“Well, dear, for a gallon of elderberry wine, I take one teaspoonful of arsenic, and add half a teaspoonful of strychnine, and then just a pinch of cyanide.”

Joseph Kesserling Arsenic and Old Lace

Carbon Monoxide Poisoning

During the period of 1979 to 1988 an average of 1,100 accidental deaths per year were due to CO poisoning.

An estimated 10,000 persons per year in the US seek medical attention or lose at least one day of normal activity as a result of CO inhalation. The true number of annual CO poisonings is believed to be much higher.

Unfortunately, winter time is when the use of home heating appliances rises concurrently with viral influenza. Therefore, the diagnosis of CO poisoning is often missed.

Carbon Monoxide Poisoning

Acute carbon monoxide poisoning is responsible for 3,500 suicide deaths each year in the United States. And people who survive severe carbon monoxide poisoning may have long-term psychological abnormalities that severely limit their ability to function in society.

Symptoms of CO poisoning

Blood and tissues become cherry red
Symptoms of CO poisoning

Lividity in a victim of carbon monoxide poisoning. Note the pinkish discoloration of the skin consistent with a person who has ingested carbon monoxide. This cherry red color is the result of carboxyhemoglobin, a compound produced by the exposure of the hemoglobin to carbon monoxide.

Detection of CO in blood

Gas chromatography

CO released from blood by treatment with 85% $\text{H}_3\text{PO}_4$

CO catalytically converted to methane

$$\text{CO} + 3\text{H}_2 \xrightarrow{\text{Ni catalyst}} \text{CH}_4 + \text{H}_2\text{O}$$

Methane detected by gas chromatography

Two species, (α and β) are present at unknown concentrations, $C_\alpha$ and $C_\beta$.

Measure total absorbances, $A_1$ and $A_2$ at two wavelengths, 1 and 2.

If $\varepsilon$ values of the two species (α and β) are known at the two wavelengths, say $\varepsilon_\alpha$ (for species α at wavelength 1), $\varepsilon_\beta$ (for species α at wavelength 2), $\varepsilon_\alpha'$ (for species β at wavelength 1), $\varepsilon_\beta'$ (for species β at wavelength 2), then

$$A_1 = \varepsilon_\alpha C_\alpha + \varepsilon_\beta C_\beta$$

and

$$A_2 = \varepsilon_\alpha' C_\alpha + \varepsilon_\beta' C_\beta$$

Two equations in two unknowns can be solved for $C_\alpha$ and $C_\beta$

**WILD BLACK CHERRY**

*Prunus serotina*

Healthy cherry leaves contain prunasin, a cyanide precursor that in itself is non-toxic. When the leaves are damaged, the prunasin molecule is split and free cyanide (also called prussic acid or hydrocyanic acid) is liberated. Many plants, especially those in the rose family, have the potential to produce toxic levels of cyanide under certain conditions. Chokecherry (*Prunus virginiana*) is also toxic. There are reports of peach sprouts, leaves, and pits poisoning sows. Apricot pits and apple seeds are toxic as well. Arrowgrass (*Triglochin maritima*) contains a cyanogenic glycoside and has caused poisoning in livestock.

**Prunasin hydrolysis**

$$\text{Prunasin} \xrightarrow{\text{Prunasin hydrolysis}} \text{C}_6\text{H}_5\text{N} + \text{HCN} + 2\text{H}_2\text{O}$$
Poisoning Pigeons in the Park

All the word seems in tune on a Spring afternoon
When we're poisoning pigeons in the park,
Every Sunday you'll see my sweetheart and me,
As we poison the pigeons in the park.

When they see us coming the birdies all try and hide,
But they still go for peanuts when coated with cyanide,
The sun's shining bright, everything seems all right,
When we're poisoning pigeons in the park.

Tom Lehrer

Cyanide Poisoning

The Gas Chamber in the American Police Hall of Fame and Museum

The person to be executed is strapped to the chair. The room is air tight. Just below the seat is a pan of sulfuric acid. Held above the pan of acid are 16 one-ounce pellets of cyanide. As they are released the pellets form a deadly gas as the fumes rise and are inhaled by the person being executed.

