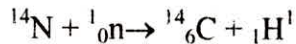

Measurement of Radiocarbon in Natural Water Samples

1. Introduction

Libby discovered radiocarbon in atmospheric CO₂ in 1946. He determined its half-life to be 5568 yrs (the Libby half-life) and recognized then its potential as a dating tool. Godwin subsequently refined its half-life to 5730 yrs.

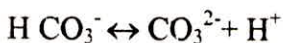
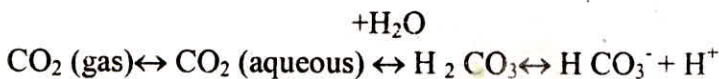
Carbon-14 is produced naturally in the atmosphere by cosmic neutrons reaction with nitrogen atoms.

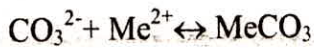


Carbon-14 is also been added to the atmosphere since 1952 as a result of testing of thermonuclear devises. In 1963, the carbon-14 concentration reached to its peak which was about 200 times the pre-bombed level +2000‰ (1000 ‰ (permill) = 100%). After coming into existence of the treaty banning the open atmospheric nuclear tests, the anthropogenic input of carbon-14 in the open environment stopped and the existing peak started reducing.

Once produced, the carbon-14 gets oxidized to carbon-di-oxide and becomes part of the atmospheric carbon-di-oxide reservoir. From the atmosphere reservoir, CO₂ enters into the water cycle mainly through two path ways:

(i) Chemical process of dissolution:





Where, Me^{2+} is generally Ca^{2+} but can include Mg^{2+} , Fe^{2+} and sometimes 2Na^+ in highly saline continental brines.

(ii) Biological pathway: In this, assimilated atmospheric CO_2 by plants is released in soil zone and also through decay of organic matter.

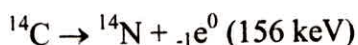
The total dissolved inorganic carbon (TDIC) in groundwater is the sum of $\text{CO}_{2(\text{aq})}$, H_2CO_3 , HCO_3^- , and CO_3^{2-} . Distribution of DIC species can be inferred from pH of groundwater (figure 1)

The age of groundwater in confined aquifer is the time elapsed since its infiltration in recharge area or in general it is an average turnover time. At the time of recharge if the specific ^{14}C activity of DIC of groundwater is A_0 and at the point of sampling if it decays and remains to A then radiocarbon age of groundwater in years is given by:

$$t \text{ (yrs)} = -8267 \ln (A/A_0).$$

(This is deduced from the radioactive decay equation $A = A_0 e^{-\lambda t}$)

The activity of ^{14}C is measured using ultra-low-level liquid scintillation counter by monitoring β emission of ^{14}C active carbon.



The measured ^{14}C value is expressed in terms of percent modern carbon (pmc).
The modern carbon is an international standard that refers to the specific activity

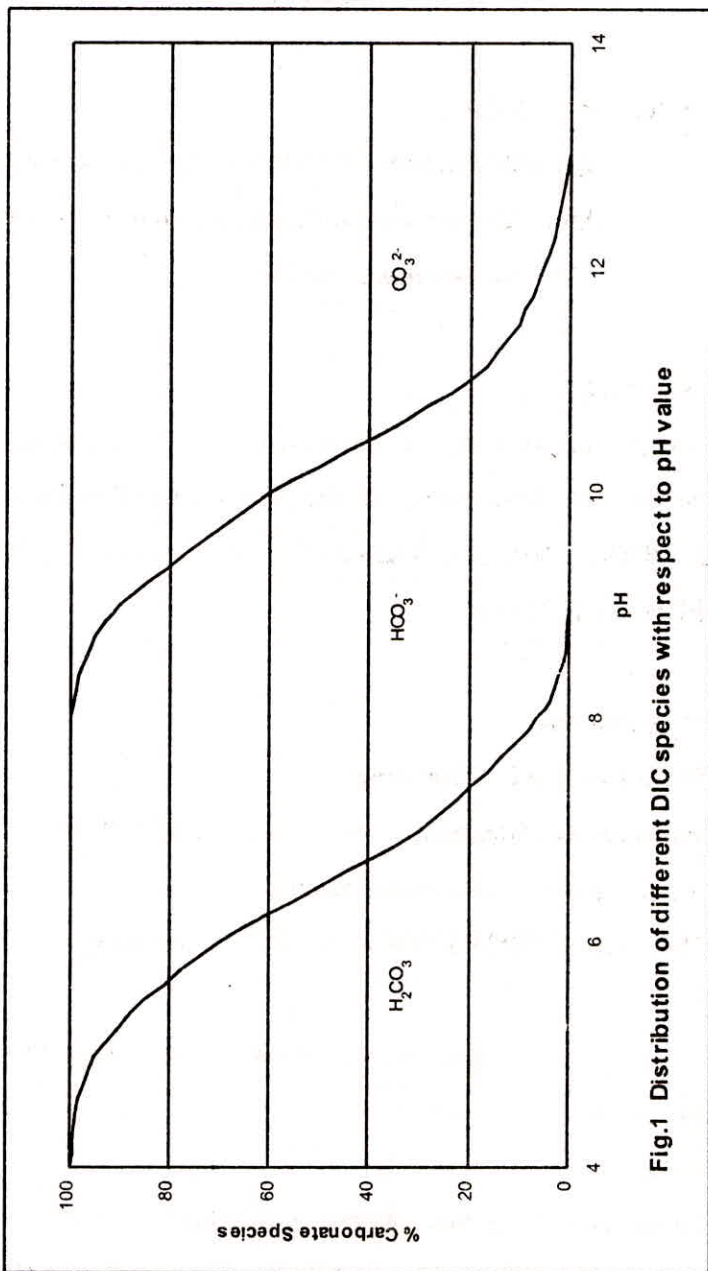


Fig.1 Distribution of different DIC species with respect to pH value

of wood grown in 1890 (unaffected by any fossil fuel combustion). The activity of this standard is 0.226 Bq (13.56 dpm) per gram of carbon and corresponds to 100 pmc. The Carbon-14 activity of a sample is also expressed in terms of permil that refers to as permil variation from the standard ($\delta^{14}\text{C}$).

Count Rate: 1 Bq = 1 dps

dps: abbreviation for disintegration per second.

dpm: Abbreviation for disintegration per minute

1dps corresponds to 60dpm.

Stable Isotope Standard:

PDB- Stable isotope standard for ^{13}C measurement. It is a calcite from a fossil Belemnite (*Belemnitella Americana*) of the Cretaceous Pee Dee formation of South Carolina (PDB-1). VPDB is Vienna PDB. It is identical to PDB. The ratio ($^{13}\text{C}/^{12}\text{C}$) in VPDB = 1.1237×10^{-2}

International ^{14}C Standards:

0.226 Bq (13.56 dpm) per g C = 100 pmc

Primary Modern Reference Standard - NBS_{oxi} (Code-SRM 4990)

Activity = $0.95 \times (100\text{pmc})$ (ox- oxalic acid)

Activity of NBS_{Oxii} (code- SRM 4990C) = $0.7459 \times (100\text{pmc})$

The ^{14}C age of a sample having initial activity 100 pmc and present activity A is expressed by the equation.

$$t (\text{yrs}) = -8267 \ln(A \text{ in pmc}/100)$$

If the initial activity is not 100 but is diluted by a factor q due to some contamination (example, $q=0.5$ i.e., initial $A_0=50\text{pmc}$) then ^{14}C age will be expressed as, $t (\text{years}) = -8267 \ln (A \text{ in pmc}/qx100)$

1.1 ^{14}C Dating Procedure

Carbon-14 dating of groundwater is done by measuring ^{14}C activity in its dissolved inorganic carbon. Various steps involved in dating procedure are:

i) Sample collection: Groundwater sample is collected in the form of BaCO_3 by precipitating the dissolved inorganic carbon (TDIC).

ii) Extraction of CO_2 from the precipitate by acidifying it.

iii) Sample preparation: Sample can be prepared in two ways from the extracted CO_2 . These are (a) Absorption technique: The extracted CO_2 is directly absorbed in absorber (carbosorb) - scintillator mixture and (b) Benzene synthesis: The extracted CO_2 is converted into benzene using acetylene as an intermediate step. A suitable scintillator is then added to the benzene.

iv) Counting: The absorbed CO_2 - scintillator mixture or benzene-scintillator mixture is then counted in liquid scintillation counter for estimating the concentration of radioactive carbon in it.

v) Estimating ^{14}C age: Specific activity of sample is determined by comparing with standard having known specific activity and is expressed in terms of pmc. Appropriate models are used to estimate the factor q to correct the deviation of initial ^{14}C activity from 100 pmc. Groundwater age is calculated from the estimated sample pmc and q factor.

2. Groundwater Sampling for ^{14}C dating

Carbon-14 dating is normally done on groundwater older than 100 years except the measurement of initial activity in recharge areas. Therefore it is

desirable to have groundwater pre-dated by tritium or other means to identify recharge areas and old groundwater before any sampling for ^{14}C dating.

2.1 Chemicals and materials required

1. 80 or 100 l plastic bags sealed in all sides except for a small opening at the top
2. 1 litre HDPE sample shipment bottle (Tarson make)
3. Barium chloride solution in DDW ($\text{BaCl}_2 \cdot \text{H}_2\text{O}$ reagent grade)
[Preparation of barium chloride solution – Dissolve 500 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 1000 ml of double distilled water. Isolate the precipitate and collect only the supernatant clear solution]
4. 10N sodium hydroxide (NaOH) solution in DDW
[Prepare sodium hydroxide solution a few weeks in advance. Add 500 gm of NaOH pellets in 1250 ml of DDW. Isolate the precipitate and collect the clear solution only. To make the solution carbonate free, add 20ml of saturated BaCl_2 solution and then allow the solution to stand for few days. Insoluble precipitate settles out and the clear supernatant solution is carefully decanted and saved.]
5. Praestol solution - polyacrylamide-electrophoresis grade (Add 10 grams of praestol salt in one litre DDW)
6. A rope of good strength, a knife and a scissors

2.2 Sampling procedure

1. First carry out the field tests for pH, alkalinity and sulphate to determine the concentrations of bicarbonates/carbonates (H_2CO_3 (aq), HCO_3^- and CO_3^{2-}) and SO_4^{2-} concentrations in the sample water. (Alternatively use the existing data). Determine from the table given below how much barium chloride is required to precipitate the sulphate and carbonate and the amount of sample water required for 3g of carbon (assuming 60% overall

efficiency for carbonate precipitation, CO₂ extraction, its absorption or benzene preparation).

TABLE - Carbonate Sampling: Volume and Reagent Requirements

Alkalinity mg/L	Grams of Barium Chloride for a 50L sample Volume									
	0	200	400	(Per range of SULPHATE = mg/L)					1gC	3gC
			600	800	1000	1500	2000			
50	5	18	30	43	56	69	100	140	100	300
100	10	23	35	48	61	74	105	145	50	150
150	15	28	40	53	66	79	110	150	35	100
200	20	33	45	58	71	84	115	155	20	75
250	25	38	50	63	76	89	120	160	20	60
300	30	43	55	68	81	94	125	165	15	60
350	35	48	60	73	86	99	130	170	15	50
400	40	53	65	78	91	104	135	175	15	44
450	45	58	70	83	96	109	140	180	10	35
500	50	63	75	88	101	114	145	185	10	30
600	60	73	85	98	111	124	155	195	10	25
1000	100	113	125	138	151	164	195	235	5	15

- Rinse the plastic bag and the sampling bottle at least three times with sample water.
- Fill the plastic bag with sample water and allow it to overflow by at least 50%. Filling tube should preferably be in the bottom of plastic bag to avoid turbulence and dissolution of atmospheric CO₂.
- Add the necessary amount of NaOH (about 30 ml of 10N) quickly and seal the bag airtight. Roll the bag to mix thoroughly. Now check the pH with an indicator paper (pH must be >10)
- Open the bag again and add the pre-measured amount of BaCl₂.H₂O quickly according to the Table. (plus 20% extra to be on safer side) Add 50ml of praestol solution. Seal the bag tightly and again roll for well

- mixing. Hold the bag vertically and allow the precipitate to settle for a minimum of 30 minutes. Gently keep tapping the bag every five minutes.
6. Hold the bag vertically and systematically make cuts in the bag starting from top and moving towards bottom. The cuts must allow clear water to flow out without much turbulence. The cuts (slits) may be 2 inch in width horizontally. When the precipitate alone is left in the bag, tie the bag from a nearby tree branch with the rope.
 7. Hold a bottom corner tip of the bag tightly and cut it open with the scissors and let the precipitate flow into the sample bottle (1 litre – Tarson™ make).

