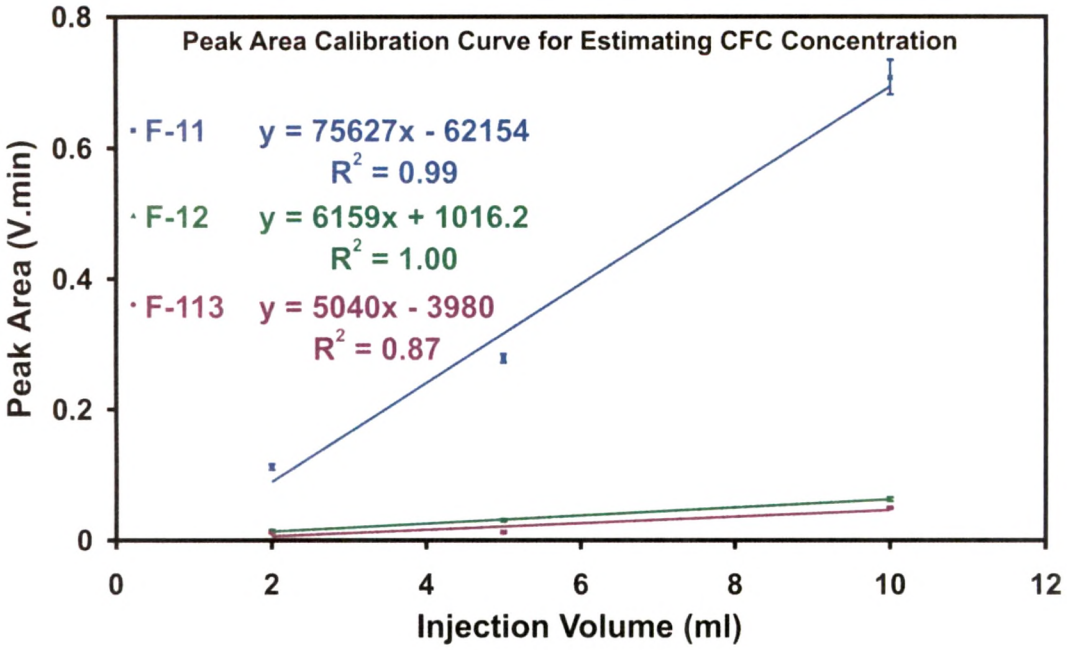

Figure 3.13 Peak area calibration curve for estimating CFC concentration in the injected gas sample. Concentration in the standard gas mixture used for calibration corresponds to: F-12 (4.834E-10 $ml.ml^{-1}$); F-11 (2.303E-10 $ml.ml^{-1}$); F-113 (7.3E-11 $ml.ml^{-1}$).

Additionally, it is also necessary to undertake peak area calibration experiments by analysing different volumes of CFC standard mixture before initiating the analyses of water samples after every few water samples and to include a background run before and after every analysis.

This completes the objective of setting up of the CFC laboratory and establishing the field and laboratory protocol for CFC analyses. Since the field sampling and analyses of groundwater samples did not form part of this study, no results of CFC analyses of groundwater have been included in Chapter 4. Results of various other field and laboratory investigations undertaken using other tracer techniques are, however, reported in Chapter 4.