AD 14
Livia kills the Emperor Augustus by poisoning his figs with cyanide

To avoid being poisoned, Augustus would drink only running water and would only eat figs off the tree.
Livia injects the figs with cyanide.
Several of Augustus' family die mysteriously.

Livia's son, Tiberius, becomes Emperor.

Cyanide Poisoning

Product tampering

TV & Movies

Novels & Short Stories

Individual nutters & mass suicides

"Lizzie Borden took an axe and gave her mother 40 whacks
When she saw what she had done, she gave her father 41"

Tylenol Killings
Chicago Sept/Oct 1982

Seven people, including a 12-year-old girl, died after taking Tylenol capsules that had been poisoned with cyanide.

After a two-month investigation, an unemployed accountant named James W Lewis was arrested at a New York library.

In June 1983 Lewis sentenced to 20 years in jail for sending a letter to Johnson & Johnson demanding $1million "to stop the killing". He was the only person ever linked to the deaths.

April 1996 Lewis paroled, after serving 13 years

New packaging and product warning laws introduced

WARNINGS: DO NOT USE IF CARTON IS OPENED OR PRINTED RED NECK WRAP OR PRINTED FOIL INNER SEAL IS BROKEN
Stella Nickell and the Excedrine Tablets

**Washington 1986**

June 11 1986, Sue Snow dies after taking headache tablets
Assistant at autopsy notes almond smell
Cyanide detected and traced to tablets

June 17 Stella Nickells informs police that her husband, Bruce, died suddenly on June 5 after taking Excedrine tablets - death recorded as emphysema
Nickells was an organ donor - cyanide found in preserved blood

Stella Nickell and the Excedrine Tablets

FDA examine ~3/4 million capsules - only 5 bottles (2 found at Nickells’ home) contaminated
Element “fingerprinting” traces cyanide to fish tank algicide
Stella Nickells found to have bought algicide (storekeeper recalls bell on her purse)
Insurance on Bruce Nickells $31K if death from emphysema, $176K if death accidental
9 May 1988, Stella Nickells sentenced to 90 years’ jail

The Sudafed saga

2 Feb 1991 Joseph Meling attempts to kill wife, Jennifer, with a cyanide-filled capsule placed in a package of Sudafed decongestant (Jennifer insured for $700K)
To divert suspicion, Meling had put adulterated capsules in five other packets on store shelves
Kathleen Daneker and Stan McWhorter died later that month from cyanide in Sudafed tablets
April 1993 Meling sentenced to life imprisonment (Jennifer divorces Meling)

Jonestown, Guyana, Nov 18 1978

The Rev Jim Jones orders 638 adult followers of his People’s Temple cult and 276 of their children to commit suicide by drinking cyanide-laced Kool-aid. Any who refused appeared to have been injected or shot

Cyanide and the comet

Astronomers detect HCN in the tail of the Hale-Bopp comet

Earth will pass through comet’s tail “we’ll all be ruined, said Hanrahan”

39 members of the Heaven’s Gate cult commit suicide in Rancho Santa Fe, Calif., with a mixture of phenobarbital and vodka
Cult leader, Marshall Applewhite and Bonnie Lu Trousdale Nettles
Cult members believed that after death they would join a spaceship hidden behind comet Hale-Bopp

Cult members believed that after death they would join a spaceship hidden behind comet Hale-Bopp
Lizzie Borden and cyanide

3 August 1892, Lizzie Borden refused any more purchases of prussic acid without a prescription.

That evening, all the family but Lizzie are violently ill

4 August 1892, Lizzie’s father, Andrew, and stepmother, Abby, are murdered in their home with an axe.

Lizzie acquitted after a 10 day trial

A botched cyanide assassination

Prince Yussoporov invites the lecherous Rasputin to the palace to meet Yussoporov’s wife.