The percentage distribution of carbonate ions in the form of CO_3^- , HCO_3^- and $\text{H}_2\text{CO}_3(\text{aq})$ contributing the total alkalinity can be estimated from pH and percentage distribution curve. Praestol accelerates the speed of precipitation it also adds 0.001g carbon i.e. 0.03% of organic carbon to the system.

Example: If the alkalinity of the sample is 300 mg/l and sulphate is 1500 mg/L, (typical of a saline groundwater having an EC of 40,000 $\mu\text{s}/\text{cm}$) then for a 50 litre sample, 125 g of BaCl_2 is added i.e., 250 ml of BaCl_2 solution (as the solution is made in 1:2 ratio). The quantity of water to be treated chemically at field site for collecting the desired amount of BaCl_2 precipitation, as per the required quantity of carbon-14 (1 gm or 3gm), can be noted down from the table given below, i.e. in the present example, 60 lt. of groundwater will be sufficient. However, it is advised to collect/treat 25 to 30% more water keeping in view the loss of ^{14}C amount of various stages of sample processing.

3. Sample Preparation

In sample preparation, the DIC is either converted into benzene (section 3.2) or is absorbed in the form of CO_2 in an absorber-scintillator mixture (see

section 3.4). Benzene analysis provide more accurate results but is an order of magnitude more expensive and requires more skill in handling the equipment compared to the CO₂ absorption technique. If a 10% accuracy can be tolerated and also if the sample age lies within a range of few hundred to 35ka then CO₂ absorption technique can be used in place of benzene synthesis technique. Both the methods require extraction of CO₂ (section 3.1) as the 1st step in their sample preparation. Therefore, CO₂ extraction and volume measurement part of benzene synthesis line can also be used in CO₂ absorption technique.

Benzene preparation is carried out in the benzene synthesis line (Fig. 2a). It contains four basic sections A (CO₂ Extraction Unit), B (gas storage and volume assessment unit), C (acetylene preparation unit), and D (benzene conversion unit). Functions of each of these sections are described below:

Section A: This contains a reaction unit and a moisture trap. CO₂ that comes out from reaction unit due to reaction with sample and reactant chemicals (H₃PO₄, KMnO₄ etc.) is made moisture free by passing through moisture trap.

Section B: This section serves as a storage and volume assessment unit for the CO₂ that is extracted. The unit inlet contains P₂O₅ trap (T₂) to remove final traces of moisture from the CO₂ entering in this unit. It also contains traps T₃ and T₄, which are kept at -195⁰C (at liq. N₂ temp.) where gaseous CO₂ is converted into dry ice. A 5L balloon with a pressure gauge is provided in this unit to measure the gas volume.

Section C is used only for benzene synthesis and section D is modified as shown in figure 2b in case of carbosorb technique, the CO₂ stored in unit C is directly transferred in the CO₂ storage cylinder.

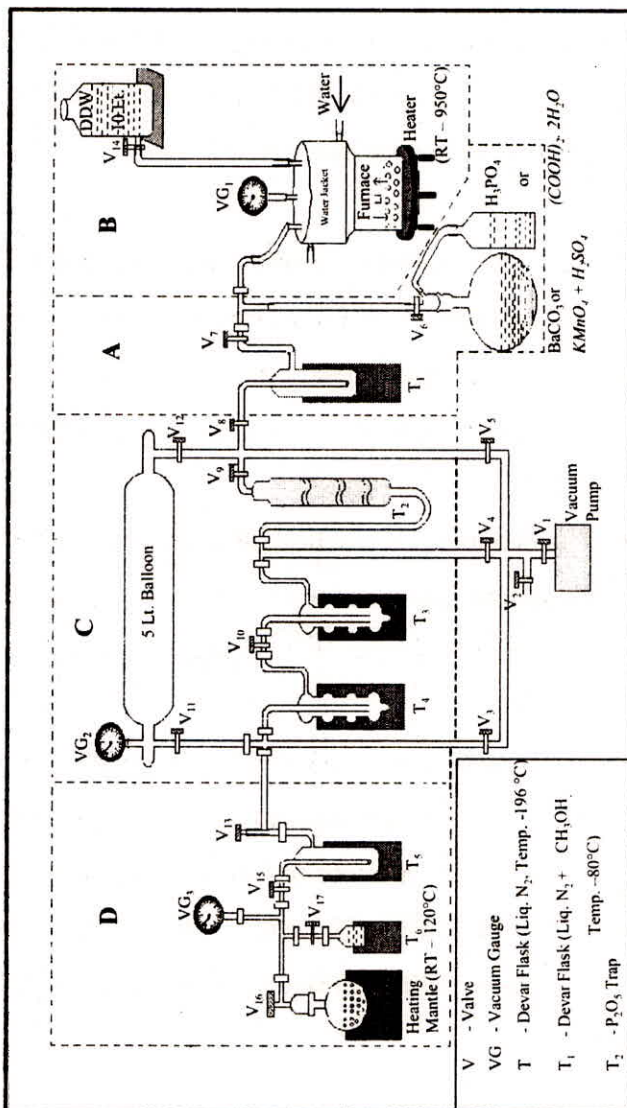


Fig. 2a Benzene Synthesis Line

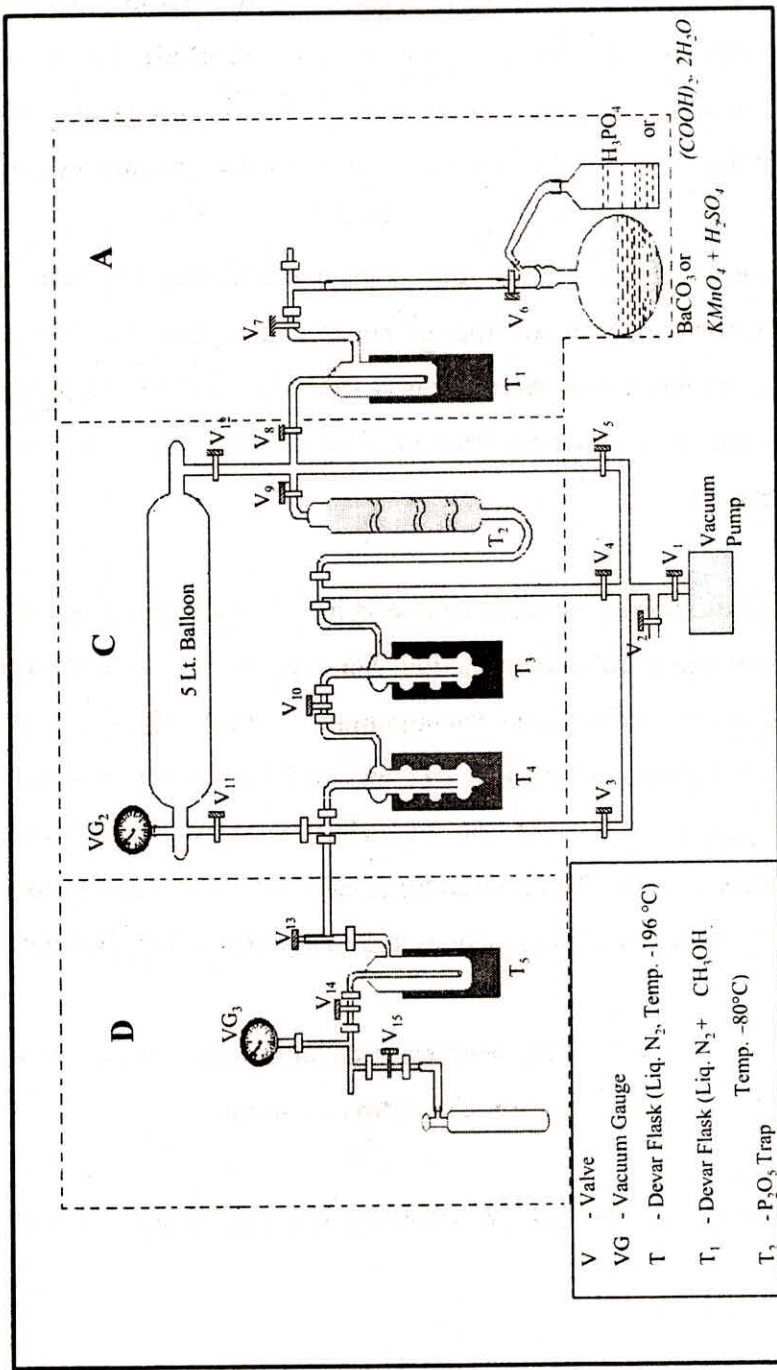


Fig. 2b CO₂ Extraction Line

Section C: In this unit, CO_2 is converted into acetylene. It contains a stainless steel furnace and a water chamber. In the furnace, lithium is heated to $\sim 700^\circ\text{C}$. At this temperature, CO_2 from the block B is let into the furnace. The reaction between CO_2 and lithium produces lithium carbide. The carbide is then hydrolyzed by water at room temperature. The reaction generates acetylene, which is then transferred to the unit B for volume measurement/storage.

Section D: This is the last unit of the benzene line. The main part of this unit is a flask containing an adsorber to trimerize acetylene into benzene at room temperature. The benzene is then released from this bottle by warming to 80°C . The benzene vapors released out from the catalyst bottle are cooled and collected in benzene trap T_6 .

Before the start of benzene synthesis line, it is ensured that the line is free of any vacuum leaks and contamination. For this, the line is brought to vacuum and is then disconnected from the vacuum pump. All the valves are closed and the line is kept for monitoring for about 10 hours to check for any vacuum leaks using the vacuum gauges VG_1 , VG_2 and VG_3 (VG_1 and VG_3 are required only for benzene synthesis). After the required time, each valve proceeding from the gauge is sequentially opened to check vacuum loss in corresponding trap/unit.

As the unit C is not used in CO_2 absorption technique, checks for vacuum leak are not required for this block for CO_2 absorption technique.

After ensuring for vacuum leaks, evacuate the line and close all the valves.

3.1. Preparation of CO₂

As shown in Fig.2a, units A and B are used for the preparation of CO₂.

Take the carbonate sample in round bottom flask (2000 ml) in the form of paste by adding little amount of distilled water and measure the pH for records. Attach the H₃PO₄ filled bottle with the help of two-way joint with one end connected to V₁. Now open V₁ and evacuate flask and bottle as in part A of the line as discussed above.

Put the trap (T₁) in Devar flask containing Methanol + Liq. N₂ (-80°C) to trap the moisture. (Trap T₂ should be filled with P₂O₅ earlier before evacuating the system). Now put the T₃ and T₄ in Liquid N₂. Open V₁, V₂ and V₅ and mix a small amount of H₃PO₄ in the sample in steps. CO₂ will evolve and is seen as bubbles. The rate of reaction should be slow to maintain gas pressure inside the reaction bottle within a limit to control any possible leak out from the connector joints. The slow reaction rate also ensures enough travel time of CO₂ through moisture retention traps T₂ and CO₂ condensing traps T₃ and T₄. The temperature of T₃ and T₄, which are maintained at -196°C by liquid nitrogen, converts CO₂ into dry ice. The non-CO₂ gases that do not get condensed in the traps may be allowed to pass into the 5L balloon to avoid development of excess pressure in the condensing traps. The residual gases collected in the 5L balloon can be quantified and used in efficiency calculation. Ensure the magnetic stirrer beneath the round bottom flask is switched on to facilitate continuous mixing of H₃PO₄ with BaCO₃/marble powder. H₃PO₄ reacts with marble much slowly (about four times slower) compared to that with BaCO₃. Raise the level of Liquid N₂ over T₃ very slowly. This may be achieved by adjusting the laboratory jack below T₃. After filling T₃ open V₁₂ for extra CO₂ to be trapped in T₄.

Theoretically, 50g of sample will produce 5.5 liters of CO₂ (that is required for 3ml benzene), and this amount can be stored in single trap T₃.

After complete extraction of CO₂ close the valves V₁, V₂, and V₅. Detach the H₃PO₄ bottle from the line for safety reasons. Measure the pH of remaining substance in flask using pH indicator paper for records. Open V₆ and V₉ and pump out the residual gases. Close V₆ and V₉. Allow transfer of CO₂ by removing the LN₂ trap into the glass balloon and note the pressure in VG₂.