Yussoporov and friends (?) feed Rasputin cakes with a huge dose of cyanide.

Rasputin does not die, so the conspirators blind, shoot, knife and kick him before dropping Rasputin through the ice into the River Neva.

3 days later, Rasputin’s corpse is recovered with one hand freed.

Monday January 26 1948 Teikoku Bank, Tokyo

“Welfare Ministry official” arrives at bank to disinfect Bank and staff because of dysentery outbreak at local well

16 staff members each given two doses of medicine

12 die – suspected KCN poisoning

After 7 month investigation, Sadamichi Hirasawa arrested, tried, convicted, sentenced to death – dies in jail in 1987

2003 – adopted son attempting to clear Hirasawa’s name – wartime poisoning unit blamed

Qualitative Tests for Cyanide

Formation of Prussian Blue

\[ 4\text{CN}^- + \text{Fe}^{2+} \rightarrow [\text{Fe(CN)}_6]^{4-} \]

\[ 4\text{Fe}^{3+} + 3[\text{Fe(CN)}_6]^{4-} \rightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 \]

Conversion to thiocyanate, SCN^-

\[ \text{CN}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SCN}^- + \text{S}_2\bar{\text{O}}_3^- \]

Schematic illustration of Prussian Blue Structure Fe (orange), C (blue), N (green)

Qualitative Tests for Cyanide

dissolution of solid black CuS

\[ 2\text{CuS} + 4\text{CN}^- \rightarrow 2[\text{Cu(CN)}_2]^2- + 2\text{S}_2\bar{\text{O}}_3^- + \text{CN}_2 \]

\[ [\text{Cu(CN)}_2]^2- \text{ very stable (K_{stab} \sim 10^{31})} \]

\( \text{Cu}^{2+} \text{ in the presence of } \text{CN}^- \text{ powerful oxidant} \)

\[ \text{Cu}^{2+} + e \rightarrow \text{Cu}^+ \]

\[ \text{Cu}^+ + 4\text{CN}^- \rightarrow [\text{Cu(CN)}_4]^{2-} \]

\[ \text{Cu}^{2+} + e \rightarrow \text{Cu}^+ \quad E^* = +0.16 \text{ V} \]

\[ [\text{Cu(CN)}_4]^{2-} + e \rightarrow [\text{Cu(CN)}_4]^3- \quad E^* = +0.54 \text{ V} \]

Formation of \([\text{Cu(CN)}_4]^{2-}\) powerful driver for reduction of \(\text{Cu}^{2+}\)

- oxidative power of \(\text{Cu}^{2+}\) considerably enhanced by presence of \(\text{CN}^-\)

Qualitative Tests for Cyanide

Combination of \(\text{CN}^-\) assisted \(\text{Cu}^{2+}\) reduction and benzidine oxidation

\[ \text{Cu(OAc)}_2 \text{ (e.g.) reacts with benzidine only in the presence of } \text{CN}^- \]

\[ \text{Cu}^{2+} + e \rightarrow \text{Cu}^+ \quad E^* = +0.16 \text{ V} \]

\[ [\text{Cu(CN)}_4]^{2-} + e \rightarrow [\text{Cu(CN)}_4]^3- \quad E^* = +0.54 \text{ V} \]

Blue - \(\lambda_{max} 410 \text{ and } 595 \text{ nm}\)

Colourless – do not interfere
Quantitative Tests for Cyanide

Titration of $\text{MCN}(aq)$ ($M =$ alkali metal) with $\text{Ag}^+$

\[
\text{Ag}^+ + 2\text{CN}^- \rightarrow [\text{Ag(CN)}_2]^+ \quad K_{\text{stab}} = 10^{+20.48}
\]

Soluble as alkali metal salt, precipitates in presence of $\text{Ag}^+(aq)$

Once $\text{CN}^-$ consumed, excess $\text{Ag}^+$ precipitates $[\text{Ag(CN)}_2]^-$

\[
\text{Ag}^+ + [\text{Ag(CN)}_2]^+ \rightarrow \text{Ag[Ag(CN)}_2] \quad K_s = 2 \times 10^{-15} \text{M}^2
\]