3.1.1 Measurement of CO₂ volume

Evacuate 5L balloon very slowly through T₄ and T₃ to trap CO₂ if left earlier. Close V₇. Remove liquid nitrogen devar flasks from trap T₃ and T₄. Warm-up CO₂ traps to release CO₂ into the 5L balloon. See that the pressure in 5L balloon does not exceed the limit 1-atmosphere. Otherwise condense the remaining gas into the trap T₄. Measure difference in pressure before and after release of gas into the 5L balloon to calculate the gas volume.

Some times we get excess carbon dioxide (> 5 lit.) from sample, which can be stored in T₃ and T₄ but can not be measured in the glass balloon because of limited capacity (5 lit). For this purpose the following action can be taken. Ensure all the valves in the line are closed except V₁₂. Remove devar flask from trap T₃ and empty it by passing all CO₂ into trap T₄ by blowing hot air over T₃ (with the help of hot-air blower). When T₃ becomes empty close V₁₂. Open V₁₃, remove devar flask from trap T₄ and pass 5 litres of CO₂ in to the glass balloon (by noting the reading in VG₂). Put T₃ in devar flask and open V₄ and V₅ to condense the CO₂ from glass balloon into T₃. When the glass balloon becomes empty remove the devar flask of trap T₄ and transfer the CO₂ from T₄ to glass balloon again. Again repeat the process to condense the gas in T₃. This way one can manage the excess CO₂ formed from the sample.

3.1.2 Extraction of CO₂ from Oxalic acid

For preparing 5 liters of CO₂ (considering 100% efficiency), take 7g of KMnO₄ dissolved in 150ml of distilled water in a reaction bottle and add 22ml of conc. H₂SO₄ to it. Take 13.1g oxalic acids dissolved in 150ml of distilled water in an acid-dropping bottle and connect it to the side arm of the reaction bottle. Connect the reaction bottle to the benzene line and evacuate the system. Attach a cooling bath to the reaction-bottle, as the reactions are exothermic. Start adding KMnO₄ slowly and collect CO₂ in liquid nitrogen cooled traps T₃ and T₄ as described in the section for CO₂ extraction from carbonate precipitate. Completion of the reaction is noted by a colorless solution and cease in the production of CO₂ bubbles.

3.2 Benzene Synthesis

Prior to conversion of CO₂ into acetylene for benzene synthesis, a small fraction of CO₂ is extracted and stored in a cylinder for ¹³C measurement. The ¹³C data is used in correcting the ¹⁴C age for carbonate dissolution.

3.2.1 Preparation of acetylene from carbon dioxide

Units B and C are used in preparation of acetylene from carbon-dioxide. This is a two step reaction. The first step involves conversion of CO₂ to lithium carbide by absorption on hot molten lithium and in the second step acetylene is generated from carbide by hydrolysis.

Step1: Absorption of CO₂ in Lithium

Lithium is normally stored in Petroleum Ether to avoid moisture or air contact otherwise it may form its hydroxide or oxide, as the case may be.

Take a quantity of lithium that is 2.5 times that of the extracted CO₂ [CO_2 (in lit) \times 2.5 = Li (in gm)]. Place the lithium in the furnace. Check V₂₁ is closed tightly. Attach the furnace with line through V₂₀. Evacuate this part (B) by

opening V_{20} , V_2 , V_3 and V_9 . Put the furnace on heater and raise the temperature to 750°C (the temperature sensor should touch only the furnace and not the heating element). The upper part of the furnace must be cooled through water jacket provided in the furnace. After 10-15 minutes evacuation should be stopped and the valves V_{20} , V_2 , V_3 and V_9 should be closed. Now start admission of CO_2 in the furnace through V_4 , V_2 and V_{20} in a controlled manner i.e. pressure should not exceed 60 mm of Hg in VG_1 . For complete reaction the speed of CO_2 admission should be low. During CO_2 admission, the temperature should be controlled between $775\text{-}790^{\circ}\text{C}$. After complete admission, close the valves V_4 , V_2 and V_{20} and raise the temperature up to 925°C and maintain it for 25 minutes. Now switch off the heater and let it be cooled down to room temperature.

Step 2: Hydrolysis of Lithium Carbide

After cooling the furnace, open V_{21} to allow double distilled water (DDW) into the furnace at a very slow rate (since the pressure in the furnace should not increase by 260 mm Hg). As a thumb rule, about 3 liters of DDW is required for 5 litres of CO_2 . Shake the furnace carefully to ensure reaction of DDW with the lithium carbide that may be sticking to the walls of the furnace. This process results in evolution of acetylene that should be trapped in T_3 and T_4 using Liquid N_2 devar flasks. The moisture of the gas will be trapped in T_1 as stated earlier (Step III(b)). For this, open V_{20} , V_2 , V_5 , V_{12} and V_{13} to trap acetylene in T_3 and T_4 and residual gases to go into the glass balloon. This should be done with utmost care.

In certain cases, the quantity of residual gases is large and hinders the flow of C_2H_2 into the line. This may be tackled by closing V_5 and opening V_7 . The volume of C_2H_2 is also measured using glass balloon as it was done in case of CO_2 .

3.2.2 Trimerization of Acetylene into Benzene

This is also a two step process. The first step is activation of catalyst and then in the second step the activated catalyst is used in trimerization of acetylene into benzene. The unit-D is used for this purpose. The catalyst activation step can be completed along with CO₂ extraction and its conversion into acetylene.

3.2.2.1 Activation of Catalyst (Al₂O₃+Cr₂O₇)*

This requires an oven for drying and unit D of benzene synthesis line. About 185g of catalyst, Aluminum Chrome (Al₂O₃+Cr₂O₇) is required for the extraction of 3ml benzene sample. The activation procedure is as given below:

[* **Catalyst performance** - Two types of catalyst can be used for trimerization of Acetylene into Benzene. These are (1) Aluminum Chrome (Al₂O₃+Cr₂O₇) and (2) Vanadium Chrome. The purity of Benzene extracted from these catalysts can be seen from fig. 3]

1. Take 150 gm catalyst and dry it in oven at 100°C for 6 hrs and then allow cooling in a vacuum dessicator.
2. Put the catalyst in a 500 ml round bottom silica flask and heat it 100°C for 2 hrs with dynamic pumping. While heating and evacuating, flush the catalyst column with dry air and re-evacuate it twice or thrice. This can be done within the benzene line (Figure 2a) by evacuating part D and keeping T₅ in Liq. N₂. Allow air from valve V₁₅, open V₁₆, V₁₇ and then V₁₉ to flush the catalyst. Close V₁₉ and V₁₅ to evacuate part D [STEP IIIa (iii)] by opening V₁₁. After few minutes open V₁₉ also to evacuate flask and check the vacuum from VG₃. Close all the valves. This process should be repeated twice or thrice.
3. Heat the catalyst column at 150°C for 3 hrs in a similar manner as in step - 2.

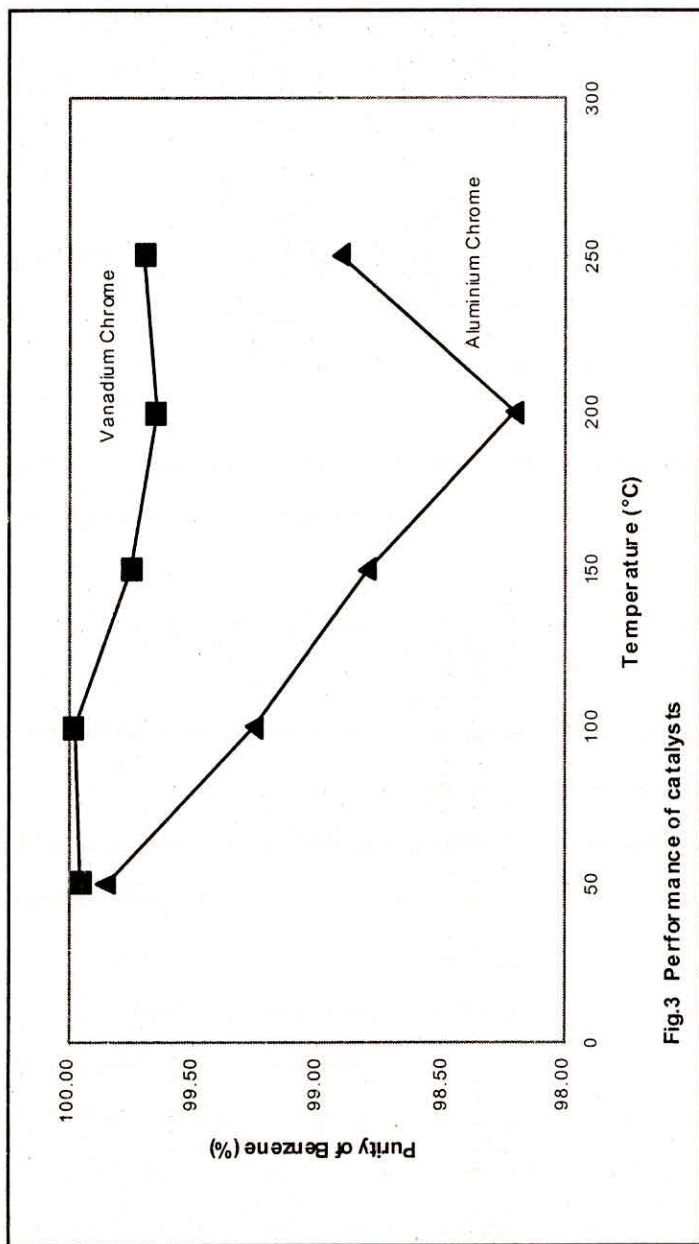


Fig.3 Performance of catalysts

4. Heat the catalyst column at 200°C for 4 hrs in a similar manner as in step - 2.
5. Heat the catalyst column at 300°C for 4 hrs in a similar manner as in step 2. Stop heating and allow it to cool it down to the room temperature. Now it is ready for the absorption of C_2H_2 .

Alternately, take, 190g of catalyst and heat it overnight (~8-12 hrs.) at 250°C under dynamic vacuum. The vacuum should reach to 10^{-3} torr. After activation, cool it down to room temperature for the acetylene adsorption. Once used, the catalyst can not be re-used for the second time.

3.2.2.2 Trimerization of acetylene:

This is the last step in the benzene synthesis and in this part of the process; acetylene is transferred from unit-B to unit-D after trimerisation it is recovered as benzene. The details of the procedure to be followed are given below.

Remove the devar flasks of T_3 and transfer C_2H_2 from T_3 to T_4 and close V_{12} . Remove the devar flask of T_4 and allow acetylene to be stored in the glass balloon through V_{13} with the help of a hot air blower. [If there is excess C_2H_2 (> 5 litres) then one can repeat the process as in case of excess CO_2 and can measure the C_2H_2] Measure C_2H_2 , and condense whole C_2H_2 in T_4 with the help of Liquid N_2 . Close V_{13} , open V_{14}, V_{16} and put T_5 in Liquid N_2 . Heat T_4 and transfer whole gas in T_5 . Close V_{14} and V_{16} .

In this last step, only part D of the line is used. Open V_{17} and V_{19} and allow C_2H_2 to react with catalyst at room temperature ($20 - 25^{\circ}\text{C}$). When complete acetylene has been absorbed, close V_{17} and V_{19} . Since the trimerization is a slow process to ensure completeness of trimerization, leave the system at room temperature for few hours after the final inlet of acetylene.

3.2.2.3 Recovery of Benzene trapped in catalyst

For recovery of benzene, put the flask containing catalyst in heater and maintain temperature between 100-110°C. Benzene will be released from the catalyst and can be trapped in T₆ (open V₁₉ and V₁₈). This process will take about 1-2 hrs for 3ml benzene*. Close V₁₉ and put T₅ in the liquid nitrogen. Pass dry air in the line by opening V₁₅, V₁₆, and V₁₇. Detach T₆ and measure the recovered benzene in volume as well as weight and transfer the benzene into a glass vial for counting.

Normally, the complete C₆H₆ is not recovered during the above process as 20% of benzene remains in the catalyst. Therefore, extra efforts are required to achieve the complete recovery of C₆H₆. Put T₅ in Liq. N₂ and open V₁₅, V₁₆ and V₁₇. The moisture of incoming air will be trapped in T₅ and only dry air will be passed. When the pressure in the part D of the line becomes equal to atmospheric pressure (VG₃, at 0 mm Hg) close V₁₆ and open V₁₉ at once and allow dry air to fill the catalyst flask then close V₁₉. Again pass air in the line by opening V₁₆. Repeat the process until the flask pressure becomes equal to the atmospheric pressure. Now close V₁₉ and evacuate the part D through V₁₁ until T₅ becomes dry. Again put T₅ in Liq. N₂, open V₁₉ and evacuate again. The dry air from the flask will mix with the remaining C₆H₆ in the catalyst. Benzene will be trapped in T₅. When pressure drops to -760 mm Hg close V₁₁ and V₁₆. Remove devar flask containing Liq. N₂ from T₅, open V₁₈ and close V₁₉. Now heat the T₅ with a hot-air blower. The trapped C₆H₆ in T₅ will be transferred to T₆ that is under Liq. N₂. This process will improve the benzene recovery from the catalyst by 20%.