Catalytic detection

Regenerated $\text{CN}^-$ turns over more substrate
colour-forming process is catalytic in the test substrate, allowing the detection of traces (1.3 ng/mL) of cyanide, since one cyanide ion generates many molecules of the dye

Colorimetric micro determination of cyanide

Chloramine T

Automated analyser

The König reaction

Several alternatives for cyanide determination

e.g., reaction of 3-(4-carboxybenzoyl)quinoline-2-carboxaldehyde) with cyanide with primary amines to form highly fluorescent isoyndoles

Electrophoresis

charged species separated on the basis of their different rates of migration through a conductive medium under the influence of a dc electric field

Slab gel electrophoresis

charged sample in electrolyte (e.g., aqueous buffer), loaded as narrow band across a slab of the stationary phase - layer of porous material (e.g., paper or gel, say, agarose or polyacrylamide), often supported on a glass plate
Electrophoresis

Both solute & buffer migrate in electric field

Normally (but not necessarily) set up so buffer migrates towards the cathode

Electroosmotic flow:
cations, anions and neutral molecules swept along with buffer

Electrophoretic flow:
Solute also migrates in response to electric field

Cation mobility added to that of buffer
Anion mobility against that of buffer
Neutral solutes migrate with buffer

Separation by “charge”

Resolution improved by:
- Isoelectric focussing
- pH gradient maintained along the support gel.

Migrating proteins reach pH regions equal to their isoelectric point, are neutralised and stop migrating.

Separated proteins become focussed into narrow bands of the gel

Disc (continuous) electrophoresis
Two different buffers with different pH.
Proteins migrating between pH domains are concentrated into sharp bands

Drawbacks
Slab gel electrophoretic techniques good for qualitative analysis (what is there)
Less useful for quantitative analysis (how much is there)

Separation efficiency related to plate counts, $N$, $N = \frac{uE}{2D}$
Best separations at high voltages, $V$
High voltages lead to undesirable heating

Heating limits the potentials used in slab electrophoresis to about 500 V

Limitation on separation efficiency

SDS-PAGE electrophoresis
rate of migration depends on charge/volume ratio
molecules of similar size, but different charge, can migrate at different rates
If charge equalised, migration rate related to molecular size
use a polyacrylamide gel (PAGE) & detergent, sodium dodecyl sulfate (SDS)
SDS dissociates proteins into polypeptide subunits
electrostatic binding of SDS to polypeptides produces aggregates of similar charge
aggregates migrate at rates dependent on their molecular weights
compare migration rates with standards of known MW

Capillary Electrophoresis
Capillary - lower power dissipation; more efficient cooling
Much higher potentials (typically 20,000 - 60,000 V)

Considerable improvements in sensitivity, resolution and analysis time
Small sample sizes (0.1 to 10 nL) and quantitative detectors
Capillary Electrophoresis

Electroosmotic flow

- small sample cross section, so capillary walls influence flow
- Si-O-H groups on glass capillary wall ionized by buffer
- Buffer cations associated with Si-O\(^{-}\) groups form immobile layer
- second layer of loosely held cations, attracted to the cathode
- as they migrate with their associated solvating molecules, the solution moves towards the cathode
- electroosmotic flow

Bufferelectroosmotic flow has a flat profile across the capillary
bands of analyte intrinsically narrower than in pressure-driven flow methods

Electrophoresis sample introduction

- Electrokinetic injection
- Pressure injection
- No electroosmotic flow, so only cations migrate to cathode
- neutral species stationary, anions go to anode (source reservoir)
Capillary Electrophoresis

Detectors

Detection by absorbance, fluorescence, electrochemistry, mass spectroscopy, etc.
Generally on-column detection
Beer Lambert Law: $A = \varepsilon c d$
Detector configurations designed to maximize path length ([analyte] often low)