The benzene is stored in a plastic or glass vial and stored in refrigerator till it goes for counting in Liquid Scintillation counter. Before counting, benzene

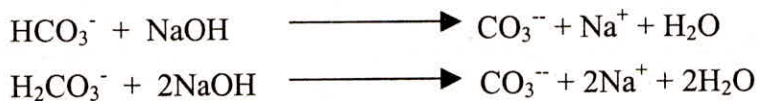
sample is mixed with a scintillator at 1:4 parts (1 part scintillator, 4 parts benzene sample).

[Scintillation Cocktail: Certain organic compounds (scintillates) fluoresce when exposed to ionizing radiation. Each fluorescent event is proportional to a radioactive decay event, and the frequency of these events is directly proportional to the number of radioactive atoms present in the sample. In ^{14}C dating, scintillate solutions are mixed with the sample before counting. The scintillators are special organic compounds and are referred as cocktail. The most normally used scintillator in ^{14}C dating is a mixture of PPO + POPOP (6 g and 0.2 g/L respectively) dissolved in toluene. This scintillator is used only with samples made from Benzene Synthesizer method. Sample and scintillator are added in 1 part to 4 parts respectively.]

3.3 Reaction Summary

Sample Collection

Step 1: Raising of pH by NaOH

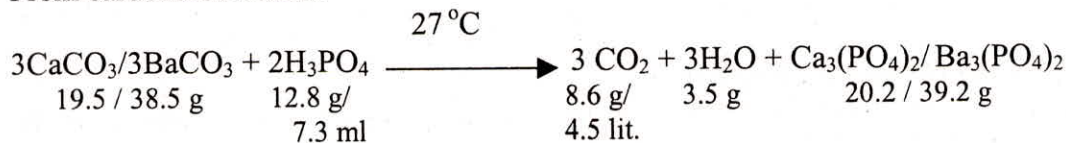


Step 2: Precipitation

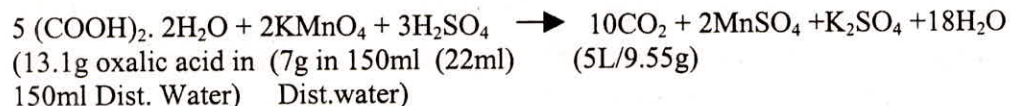


CO₂ Preparation

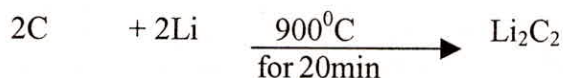
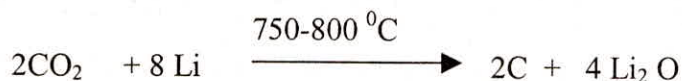
From carbonates/marble



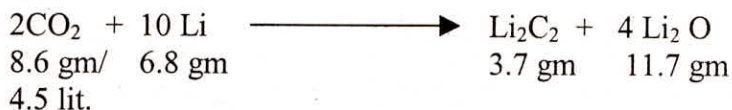
From Oxalic acid



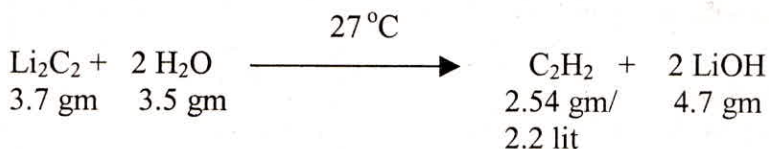
Lithium Carbide (Li₂C₂) Preparation



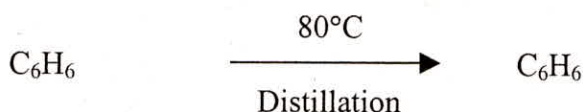
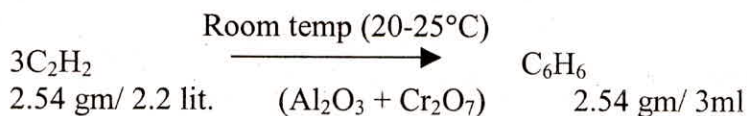
Net Reaction:



Acetylene Preparation (Hydrolysis of Li₂C₂)



Benzene Preparation from Acetylene



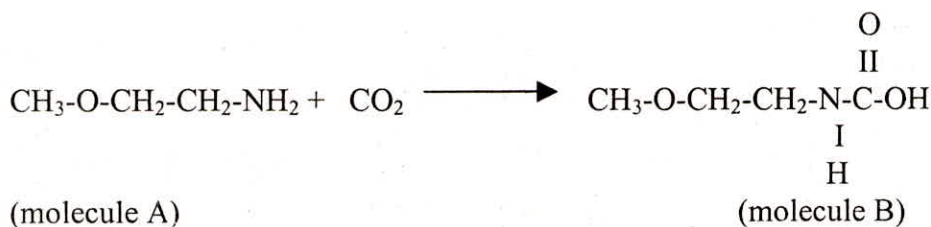
3.4 CO₂ Absorption Method

Prior to absorption, the CO₂ in cylinder must be kept stored for atleast 20 days to decay out ²²²Rn, which might have escaped out from sample matrix during the CO₂ extraction process. ²²²Rn has a half-life of 4.6 days and it has its beta peak at 5.4 MeV. After the storage period, CO₂ can be taken for absorption. Compared to benzene that takes nearly 2 days for 1 sample, the absorption method takes less than half a day to complete one sample. Moreover, it is cost

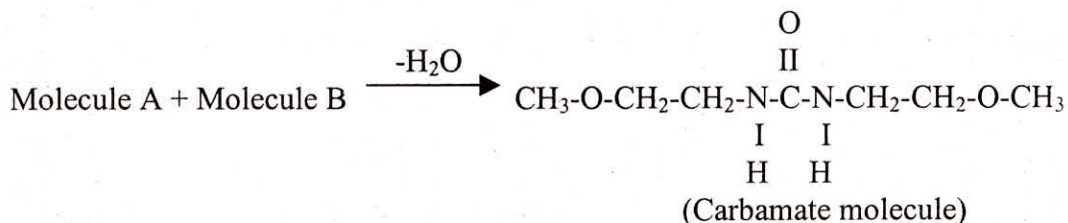
effective and requires lower level of technical skill for its maintenance, as compared to the benzene line.

For absorption of CO₂, a mixture of the absorber-scintillator liquid, CarboSorb-E[®] [i.e. *2-methoxy-ethyl-amine*(CH₃-O-CH₂-CH₂-NH₂)] and scintillator Permaflour-E+[®] [*a mixture of toluene, PPO and Bis MSB*] respectively (abbreviated here onwards as CS and PF respectively) are used. Chemically, the absorption process is a two step reaction:

1st step:



2nd step: (removal of water molecule)



Theoretically, 10 g (12ml) of CS absorbs 2.534g of CO₂ i.e. 4.8 mmole of CO₂ per ml of CS. But, practically ~7 mmole of CO₂ gets absorbed per ml of CS. The excess CO₂ that is absorbed remains in the adsorbed state and does not form the compound carbamate. However, at NIH, we take 10g (12ml) of CS+10g (11.6 ml) PF and allow about 3 g of CO₂ to get absorbed at saturation, which works out to be 5.68 mmole of CO₂ per ml of CS.

3.4.1 Absorption Procedure

The CS and PF are taken in the ratio of 10:10 g in the absorption-column (Fig. 4). Pour the CS and PF mixture in the column through the 'column inlet' while the gas inlet (V1) is kept closed air tight to avoid the downward percolation of the CS-PF mixture through the sintered disc. Once the mixture is added, a 'glass cap' is placed on the 'column inlet'. Weigh the column along with the CS-PF mixture, glass cap, the tubings and V1 by placing the entire set-up inside a thermocoal container. Note the weight in $1/100^{\text{th}}$ of a g, as 'initial weight'. Connect the column to the gas line at V1.

A water bath at room temperature (25°C) is attached to the absorption column. This is done as during the absorption process, temperature of the solution rises above 40°C , which causes change in viscosity and absorption coefficient of the solution. Even at the 25°C , there could be a loss of solvent due to evaporation. However, this should not affect the results since all the samples, including the standard, are prepared in similar conditions. The temperature of water bath should not be below 15°C as this may cause crystallization in absorption column.

The valve (V3) of the CO_2 gas cylinder is opened. The valve (V2) of the flow meter is gently opened to let the gas in the line upto V1, so that a slight positive pressure is maintained at V1. Now close V2. These steps prevent the backflow of CS-PF mixture towards V1, while V1 is opened. Open V1, while gently pressing the 'glass cap' over the column. The CO_2 gas is passed into the column by adjusting V2, such that the upper black ball and lower white ball are maintained to a scale mark 60 and 30 respectively in the flow meter. This state corresponds to a constant flow rate of 60 ml/min. As absorption progresses, the bubbles start evolving and pass through this solution sluggishly. The end point of the absorption process is marked by a rapid rise in the frothy solution level up to the bulb (as shown in Fig. 4). It takes about 25 minutes for absorbing 3g(or 1.57 l)

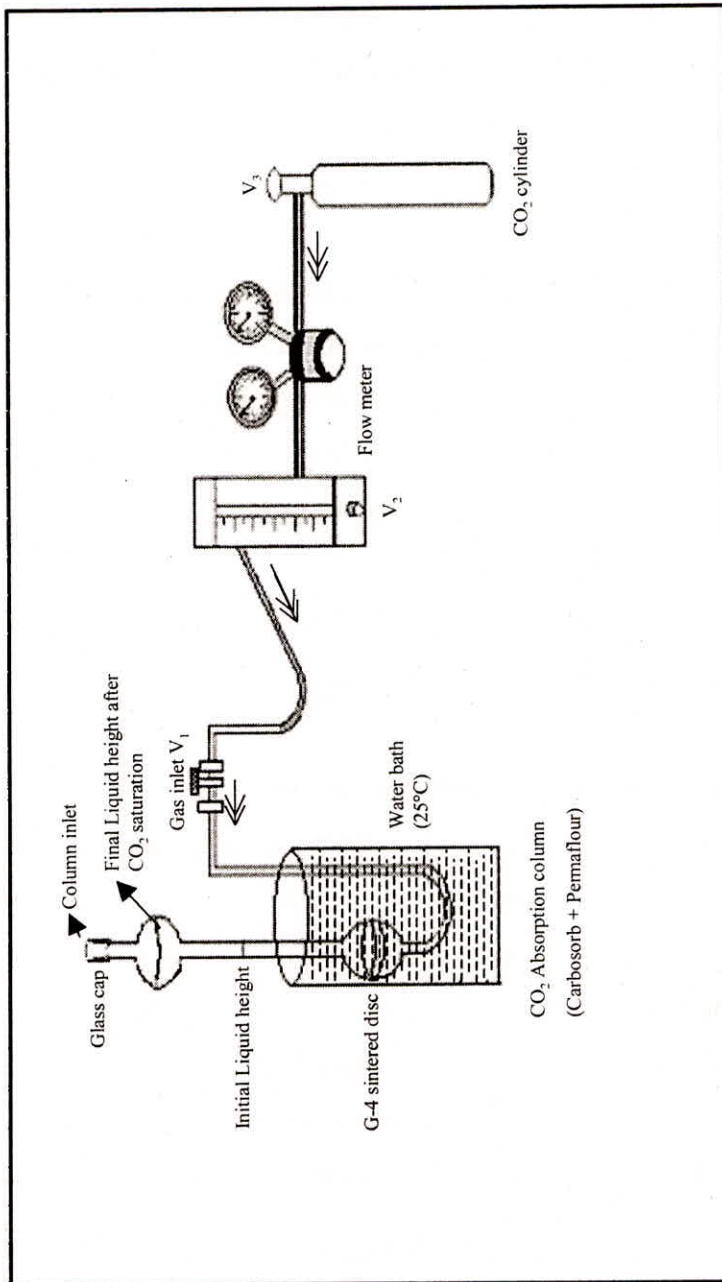


Fig. 4 CO₂ Absorption Line

of CO₂ at the flow rate given above. In practice, considering the efficiency of the absorption of about 90%, it requires nearly 30 min (i.e., 3.3 g of gas) to reach the end point. Detach the column along with the tubing, CS-PF-CO₂ mixture, glass cap and V1, and weigh them by placing inside a thermocoal container. Record the weight in 1/100th of a g, as 'Final weight'. The absorbed weight of CO₂ can be determined by deducting 'initial weight' from 'final weight'. The weight of the absorbed CO₂ may be made consistent by maintaining same flow rate in all the samples. Variation in absorbed CO₂ can lead to errors in the counting process.

After completion of absorption, the sample is transferred to a pre-weighed empty polypropylene vial and the weight of the transferred solution is also noted. This is done, as there may be some loss of solution that adheres to the column. The weight of the sample transferred into the vial is required to calculate specific activity of the sample (count rate per gram of carbon).

In two days, 8 samples including 1-standard and 1-background can easily be prepared using CO₂ absorption technique.

3.4.2 Cleaning of Carbosorb absorption column

After removal of the sample from the absorption column, clean the column with hot methanol by pouring methanol in the absorption column and dipping the column in hot water bath (~70°C). Leave it under the hot condition for about 15 minutes and decant thereafter. Repeat the procedure for 3 times. Dry and remove the traces of methanol from it by keeping it in vacuum and simultaneously warming it with a drier. One should ensure that while cleaning the 'absorption column', no traces of methanol or moisture remain within the column and in the sintered disc. The traces shall cause deterioration of the absorbed sample and lead to discoloration.

4. Radioactivity Measurement

The sample prepared as per the procedure described under section 3.4.1 is taken in a 22-ml polypropylene vial while benzene samples described under section 3.2 can be taken in a copper or Teflon capped 6-ml capacity Teflon vial. The procedure for cleaning the Teflon vials is given in section 4.2. The residual ^{14}C activity of the samples is estimated by counting the number of disintegrations per minute per gram of Carbon (dpm/g of C) of carbon with the help of Ultra low-level liquid scintillation spectrometer (LKB Wallac 1220 Quantulus). From the residual activity, the age of the sample is calculated using the decay equation. This is calculated through the careful measurement of net residual activity remaining in a sample whose age is unknown, compared with the net activity present in standard samples. Thus the samples are to be accompanied by background and standard samples prepared in the same way and with similar geometry.

4.1 Sample size

For counting benzene, standard sample size is taken as 3ml (2.64 g of C). On certain occasions, when the benzene yield is less than 3ml in the synthesising of benzene, dead benzene is added to bring the volume to 3ml during the sample weighing process. The scintillator used is PPO (6g) + POPOP (0.2 g) dissolved in one litre of toluene. This is added to the benzene in 1:3 ratio i.e., 1 ml of the scintillator is added to 3ml of the benzene.

For the absorption method, the amount of CO_2 required is 3.6 gms (i.e., 1gm of C). However, if the sample size is insufficient, a calibrated amount of dead CO_2 is added to the sample CO_2 to ensure saturation of the absorption of the mixture.

4.2 Procedure for cleaning of Teflon vials

The Teflon vials used in counting of benzene/carbosorb are washed twice in benzene/methanol and then with double distilled water. Finally these are rinsed with benzene/methanol and then dried in vacuum oven. The vacuum oven helps in maintaining the drying atmosphere moisture free. The dried vials are wrapped in clean tissue paper and are opened only at the time of transfer of sample benzene.

4.3 Standard Sample:

For radiocarbon dating, the activity of the ^{14}C reservoir (A_0) is defined as that of modern carbon (100 pmc). The term 'modern' refers to wood grown in 1890 in a fossil CO_2 -free environment with ^{14}C activity being 13.56 dpm/g of carbon.

4.3.1 Primary Modern Reference Standard

For laboratory calibrations, the National Bureau of standards (NBS) prepared an oxalic acid as a Primary Modern Reference Standard (NBS code-SRM 4990). Its isotopic ratio is $\delta^{13}\text{C} = -19.3\text{‰}$ with respect to the PDB limestone (Craig 1961). 95% of the count rate of this oxalic acid standard (0.95 A_{ox}) corresponded to the ^{14}C activity of the modern carbon i.e. 100pmc (100pmc = 0.95 A_{ox}). Then, the ^{14}C dating modern reference standard, denoted 0.95 O_x is the measured net activity derived from the NBS oxalic acid normalized to $\delta^{13}\text{C} = -19.3\text{‰}$ with respect to PDB.

This is expressed as:

$$\begin{aligned} A_{\text{on}} &= 0.95 O_x \\ &= 0.95 A_{\text{ox}} [1 - 2.3(\delta^{13}\text{C}_{\text{ox}} + 19)/1000] \text{ (w.r.t. PDB)} \end{aligned}$$

Where,

- A_{on} = measured net activity of the ^{14}C reservoir
- A_{ox} = measured net activity of the NBS oxalic acid standard
- $\delta^{13}\text{C}_{\text{ox}}$ = measured $\delta^{13}\text{C}$ of NBS Oxalic acid w.r.t PDB

Like stable isotopes, ^{14}C fractionate during organic and inorganic phase transformations and reactions. To maintain universality for dating purposes (^{14}C dating) ^{14}C activities must be normalized to a common $\delta^{13}\text{C}$ value of $-25^0/_{00}$ w.r.t. PDB.

4.3.2 New Reference Standard:

As the primary reference is completely exhausted a new international standard is prepared by NBS. This is **NBS Oxalic acid-ii, SRM 4990C**. 74.59 % activity of this standard corresponds to the 100% ^{14}C activity of modern carbon (100 pmc). Its isotopic ratio is $\delta^{13}\text{C} = -25^0/_{00}$ w.r.t. PDB (Stuiver, 1983).

This is expressed as:

$$A_{\text{on}} = 0.7459 A_{\text{oxii}} [1 - 2.3(\delta^{13}\text{C}_{\text{oxii}} + 25)/1000] \quad \text{w.r.t. PDB}$$

Note:

Oxalic acid-ii	= 18.1794 dpm/g
0.7459x A _{oxii}	= 0.7459x18.1794 dpm/g of C.
	= 13.56 dpm/g of C, this corresponds to 100pmc

4.3.3 Sample for Background activity

Background activity corresponds to the observed count rate with a sample that does not contain any radionuclide. There are many sources of background counts in LS counting. Some are produced in the sample solution including the vial, and some result from events that have no connection with the sample. The background sources are such as system electronic perturbations/noise, ambient activity - cosmic rays, back scattering phenomenon, activity in air and shielding materials etc.

A sample with no radiocarbon in it is taken to record the background activity/counts. In the present case, commercial benzene or CO₂ absorbed samples prepared from marble or dead calcite (¹⁴C activity ~0 pmc) are taken as background samples because of very high ages. They do not have any ¹⁴C activity. Dead benzene or CO₂ from deep underground mines can also be examined and used for preparing background samples. It is also important to note that non-Teflon vials may show some activity. Therefore it is preferable to use pure Teflon vials for such activity measurement.

In the presence of sample having no ¹⁴C activity, all the observed background counts limits to the system electronics and ambient activity (cosmic rays and back-scattering events, activity in the air and shielding bricks etc). The observed background activity measured with background samples determines the accuracy, precision, and upper age limit of the radiocarbon dating method because finite ages can only be calculated where sample activity is at least 3 standard deviations above background activity (Gupta and Polach, 1985). Consequently, each of the components of the LS counting system needs to be totally optimized for low level counting, so as to maintain high counting efficiency while significantly reducing the background counts. The 'total optimization concept' has been applied in the design of the Wallac 1220 Quantulus.

Counts generated from ambient radioactivity (cosmic and environment) are reduced in the Quantulus through shielding of the counting environment. This may be active or passive shielding. The passive one consists of layers of purified Boliden lead (650 kg), copper and cadmium, which shields the counting chamber from external radiation. The term 'active shielding' describes electronic means of recognizing and eliminating background causing event form the sample beta spectrum. The Wallac Quantulus utilizes an electronic anti-coincidence guard, comprising of a liquid scintillator guard, surrounding the counting chamber and

sample PMTs. Ionizing radiation from non-sample external sources passing through the guard scintillator leaves excited atoms and molecules in it, which are detected by the guard PMTs. If an ionizing event is recorded simultaneously in the guard and sample tubes, it is rejected as a background count.

4.4 Counting Procedure

Each batch for counting includes the samples, a background sample and a standard sample. All the samples are taken in Teflon vials and should contain equal volume of liquid scintillator and sample/background or standard and with same amount of absorbed CO₂ or benzene in them. All the samples should have same uniform transparency. All the samples in a set should spent nearly same time delay between their preparation and counting.

The counting vials are placed into one of the three trays located beneath the shield, and the counting data (tray position number, 1-60; sample identification number; counting requirements etc) are entered into the computer. They are counted for 1000 minutes, in 20 cycles with each cycle having 50 minutes. The LS vial is housed in a stepped stainless steel sleeve, which forms a light seal when the sample is loaded through the bottom of the shield assembly, by low activity copper piston. The sample changer and the shield areas are refrigerated to about 15°C to reduce benzene evaporative loss, and also ventilated, to prevent condensation on vials and to eliminate possible radon build-up. But while counting sample from the absorption method, the temperature of the counter is maintained at 20°C since at 15°C solute crystals has been observed in case of few cocktails. More operating instructions are given in the Quantulus operating manual (LKB-Wallac, 1980).

4.5 Quenching:

Quenching refers to the reduction in signals due to the inhomogeneous or improper mixing of sample and cocktail. In some cases the improper mixing may lead to change in colour etc. The ease of measuring the beta activity of a sample by liquid scintillation counting is dependent upon the preparation of a reproducible quality counting solvent. Elimination of variable quench will enhance the counting accuracy. LKB Wallac 1220 Quantulus ULLSS use dedicated microprocessor computers and present the user with the choice of programs for automated quench correction.

4.6 Noise reduction in Ultra Low Level Liquid Scintillation Counter:

The Quantulus has two Photo Multiplier Tubes between which the sample is kept to detect the scintillating pulses. These are, left (L) and right (R) phototubes. In addition to the sample scintillation, these phototubes may generate output due to their inherent thermal noise, cosmic ray background, electronic noise, ambient radioactivity etc. These noises are removed by various filtering modes. A coincidence condition LxR is used to remove thermal noise of PMT. The output in this logic is detected only when both the PMT generates output at same time (con-incidence counting). A logical condition true (i.e. select LxR) transfers all the coincidence pulses to the second half (MCA2) of the MCA else the total pulses (coincidence Pulses + anti-co-incidence pulses = L+R) pulses get transferred to first half. Similarly, a scintillation due to cross-talk or background will produce pulses of unequal amplitudes at the common output of these phototubes. A pulse amplitude comparator (PAC) is set in MCA to such a level that it selects those events which generates pulses of similar amplitude in both the phototubes. PAC=1 allows largest deviation between the L and R PMT while PAC=256 corresponds roughly to selection of amplitude ratio (amplitude of L:R=) 0.8:1.0 This discards events due to crosstalk or any other background. The system also contains a guard counter to detect events (Left Guard detector pulse =

GL and Right Guard Detector pulse = GR) due to external radiation such as from cosmic source, ambient environmental activity etc. Removal of guard events from combined LxR and PAC output extracts signal that is generated purely from the sample scintillation. These pulses are further divided into alpha and beta counts on the basis of their pulse shapes. Longer one is beta originated and shorter due to alpha events.

4.7 Data filtering:

A signal spectrum that is obtained after filtering out all the background contains count-rate along the y axis and channel number along the x axis. The total spectra can be saved in maximum 1024 channels (for low resolution, the spectra can be saved in 16, 32, 64, 128, 256 and 512 channels).

The raw spectrum of any nuclear measurement appears noisy due to the low total number of counts in a given channel number. Therefore, it is smoothened and filtered out for erroneous data before any calculations. A simple smoothening of the data is nothing but a box-car averaging of data using a bunch factor. For example, a bunch-factor 4 means smoothening of the spectra by taking average of channels 1-4, 5-8 etc.

The first part in statistical analysis is fixing-up of beta emission window (^{14}C emission is at 156keV and is observed in channel00-269). This is done on the basis of visual observation of peak and applying the figure of merit criteria on it.

Beta emission peak can be observed by comparing cumulative spectra of standard of high activity with the background. A parameter 'Figure of Merit' is then used to select part of this peak (W) that suits best for any inter sample comparison. The parameter figure of merit, $FM = E^2/B$. Where, $E = \% \text{ efficiency}$ i.e. $(\text{cpm/dpm}) * 100$ of radioisotope; $\text{cpm} = \text{counts per minute}$ as observed by the

counter; dpm = disintegrations per minute (theoretical value); B = background cpm under identical conditions.