Capillary Electrophoresis

Some variations:
- Capillary zone electrophoresis (CZE)
- “normal” (simplest) configuration
- Capillary Gel Electrophoresis (CGE)
- Capillary filled with polymeric gel – good for separations based on molecular size
- Capillary Isoelectric Focussing
- Uses 2 buffers – analytes concentrated into narrow bands – good sensitivity
- Capillary Isoelectric Focussing
- pH continuum established – excellent resolution of amphoteric molecules (e.g. proteins)
- Micellar Electrokinetic Capillary Chromatography (MEKC or MECC)
- Uses surfactant micelles to separate neutral analytes
- Capillary Electrochromatography (CEC)
- Capillary loaded with coated SiO$_2$ spheres – also good for neutral analytes

The Shroud of Turin

The Shroud of Turin is a centuries old linen cloth that bears the image of a crucified man. A man that millions believe to be Jesus of Nazareth. Is it really the cloth that wrapped his crucified body, or is it simply a medieval forgery?

The Shroud of Turin chronology

1357 Earliest authenticated document mentioning the Shroud
Shroud called a forgery by Bishop Henri De Poitiers of Troyes “cunningly painted as attested by the artist who had painted it”
1532 Shroud survives chapel fire (slightly scorched by molten silver from casket and stained by water
1977 Analyses of pollen samples shows pollens from Turin, France (where it had been exhibited), Palestine and Turkey
1978 Shroud of Turin Research Project scientists examine the Shroud in Turin and conclude that the image contains blood and cellulose

The Shroud of Turin chronology

1981 Polarised light microscopy studies interpreted as indicating that the red component of the Shroud contains the red pigments Fe$_2$O$_3$ and vermilion, HgS
1988 Radiocarbon dating (University of Arizona, Tucson; University of Oxford; University of Zurich) date the Shroud between 1260 and 1390 AD
1990 X-Ray diffraction suggests blood areas to be a paint pigment made from a mixture of vermilion, calcite (CaCO$_3$) and hematite (anhydrous Fe$_2$O$_3$)
Electron microprobe analysis confirms presence of red-ochre pigment on the Shroud

Shroud website
http://www.shroud.com/
X-Ray diffraction

One of several diffraction techniques (electron, neutron diffraction)

Crystals
Made up of repeats of the unit cell

The Unit Cell
Contains the minimum contents which, if repeated through space, are sufficient to specify the whole of the crystal. In a 3-D lattice, the unit cell is a volume element and may be defined as the parallelepiped which produces the macroscopic crystal when repeated side by side in 3 dimensions.

The Unit Cell - an example in 2D

Unit cell is the smallest part of the drawing which, if repeated in all directions will generate the pattern. Find several examples of such a repeat unit (note that all are the same size).

The Unit Cell in a crystal

Atoms of a crystal are repeated regularly in 3D space and may be considered to form a grid (or several interpenetrating grids) made up of planes of atoms

E.g., cristoballite (SiO₂)
The Bragg equation

If X-ray energies are chosen such that the wavelength of the X-rays – the distance between the atoms in a crystal, then the X-rays “see” a series of planes within the crystal, the crystal acting as a “diffraction grating”.

In 1913, Bragg treated diffraction as equivalent to reflection from planes within the lattice.

Consider 2 parallel incident rays making an angle $\theta$ with two parallel planes. The 2 rays will reinforce (be in phase) if the path difference of the 2 rays is some integral multiple of the wavelength.

Path length difference = $2x$

Thus, for reflected waves to be in phase, $2x = n\lambda$,

Since, $\sin \theta = x/d$

Thus, $x = d \sin \theta$

and so, to get x-rays in phase, for which $2x = n\lambda$

$2x = 2d \sin \theta = n\lambda$ or $n\lambda = 2d \sin \theta$

The Bragg Equation

The Generation of X-rays

Electrons accelerated by electric field to hit a metal target (generally Cu or Mo). As electrons are slowed by the collisions X-rays (white radiation) is emitted.