To determine the useful part of this peak W, the individual cycles of standard and background are cumulated, smoothened by bunch averaging and then examined to make the first order selection of the window-spectrum (say W_i) that gives maximum figure of merit. The automated FM criteria, integrates counts inside the selected window (within right and left-hand limits) for standard and background and computes FM. The window width and channel limits are adjusted in such a way that FM is maximized.

The window width determined as above is from gross data without any removal of erroneous data (cycle) present in the standard or background. To remove erroneous data, integrate data (cycle) inside the spectrum width W_i and examine the statistical distribution of these counts. Two aspects are looked in statistical distribution (i) data trend and (ii) scattering in the data. A trend such as increasing count rate or decreasing count rate with the cycle number can be due to sample weight loss, time dependent change in sample transparency/viscosity, electronic drift etc. Such unacceptable drifts if found then the sample should be remeasured after correcting the problem. The other observation is about the sample scatter. From the data distribution, remove the high scatter points using 2σ criteria. This statistical facility is available in the statistical analysis part of the Spectrum Analysis Program of Quantulus. Now re-determine the spectrum window width W_f using the filtered data for standard and background using the criteria FM_{max} . The entire analysis hereafter is done on the determined window width W_f .

The measured spectrum of individual cycles are smoothened, integrated over a window width W_f and examined for statistical distribution. The data points

(cycles) lying outside 2σ are discarded. The filtered cycles are cumulated for individual samples and smoothened out using bunch averaging 3 or 5. For the statistical operation on the data it is recommended that the number of counts in the defined window per cycle is greater than 50 and there should be about 30 cycles measured for samples, standard and background. .

With the above statistical procedure an integrated data within the peak area W_f from the cumulated and smoothened spectra for sample, standard and background is obtained. From this filtered data, count rate and its error for sample, background and standard is determined.

4.8 Counting and Data Synthesis:

counting period = t (say 50min)

No. of cycles (or times the sample is counted) = n (=20 say)

Total counting time $T = n*t = (20*50) = 1000$ min

If the total counts = $\sum N_i$ in 10 cycles, then average count rate per cycle = $\sum N_i / 10$

Discard 3 sigma from the average

(i.e. data lying outside $[(\sum N_i / 10) \pm 3x(\sqrt{\sum N_i} / 10)]$)

From the new count rate find the following parameters:

Gross sample count rate (cpm):

$$C_{s+b} = \sum N_i / T, \text{ counts of both standard + background}$$

$$C_{s+b} \pm \sigma C_{s+b} = \sum N_i / T \pm (\sigma C_{s+b} / T)$$

$$C_{s+b} \pm \sigma C_{s+b} = \sum N_i / T \pm (C_{s+b} / T)$$

Gross sample activity in units of cpm/3ml (2.6359 g C) benzene:

$$A_{s+b} \pm \sigma A_{s+b} = 2.6359/m * C_{s+b} \pm 2.6359/m * \sigma C_{s+b}$$

where m = benzene weight

Net sample activity:

Benzene Samples:

$$A_s \pm \sigma A_s = (A_{s+b} - B) \pm [(A_{s+b})^2 + (\sigma B)^2], \text{ activity of standard}$$

CO₂ Absorption samples:

$$A_s \pm \sigma A_s = (C_{s+b} - B^1)/\text{carb} \pm [((\sigma C_{s+b})^2 + (\sigma B^1)^2)/\text{carb}]$$

where,

B = background normalized to 2.6359 gm of benzene

B¹ = background for 20 ml pure absorption solution

carb = grams of carbon / absorbed in 20 ml absorption solution

In case the sample has been diluted at the weighing of benzene stage, a dilution factor has to be calculated as follows:

Net sample activity corrected by dilution:

$$A_{sc} \pm \sigma A_{sc} = A_s/D \pm \sigma A_s/D, \text{ activity of standard corrected for dilution}$$

where, D = initial benzene weight / final benzene weight after diluted by dead benzene.

5.0 Age Determination

5.1 Age Equation and Counting Errors

The ¹⁴C age is estimated using the relation:

$$A = A_0 e^{-\lambda t}$$

where, A = residual ¹⁴C activity of the sample

A₀ = original ¹⁴C activity of the reservoir

λ = decay constant

t = years elapsed since the sample was removed from the equilibrium condition in the ¹⁴C reservoir

By convention, Libby's half-life of 5568 years is still being used. Then, the ^{14}C dates are referred to as conventional radiocarbon ages, BP (before present). However, if somebody wants to use Godwin's half-life of 5730 years, just multiply the results of Libby's by 1.0291.

$$t_{1/2} = 5568 \text{ yr (Libby's half life)}$$

Rearranging the decay equation gives:

$$t = \ln(A_0/A)/\lambda$$

$$t = 8033 \ln(A_0/A) \text{ radiocarbon ages, BP}$$

$$t = 8267 \ln(A_0/A) \text{ BP, in case 5730 yr taken as half-life (Godwin, 1962).}$$

From the estimated count rate of sample, background and standards, the net sample and standard activity per gram of carbon is determined. In case the sample has been diluted at the weighing of benzene stage, a dilution factor has to be calculated as follows:

Net sample activity corrected by dilution:

$A_{sc} \pm \sigma A_{sc} = A_s/D \pm \sigma A_s/D$, activity of standard corrected for dilution where, $D = \text{initial benzene weight / final benzene weight after diluted by dead benzene}$].

Activity of sample with respect to standard is compared to get percent modern carbon. These are defined in various ways as:

Fraction modern (f):

$$f \pm \sigma f = A_{sc}/A_{on} \pm (A_{sc}/A_{on}) * [(\sigma A_{sc}/A_{sc})^2 + (A_{on}/A_{on})^2]$$

where, $A_{on} = 0.7459 A_{oxii} [1 - 2.3(\delta^{13}\text{C}_{oxii} + 25)/1000]$

Enrichment or depletion wrt A_{on} ($D^{14}\text{C}$):

$$D^{14}\text{C} = (A_{sn}/A_{on} - 1) * 1000 \%$$

where, $A_{sn} = A_{sc} [1 - 2.3(\delta^{13}C_{oxii} + 25)/1000]$ then

$$D^{14}C \pm D^{14}C = 1000 (f - 1) - 2f(\delta^{13}C_{oxii} + 25) \pm 1000(f - 1)$$

Percent Modern Carbon (pmc):

$$pmc \pm \sigma pmc = 100 + D^{14}C / 10 \pm \sigma D^{14}C / 10$$

The ^{14}C age is estimated by substituting these values.

Age:

$$t = 8267 \ln(A_{sn}/A_{on}) = 8267 \ln(1 + D^{14}C / 1000)$$

$$t = 8267 \ln(pmc \%) \text{ yr Before Present (BP).}$$

Error in age (σt):

$$+\sigma t = 8267 \ln[1 + (D^{14}C - \sigma D^{14}C)/1000] - t$$

$$-\sigma t = 8267 \ln[1 + (D^{14}C + \sigma D^{14}C)/1000] + t$$

5.2 Age correction for contamination

The age in the radiometric dating techniques relies on estimation of present day sample activity with the initial activity of the sample. Of these two, the major uncertainty comes from the assumed initial activity, which is not constant but varied in the past. The variation in production of ^{14}C in the past is due to anthropogenic, and geo-cosmic reasons. The anthropogenic activities caused variation in ^{14}C activity mainly within the last one-century whereas geo-cosmic reasons caused variations throughout the history of the earth. The record of variations in ^{14}C activity at high, low and coarse resolutions is available for various sites in the world for the period up to last one-century, for period up to 5.5ka and for a period 5.5-30ka respectively. These are deciphered by comparison with known age samples and by comparing dates obtained with other dating techniques such as with dendrochronology, thermoluminescence, U-Th

disequilibrium etc. (see Bard et.al. 1993 Nature 345:405). In addition to the error in age due to variation in atmospheric ^{14}C activity, error also comes from change in ^{14}C activity of water parcel during its infiltration and flow in aquifer. This take place due to various geo-chemical and isotope exchange reactions with matrix minerals In the age equations, all these correction are incorporated before expressing the radiocarbon age in calendar years. In what follows is discussed the approaches to correct apparent ^{14}C age of groundwater due to dissolution of carbonate and dolomite during its infiltration or flow in an aquifer. For other complications such as due sulphate reduction, methanogenesis, variation in atmospheric ^{14}C activity texts such as Clark and Fritz (1997), Bard et. al. (1993) etc. and the references there in can be consulted.

5.2.1 DIC in unsaturated zone

The radiometric age of groundwater is derived from measurement of ^{14}C activity of its dissolved inorganic carbon. This carbon enters into the water from the dissolution of CO_2 released by plant roots during respiration in the soil zone or from the fermentation and decay of organic matter (fulvic, flavic and humic acids).

The dissolution of biogenic CO_2 produces carbonic acid. The amount of CO_2 that can dissolve depend on the temperature, the pH of the water, the partial pressure of the CO_2 , and the weathering reactions that take place in the soil.

The distribution of DIC species in water H_2CO_3 , HCO_3^- , and CO_3^{2-} is a function of pH. The dissolution and formation of DIC from soil CO_2 changes $\delta^{13}\text{C}$ (Fig. 5) (and corresponding ^{14}C) to some extent and this is a function of temperature. But, roughly it can be said that open system condition (continuous exchange with soil CO_2) maintains ^{14}C activity of DIC is close to 100 pmc. Typical Change in $\delta^{13}\text{C}$ at 25°C for 1890 atmosphere are:

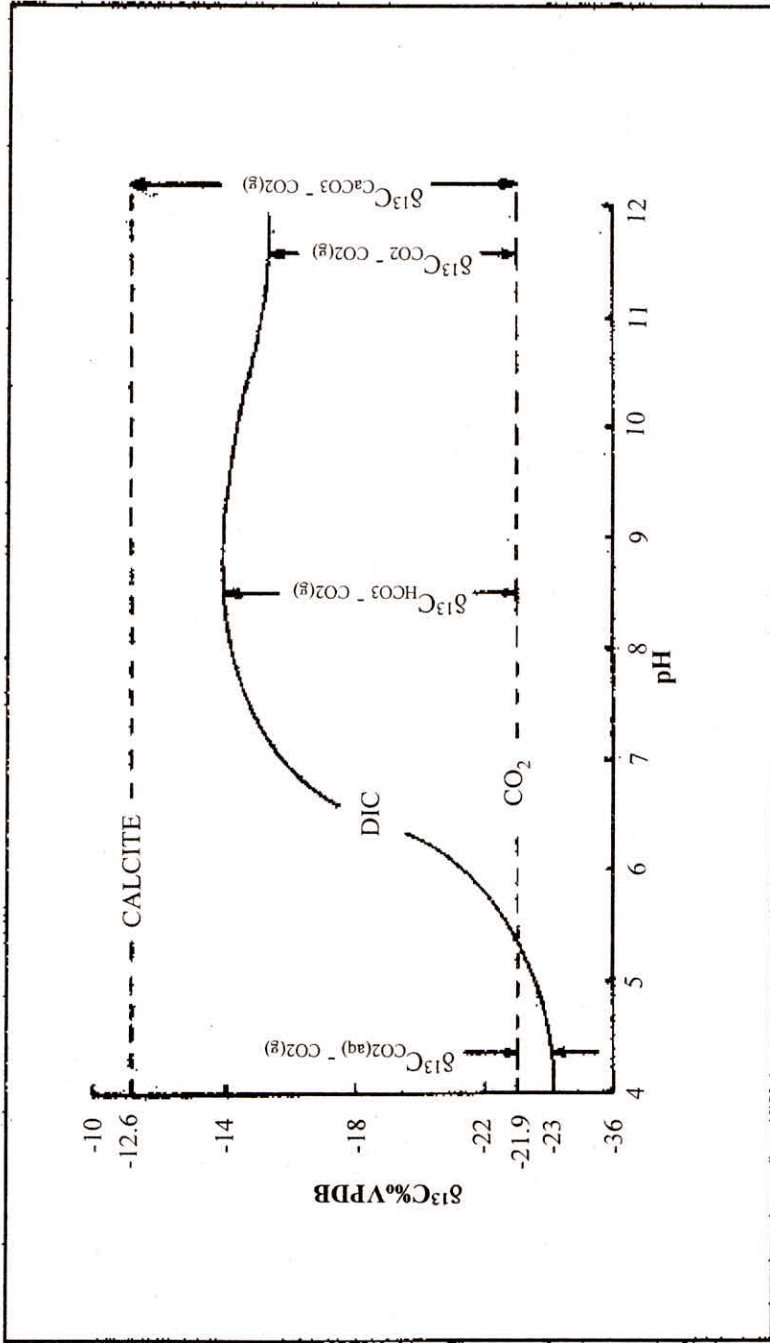
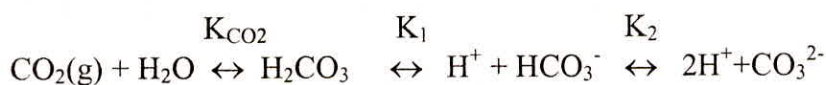


Fig. 5 $\delta^{13}\text{C}$ composition of dissolved inorganic carbon (DIC) in equilibrium with soil CO_2 at 25°C. (assumed for soil CO_2 , $\delta^{13}\text{C} = -25$ ‰)

$\epsilon = 2$	$\epsilon = -1.1$	$\epsilon = -9.1$	
Carbon in Vegetation	Soil CO ₂	CO ₂ (aq)	HCO ₃ ⁻
$\delta^{13}\text{C} = -25\text{‰}$,	$= -23\text{‰}$,	$= -24.1\text{‰}$	$= -15.1\text{‰}$
$^{14}\text{C} = 100\text{pmc}$	$= 100.5\text{pmc}$	$= 100.2\text{pmc}$	$= 102.3$
	pH < 4.0	~ 4.5	~ 8.0

Where, ϵ is an enrichment factor and $\delta^{13}\text{C}$ are with respect to VPDB.