In addition, the incident electrons of appropriate energy can knock electrons out of the innermost ($K$) shell. An electron then falls from an outer shell ($L$ or $M$) to fill the vacancy in the $K$ shell. As this occurs, nearly monochromatic, high intensity X-radiation ($K_{\alpha}$) is emitted. The extraneous radiation is removed by a filter (monochromator) and the nearly monochromatic $K_{\alpha}$ radiation used in the diffraction experiment.

The powder diffraction experiment

X-rays directed upon a powdered sample (~ 1/2 g).

Either:

(i) Electronic detector moves in an arc around the sample, measuring the intensity of the diffracted X-rays as a function of the angle $2\theta$.

Or

(ii) Detector remains constant and the sample is rotated

Intensity of diffracted X-rays plotted as a function of the angle $2\theta$.

E.g., for clay minerals

“Side view” of two layers of the layered silicate, lizardite. Tetrahedra, SiO$_4^2-$ ions, large circles, OH$^-$ anions, small circles Mg$^{2+}$ ions

Each pattern gives unique “fingerprint” data for that clay mineral
Carbon dating

Technique developed by William Libby (U Chicago) in 1946 (won Nobel Prize for chemistry in 1960)

Recall, production of $^{14}$C in atmosphere:

$$^{14}_7N + ^1_0n \rightarrow ^{14}_6C + ^1_1H$$

And decay of $^{14}$C

$$^{14}_6C \rightarrow ^8_0e + ^4_1N$$

Amount of $^{14}$C in atmosphere assumed to be relatively constant.

Incorporated into living tissue (as an equilibrium, generally through $CO_2$ in photosynthesis)

At death, no more $^{14}$C produced in organism, decay to $^{14}$N only process

Radioactive decay is a first order process - the rate of decay is proportional to the amount of material present

$$\frac{dA}{dt} = -kA$$

for $A = 1/2 A_0$, then

$$\ln 2 = 0.693 = k \tau$$

i.e.,

$$k = \frac{0.693}{\tau}$$

$$\ln \frac{A_0}{A} = \frac{0.693}{\tau}(t - t_0)$$

For $^{14}$C, $\tau = 5730$ years

$t - t_0$ represents the time since the artifact died ($\Delta t$)

Assume that the levels of $^{14}$C production have not changed since the artifact died. The current rate of decay of $^{14}$C is 15.3 disintegrations/min/g of sample. This will be proportional to $A_0$.

Let the current rate of disintegration of $^{14}$C be $R$, then,

$$\ln(15.3 / R) = (0.693 / 5730) \Delta t$$

i.e.,

$$\Delta t = \frac{5730}{0.693} \ln(15.3 / R)$$

$\Delta t = 8268\ln(15.3/R)$

Detection

Formerly, $\beta$ particles counted in gas proportional counter or liquid scintillation counter

Large amounts of sample were needed - burned to produce $CO_2$, trapped as $CaCO_3$ and measured

Accelerator Mass Spectrometer provides accurate counts on $^{14}$C and $^{12}$C on minute samples (tens of mg)

For Shroud of Turin, analysis used ~ 50 mg

The charcoal sample excavated from Stonehenge had a disintegration rate of 9.65 disintegrations/min/gm of sample.

Thus,

$$\Delta t = 8268\ln(15.3/9.65)$$

and the sample is 3810 years old

for Shroud, $R = 14.1$ disintegrations/min/gm of sample

$\Delta t = 675$ years,

i.e., vegetable matter for Shroud (flax used to make the linen) died 675 years ago, in ~ 1313

for Shroud to date from 0 AD, $\Delta t = 1988$ and $R = 12.0$
Isotope Ratios

Difference in ratio of isotopes of an element can be distinctive

Isotopes of Sr

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Stable</th>
<th>84Sr</th>
<th>86Sr</th>
<th>87Sr</th>
<th>88Sr</th>
<th>82Sr</th>
<th>85Sr</th>
<th>89Sr</th>
<th>90Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.56</td>
<td>25.6</td>
<td>64.8</td>
<td>50.5</td>
<td>29</td>
<td>0.56</td>
<td>9.86</td>
<td>7.01</td>
</tr>
</tbody>
</table>