The molar concentration of DIC species is calculated on the basis of pH or pCO₂ as follows:



At chemical equilibrium, the reaction constants are given by (at 25⁰C):

$$K_{\text{CO}_2} = \frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2} \cdot [\text{H}_2\text{O}]} = 10^{-1.46} \quad \{\text{note that } [\text{H}_2\text{O}] = 1 \text{ for dilute solutions}\}$$

So,

$$K_{\text{CO}_2} = \frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2}} = 10^{-1.46} \quad \{\text{for dilute solutions}\}$$

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{-6.35} \quad (\text{in this dissociation reaction } [\text{H}^+] \text{ can be assumed to be equal to } [\text{HCO}_3^-])$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{-10.33}$$

Temperature dependence of pK values (-ve log of K) can be calculated from the following equations for a temperature up to 50⁰C.

$$pK_{CO_2} = -7 \times 10^{-5} T^2 + 0.016 T + 1.11$$

$$pK_1 = 1.1 \times 10^{-4} T^2 - 0.012 T + 6.58$$

$$pK_2 = 9 \times 10^{-5} T^2 - 0.00137 T + 10.62$$

$$pK_{CO_2} = 6 \times 10^{-5} T^2 + 0.0025 T + 8.38$$

Example: Let the major DIC species in groundwater are $CO_{2(aq)}$, H_2CO_3 and HCO_3^- and $P_{CO_2} = 10^{-2}$ (say): then,

$$[H_2CO_3] = 10^{-1.46} \cdot P_{CO_2} = 10^{-1.46} \cdot 10^{-2} = 10^{-3.46}$$

$$\text{and } [H^+] = 10^{-6.35} \cdot [H_2CO_3] / [HCO_3^-] = 10^{-9.81} / [HCO_3^-]$$

Since for dissociation $[H^+] \sim [HCO_3^-]$

$$[H^+] = 10^{-9.81} / [H^+]$$

$$\therefore [H^+]^2 = 10^{-9.81}$$

or $[H^+] = [HCO_3^-] = 10^{-4.9}$. Therefore, pH (-ve log of $[H^+]$) = 4.9 and the distribution of DIC species will be:

$$DIC = [H_2CO_3] + [HCO_3^-] = 10^{-3.46} + 10^{-4.9} = 10^{-3.44} \text{ mole/L}$$

5.2.2 Carbonate dissolution

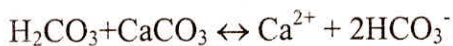
Calcite dissolution can occur both in unsaturated zone (open system) and also in the saturated zone (closed system). In the unsaturated zone, $CO_{2(g)}$ and

CO_{2(l)} coexist. With the continuous replenishment of CO₂ from the atmosphere and root zone, the pH of the groundwater decreases. The decrease of pH increases weathering capacity of groundwater and dissolves calcite minerals of the matrix. This is a simple dissociation reaction:



Although, the solubility constant of the reaction is very low ($K_{\text{CaCO}_3} = 10^{-8.48}$) the final equilibrium constant is high and large amount of calcite is dissolved due to continuous replenishment of CO₂.

Further, dissolution of calcite can take place in the saturated zone. Here the groundwater is closed off from the source of soil CO₂ (closed system condition). The fixed concentration of CO₂ gained in the soil is not replenished as carbonate dissolves according to the reaction:



i.e., $\text{CO}_{2(g)} + \text{H}_2\text{O} + \text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$ (Equilibrium constant $K = 10^{-6.41}$)

The closed conditions are typical of recharge areas where infiltration to the water table is fast (e.g. karst) or in unsaturated soils with little or no carbonate content.

Unlike calcite dissolution, silicate weathering does not change ¹³C or ¹⁴C content of the system. It only hydrolyses the silicates (in the presence of CO₂ and H₂O) into their corresponding silicate or metal hydroxides. For example, Sodium aluminum silicates (albite) become aluminum silicate hydroxides (kaolinites) or aluminum-hydroxides. Formation of hydroxides increases pH of the system and

more CO₂ and H₂O is added into the system. The CO₂ and H₂O forms HCO₃⁻ ion due to high pH of the system.

5.2.3 ¹³C as a tracer to correct ¹⁴C:

Changes in ¹⁴C in geo-chemical reactions can be traced using δ¹³C due to difference in isotope mass effect. Fractionation for ¹⁴C is 2.3 times that of δ¹³C and the correction can be written as:

$$\text{Correction in } ^{14}\text{C} = 2.3 \times (\text{final } \delta^{13}\text{C value} - \text{initial } \delta^{13}\text{C value})$$

Example 1. Say, initial values of the water system are δ¹³C = 1.5 ‰ and ¹⁴C = 65 pmc. If final value of δ¹³C = -25‰ then corresponding value of ¹⁴C would be:

$$2.3 \times (\text{final } \delta^{13}\text{C value} - \text{initial } \delta^{13}\text{C value}) = 2.3 \times (-25 - 1.5) = -61\text{‰ or } -6.1\%$$

Therefore, ¹⁴C value would be 65 - (65 × 6.1/100) = 61 pmc.

Example 2. Say for wood grown in 1890 having its ¹⁴C = 100 pmc and δ¹³C = -25‰. If δ¹³C of the atmosphere in 1890 was -6.4‰, then ¹⁴C of the atmosphere in 1890 would be,

$$2.3 \times (-6.4 - (-25)) = 2.3 \times 18.6 = 42.78\text{‰ i.e., } 4.3\% \text{ enriched.}$$

Therefore, ¹⁴C of the atmosphere would be, 100 + 100 × (4.3/100) = 104.3 pmc.

5.3 ¹⁴C Age correction Models

The standard radiometric age equation is:

$$A = A_0 \cdot e^{-\lambda t}$$

Where A and A₀ are initial activity and activity after the sample age t. λ is the decay constant.

If dissolution of calcite dilutes the initial activity by a factor q then the age equation becomes,

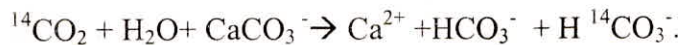
$$A = (q \cdot A_0) \cdot e^{-\lambda t}$$

$$\text{Or } t = -8267 \cdot \ln \left[\frac{A}{qA_0} \right]$$

Although, the value of q depends upon reactions like calcite dissolution, dolomite dissolution, isotope exchange with aquifer matrix, oxidation of old carbon in soils and dissolution of its CO₂ etc. but what discussed below is change in q due to carbonate dissolution.

Under open system condition with the continuous exchange of carbon isotopes with infinite reservoir of soil CO₂, the ¹⁴C activity of DIC reaches to 100 pmc (i.e. activity of soil CO₂) and remains unchanged thereafter. Therefore, under open system, q=1. For soil CO₂, δ¹³C = -25‰ VPDB.

Under closed system, the calcite dissolution imparts 50% dilution to the initial ¹⁴C activity (q=0.5):



In most ground waters, the situation is in between and this reflects in the δ¹³C of the DIC. Marine carbonates have ¹³C similar to the VPDB with δ¹³C = 0‰. For soils δ¹³C = -23‰. With fractionation during conversion of H₂CO₃ to CO₃⁻ and due to dissolution of carbonates δ¹³C starts increasing from -23‰ (starts becoming more positive). For example, CO₂ dissolution in open system

enriches $\delta^{13}\text{C}$ to -16‰ and with further dissolution of carbonate in closed system it can get enriched to value about -12‰ .

Thus, the geochemical reactions necessitate appropriate correction models to correct the initial ^{14}C activity of the system.

5.3.1 Statistical Correction:

On the basis of large number of data for ^{14}C activity, Vogel (1970) reported following q values for various recharge systems

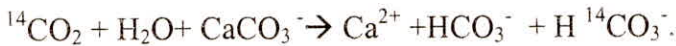
System	Dilution factor 'q'
Karst system	0.65-0.75
Sediments with fine grained carbonates such as loess.	0.75-0.90
Crystalline rocks	0.90-1.00

Higher q values indicate enriched carbonate systems hence more dilution. Crystalline rocks contain little carbonate with q values close to 1.

The q's can be estimated by comparing ^{14}C activity of groundwater with that of atmosphere. For example, if atmospheric ^{14}C activity = 114 pmc and that in groundwater = 65pmC then the dilution factor $q = 65/114 = 0.57$. The statistical model considers dilution within the recharge area. The model does not take into account dilution beyond the recharge area.

5.3.2 Alkalinity correction model (Tamer's, 1975):

Under closed system, the DIC contains a fraction of carbon originated from soil CO_2 and part is supplied by soil carbonate particles (the activity of it is generally very low):



If A_g is the ^{14}C activity of the soil $\text{CO}_{2(\text{aq})}$ (~100pmc) and A_c is activity of soil carbonate (generally close to zero) then initial activity of DIC is

$$A_0 = \frac{(m\text{CO}_2 + 0.5m\text{HCO}_3^-)A_g + (0.5m\text{HCO}_3^-)A_c}{m\text{CO}_2 + m\text{HCO}_3^-}$$

Where m are molalities (measured for HCO_3^- and evaluated on the basis of pH and alkalinity for aqueous CO_2). The model assumes no exchange with solid carbonate within the aquifer.

If $A_c \sim 0$, then equal amount of dead carbon from carbonate to that of active carbon from soil will make the overall activity half. Thus for equal fraction of dead calcite and active carbonic acid reaction ($\text{H}_2\text{O} + ^{14}\text{CO}_2 = \text{H}_2^{14}\text{CO}_3$), the dilution factor $q = 0.5$.

This model does not take into account any isotopic exchange process with gaseous CO_2 and does not indicate how much carbon is derived from soil CO_2 . The model works well for the area with low CO_2 production soil zone and unsaturated zone is not porous enough to allow a large contact between aqueous and gaseous phase. The model is applicable in semi-arid regions covered with porous, thin sediments, with poorly developed soils and where aquifer matrix is poor in carbonates.

5.3.3 Chemical Mass Balance (CMB) correction (Fontes and Garnier, 1979):

The model is applicable to closed system. It estimates correction factor q from the additional DIC gained by groundwater below the root zone (open system). The correction factor q is calculated from:

$$q = \frac{mDIC_{rech}}{mDIC_{final}}$$

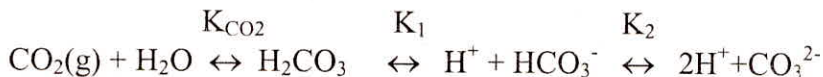
Where $mDIC_{rech}$ is the molalities of ^{14}C active carbonate incorporated from soil CO_2 dissolution during recharge and $mDIC_{final}$ is the molalities of the total carbonate (^{14}C active and ^{14}C dead) of the groundwater sample.

$mDIC_{rech}$ is calculated from pH and pCO_2 conditions of recharge environment and $mDIC_{final}$ is the measured alkalinity (CMB -Alkalinity model) or the value derived from chemical data (CMB-Chem model):

$$mDIC_{final} = mDIC_{rech} + [mCa^{2+} + mMg^{2+} - mSO_4^{2-} + 1/2(mNa^+ + mK^+ - mCl^-)]$$

The $mDIC_{final}$ thus accounts for Ca^{2+} , Mg^{2+} and SO_4^{2-} added through carbonate and sulphate dissolution and lost Ca^{2+} through ion exchange with Na^+ , K^+ or Cl^- through incorporation of salinity from seawater or halite dissolution.