Stable

Rb and Sr present in primordial sediment and/or rock

\[ \text{Rb} \rightarrow \text{Sr} \]

After time, \( t \)

\[ [^{87}\text{Rb}]_t = (^{87}\text{Rb})_0 \cdot e^{- \lambda t} \]

\[ [^{87}\text{Sr}]_t = [^{87}\text{Sr}]_0 - (^{87}\text{Rb})_0 \cdot e^{- \lambda t} \]

Isotope Ratios

Rock weathers, becomes soil, Sr absorbed by plants, enters food-chain

Sr isotope of human/animal will match that of their diets

Sr (c.f. Ca) deposited in teeth (enamel) and bones

Dental enamel laid down by age 4 then unchanged, bones continually growing

Sr isotope ratio of teeth characteristic of location in early childhood

Sr isotope ratio of bone characteristic of location of most recent years of life

Difference in Sr isotope ratio of teeth and bones indicates migration

The Iceman dieth

Sr isotope ratio in teeth matches that in Feldhurns – likely childhood home (conclusion supported by O isotope analysis)

Origin and Migration of the Alpine Iceman,
Wolfgang M"uller et al, Science, 31 October, 2003

Site of Iceman discovery 1991

Ariel photo of the site of the discovery of the iceman


Site of Iceman discovery 1991

First photograph of discovery of the Iceman 19 September 1991

Mountaineers Reinhold Messner (r) and Hans Kammerlander (l) with partially freed Iceman 21 Sept 1991

Site of Iceman discovery at completion of excavation 1992

Constancy of atmospheric CO₂?

Libby assumed atmospheric ¹⁴C constant

¹⁴C produced by neutrons from cosmic rays

Cosmic rays deflected by magnetic fields of sun and earth (variable) & cosmic flux influenced by sunspot activity (periodic ~ 11 year cycle)

So, atmospheric ¹⁴C from the N(np) reaction varies with time

Earth has several linked CO₂ reservoirs

Redistribution of global CO₂ between reservoirs varies with climate change

Natural levels of CO₂ variable

Variation in atmospheric ¹⁴CO₂ by examination of tree ring data

Carbon isotopes and plants

photosynthesis

\[ \text{CO}_2(g) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 + \text{O}_2 \]

\[ 6\text{CO}_2(g) + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2(g) \]

[glucose] C₄ plants
Carbon isotope ratios determined by accurate mass spectroscopy

Original reference for $\delta^{13}C$ was Cretaceous marine fossil, *Belemnitella americana*, found in the PeeDee formation in South Carolina.

Chosen as it has one of the highest $^{13}C/^{12}C$ ratios of all natural sources.

PeeDee standard assigned a $\delta^{13}C$ value of zero; almost all naturally-occurring samples have negative $\delta^{13}C$ values.

Currently, secondary standards, prepared by the US National Bureau of Standards used as reference materials.

C4 plants have higher $\delta^{13}C$ values ranging from $-17$ % to $-9$ %; mean of $-13$ % relative to PDB.

C3 plants show $\delta^{13}C$ values ranging from $-32$ % to $-20$ %; average value of $-27$ %.

Largest stable carbon isotope fractionation involves atmospheric CH$_4$, $\delta^{13}C$ values of $-58$ % recorded.

Atmospheric CO$_2$ has a $\delta^{13}C$ values of $-7$ %.

The $\delta^{13}C$ value used routinely by plant physiologists to distinguish between the C3 and C4 plant groups for applications such as determining drought resistance in plants, monitoring attempts to breed in drought resistance, and in detecting adulteration of foods.

Recent application:
testosterone testing in athletes

Synthetic testosterone has $\delta^{13}C$ values in the range $-28$ to $-29$.

Endogenous testosterone has $\delta^{13}C$ values in the range $-21$ to $-26$.