In the equation, $mDIC_{rech}$ is calculated using the carbonate dissolution equation discussed previously:



With chemical equilibrium constants at 25°C:

$$K_{CO_2} = \frac{[H_2CO_3]}{P_{CO_2}} = 10^{-1.46} \quad (\text{for dilute solutions})$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.35} \quad (\text{in this dissociation reaction } [H^+] \text{ can be assumed to be equal to } [HCO_3^-])$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.33}$$

Example: Calculate $mDIC_{rech}$ if pH of groundwater is 6.3 and $P_{CO_2} = 10^{-2.2}$,

$$K_{CO_2} = \frac{[H_2CO_3]}{P_{CO_2}} = 10^{-1.46}$$

$$[H_2CO_3] = 10^{-1.46} \cdot P_{CO_2} = 10^{-1.46} \cdot 10^{-2.2} = 10^{-3.66}$$

$$\text{So } [H_2CO_3] = 10^{-1.46} \cdot 10^{-2.2} = 10^{-3.66}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.35} \quad \text{Therefore, } [HCO_3^-] = 10^{-6.35} \times [H_2CO_3]/[H^+]$$

Substituting value of $[H_2CO_3]$ and also as $pH = 6.3$, so $[H^+] = 10^{-6.3}$

$$\text{Therefore, } [HCO_3^-] = 10^{-6.35} \times (10^{-3.66})/10^{-6.3} = 10^{(-6.35-3.66+6.3)} = 10^{-3.71}$$

$$\text{Therefore, } [HCO_3^-] = 10^{-3.71}$$

$$\begin{aligned} \text{Therefore, initial DIC i.e., } mDIC_{rech} &= [H_2CO_3] + [HCO_3^-] = 10^{-3.66} + 10^{-3.71} \\ &= 4.137 \times 10^{-4} \quad \text{or } 41 \text{ mg/L} \end{aligned}$$

5.3.4 . $\delta^{13}C$ mixing model:

The early version of this model was by Pearson and Hanshaw (1970). The q factor in this model is derived from the change in the $\delta^{13}C$ of the DIC of the infiltrating water with that of the water in saturated zone (closed condition).

The dissolution of carbonate mineral will cause change in $\delta^{13}C$ of DIC of infiltrating water by an amount:

$\delta^{13}\text{C}_{\text{soil}} - \delta^{13}\text{C}_{\text{carb}}$ where $\delta^{13}\text{C}_{\text{soil}}$ is $\delta^{13}\text{C}$ of soil CO_2 (usually close to -23‰) and $\delta^{13}\text{C}_{\text{carb}}$ is $\delta^{13}\text{C}$ of calcite (usually close to 0‰)

and

$\delta^{13}\text{C}$ of DIC in the closed system is given by:

$\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_{\text{carb}}$ where $\delta^{13}\text{C}_{\text{DIC}}$ = measured ^{13}C in groundwater.

The dilution factor q is:

$$q = \frac{\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_{\text{carb}}}{\delta^{13}\text{C}_{\text{soil}} - \delta^{13}\text{C}_{\text{carb}}}$$

However, due to open condition, $\delta^{13}\text{C}$ of infiltration water gets enriched over $\delta^{13}\text{C}_{\text{soil}}$ as function of pH and temperature. (fig. 5). $\delta^{13}\text{C}_{\text{soil}}$ is therefore replaced by $\delta^{13}\text{C}_{\text{rech}}$ as,

$$\delta^{13}\text{C}_{\text{rech}} = \delta^{13}\text{C}_{\text{soil}} + \epsilon^{13}\text{C}_{\text{DIC-CO2(soil)}}$$

The equation therefore gets modified as;

$$q = \frac{\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_{\text{carb}}}{\delta^{13}\text{C}_{\text{rech}} - \delta^{13}\text{C}_{\text{carb}}}$$

Example:

Input	Case A	Case B
pH	6.0	7.0
$\text{mCO}_2(\text{aq})/\text{mHCO}_3^-$	2.5	0.25
$\delta^{13}\text{C}_{\text{DIC}}$ (measured)	-12.5‰	-12.5‰
$\delta^{13}\text{C}_{\text{soil}}$ (assumed)	-23‰	-23‰
$\delta^{13}\text{C}_{\text{carb}}$ (assumed)	0‰	0‰
^{13}C activity	35	35

From the figure 5, $\epsilon^{13}\text{C}_{\text{DIC-CO2}(\text{soil})}$ at 6 and 7 pH are 1.5 and 5.7 respectively.

$$\begin{aligned}\delta^{13}\text{C}_{\text{rech}} &= \delta^{13}\text{C}_{\text{soil}} + \epsilon^{13}\text{C}_{\text{DIC-co2}(\text{soil})} \\ &= -23+1.5 \text{ (for pH=6) and } =23+5.7 \text{ (for pH=7)} \\ &= -21.5 \text{ (for pH=6) and } = -17.3 \text{ (for pH=7)}\end{aligned}$$

$$\begin{aligned}q &= \frac{\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_{\text{carb}}}{\delta^{13}\text{C}_{\text{rech}} - \delta^{13}\text{C}_{\text{carb}}} \\ &= \frac{-12.5 - 0}{-21.5 - 0} \text{ (for pH = 6) and } = \frac{-12.5 - 0}{-17.3 - 0} \text{ (for pH =7)} \\ &= 0.58 \text{ (for pH = 6) and } 0.72 \text{ (for pH =7)}\end{aligned}$$

Age uncorrected on the basis of 35pmc activity is
 $-8267 \times \ln(35/100) = 8678 \text{ yrs}$

$$\begin{aligned}\text{Corrected age} &= -8267 \times \ln[(\text{pmc}/100)/q] \\ &= -8267 \times \ln(0.35/0.58); \text{ (for pH = 6) and } = -8267 \times \ln(0.35/0.72); \text{ (for pH =7)} \\ &= 4175 \text{ yrs (for pH = 6) and } 5963 \text{ yrs (for pH=7)}\end{aligned}$$

The model shows that with the introduction of the model parameters the uncorrected age 8678 becomes almost half (4175 for pH = 6 and 5963 for pH=7). This is due to mole fraction of DIC species with pH.

Limitation: The model assumes that pH of the groundwater during recharge did not change in the past.

5.3.5 Matrix Exchange Model (Fontes and Garnier Model):

This is basically an isotope mass balance model. In this model it is assumed that a part of the DIC generated by dissolution of carbonates is replaced by soil CO₂ in the open system (unsaturated zone) due to continuous flushing of soil CO₂ and this is given by a term mDIC_{CO₂-exch} in the model equation.

Therefore, net ¹⁴C active DIC in the system is

$$mDIC_{meas} - mDIC_{carb} + mDIC_{CO_2-exch}$$

Where, mDIC_{meas} is the moles of dissolved inorganic carbon in the groundwater, mDIC_{carb} is the moles of DIC generated due to dissolution of carbonate and mDIC_{CO₂-exch} represents moles of DIC generated from the flushing of soilCO₂ replacing the dissolved carbonate mineral generated DIC.

The dilution factor is given by,

$$q = \frac{mDIC_{meas} - mDIC_{carb} + mDIC_{CO_2-exch}}{mDIC_{meas}}$$

The term mDIC_{carb} is calculated as:

$$mDIC_{carb} = mCa^{2+} + mMg^{2+} - mSO_4^{2-} + \frac{1}{2}(mNa^+ + mK^+ - mCl^-)$$

In this, the total matrix (carbonate minerals) derived DIC is considered as due to addition of Ca²⁺, Mg²⁺ ions due to carbonate dissolution, correction for Ca²⁺ through gypsum (SO₄²⁻) dissolution and lost Ca²⁺ ions through Na⁺, K⁺ and Cl⁻ ions through incorporation of salinity or halite dissolution. In this equation, the term mNO₃⁻ is dropped, as it is negligible in old water.

The term mDIC_{CO₂-exch} is given by:

$$mDIC_{CO_2-exch} = \frac{\delta^{13}C_{meas} \cdot mDIC_{meas} - \delta^{13}C_{carb} \cdot mDIC_{carb} - \delta^{13}C_{soil} \cdot (mDIC_{meas} - mDIC_{carb})}{\delta^{13}C_{soil} - \epsilon^{13}C_{CO_2-CaCO_3} - \delta^{13}C_{carb}}$$

Limitation: The model does not take into account any source other than carbonate dissolution for DIC in the groundwater.

Example : Find dilution effect in ^{14}C age for the following input parameters.

Input parameters:

Concentrations in meq/L:

$mCa^{2+} = 7.19$; $mMg^{2+} = 12.24$; $mSO_4^{2-} = 8.92$; $mNa^+ = 25.83$; $mK^+ = 0.36$;

$mCl^- = 34.57$; $mHCO_3^- = 1.97$

$\delta^{13}C_{meas} = -4.6\text{‰}$; $\delta^{13}C_{carb} = 2$; $\delta^{13}C_{soil} = -18$; $\epsilon^{13}C_{CO_2-CaCO_3} \sim 7$ (taken from fig 5)

$pH = 7.45$ and $^{14}C = 7.9\text{pmc}$.

Ans: Converting concentrations from meq to moles per liter using the relation:

(1mmole/L = Valence* meq/L)

$mCa^{2+} = 3.595 \times 10^{-3}$; $mMg^{2+} = 6.12 \times 10^{-3}$; $mSO_4^{2-} = 4.46 \times 10^{-3}$;

$mNa^+ = 25.83 \times 10^{-3}$; $mK^+ = 0.36 \times 10^{-3}$; $mCl^- = 34.57 \times 10^{-3}$; $mHCO_3^- = 1.97 \times 10^{-3}$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 10^{-6.35}$$

$$\text{so } [H_2CO_3^*] = [H^+][HCO_3^-]/10^{-6.35}$$

$$= 10^{-7.45} \times 1.97 / 10^{-6.35}$$

$$(pH=7.45 \text{ means } [H^+] = 10^{-7.45})$$

$$= 10^{-1.1} \times 1.97 = 0.1565$$

$$mDIC_{\text{meas}} = [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] = 1.97 + 0.1565 = 2.1265 \text{ moles/L}$$

$$mDIC_{\text{carb}} = [3.59 + 6.12 - 4.46 + \frac{1}{2}(25.83 + 0.36 - 34.57)] \times 10^{-3}$$

$$= [5.25 + \frac{1}{2}(-8.38)] \times 10^{-3}$$

$$= 1.06 \times 10^{-3}$$

$$mDIC_{\text{CO}_2\text{-exch}} = \frac{-4.6 \times 2.1265 - 2 \times 1.06 \times 10^{-3} - (-18)(2.1265 - 1.06 \times 10^{-3})}{-18 - 7 - 2}$$

$$= [-9.7819 - 2.12 \times 10^{-3} + 38.25792] / [-27]$$

$$= -1.05$$

$$q = [2.1265 - 1.06 \times 10^{-3} + (-1.05)] / 2.1265 = 0.5057$$

Uncorrected age for 7.9 pmc = $-8267 \ln(7.9/100) = 20984$ yrs. Corrected age for 7.9 pmc and $q = 0.5057$

$$= -8267 \ln[(7.9/100)/0.5057] = 15347 \text{ yrs}$$

5.4 Reporting of ^{14}C age

In the presence of so many models it is better to collect as much field data as possible. Considering errors in the available data examine sensitivity analysis in getting ages by individual models. Compare the results obtained from various models. Consider only those ages that are less vulnerable to errors in the observed parameters, which satisfy the limitations considered in the models. The applicability of various models is summarized below:

CO ₂ production	Soil type	Aquifer type	System type	Correction model
High	Porous soil	Non carbonate aquifer/ carbonate aquifers	Open system	No correction required.
Medium	Low porosity	Non carbonate	Complete transfer of CO ₂ into TDIC	No correction required.
Low	Carbonated soil, low porosity	Non-carbonate	Closed system with few isotopic exchange	Tamer's, Pearson's, Fontes & Garnier, Mook, and Plummer et al.
High	Carbonated soil	Miscellaneous rock aquifers	Closed system with CO ₂ exchange	Tamer's, Pearson's, Fontes & Garnier, and Plummer et al.
Medium	Carbonated soil, low porosity	Carbonated rock	Closed system, partial exchange	Pearson's, and Fontes & Garnier

