A charcoal artifact, excavated near the Museum of Contemporary Art, is thought to have come from Australia’s first dockyard which operated until 1790. The object is analysed by radiocarbon dating. What would the $^{14}$C decay rate be in 2006 if the object were genuine? The current rate of $^{14}$C decay in living matter is 15.3 disintegrations/min/g of carbon and the half life of $^{14}$C is 5730 years.

$$\ln\left(\frac{N_0}{N}\right) = k t = \left(\frac{0.693}{t_{1/2}}\right) t$$

for $^{14}$C, $t_{1/2} = 5730$ years

$N_0 = 15.3$

from the question, $t$ will be $2006-1790 = 216$ years

It is necessary to determine $N$,

Therefore,

$$\ln\left(\frac{15.3}{N}\right) = \left(\frac{0.693}{5730}\right)216$$

$$\ln(15.3) - \ln(N) = 0.026$$

$$\ln(N) = \ln(15.3) - 0.026 = 2.728 - 0.026 = 2.702$$

$$N = 14.91$$

NOTE: if the students calculate the measured disintegrations from 2.0 gm of CaCO$_3$, then they need to calculate as follows:

Formula weight of CaCO$_3$ = 40 + 12 + 3 x 16 = 100

%C by weight in CaCO$_3$ = 12/100 = 12%

mass of C in 2.0 g of CaCO$_3$ = 2.0 x 0.12 = 0.24

Therefore, specific disintegration rate of artifact = $N$ disintegrations/min/g carbon, and a disintegration rate of $N(0.24) = 3.58$, disintegrations/minute would be expected. (Note, however, that these are not the units used in the question).

If they mix $N$ and $N_0$, then the calculation is:

$$\log\left(\frac{N}{N_0}\right) = \left(\frac{0.693}{t_{1/2}}\right) t$$

and so .

$$\ln\left(\frac{N}{15.3}\right) = \left(\frac{0.693}{5730}\right)216$$
lnN - ln(15.3) = (1.209 x 10^{-4}) \times 216
lnN = 2.7279 - 0.0261
lnN = 2.7279 + 0.0261 = 2.7540
N = 15.70, disintegrations/minute/gm carbon

If students use

\[ \log \left( \frac{N_0}{N} \right) = \left( \frac{0.693}{t_{1/2}} \right) t \]

Then their answer will be 14.444.

(b) Characterisation of the bullet lead used in the assassination of President Kennedy was performed by Instrumental Neutron Activation Analysis.

(ii) A standard containing 17.5 \( \mu \)g of antimony (Sb) and a bullet sample weighing 333 mg were irradiated simultaneously in a nuclear reactor. The standard and sample were removed from the irradiation source. The standard was counted 3.50 minutes after the end of the irradiation and the \(^{124}\text{Sb}\) counting rate was determined to be 7.11 \times 10^3 cpm. Then the sample was counted 5.25 minutes after the end of the irradiation and had a \(^{124}\text{Sb}\) counting rate of 1.73 \times 10^3 cpm. What is the concentration of Sb in the sample? For \(^{124}\text{Sb}\), the half life is 1.54 minutes.

\[
\frac{R_{\text{std}}}{R_{\text{sam}}} = \frac{W_{\text{std}}(e^{-\lambda T})_{\text{std}}}{W_{\text{sam}}(e^{-\lambda T})_{\text{sam}}}
\]

where:

- \( R \) = counting rates of standard (\( R_{\text{std}} \)) and sample (\( R_{\text{sam}} \))
- \( W \) = mass of the element in the standard (\( W_{\text{std}} \)) and in the sample (\( W_{\text{sam}} \))
- \( T \) = elapsed time since irradiation
- \( \lambda = 0.693/\tau_{1/2} \)

here:

\[
\lambda = 0.693/\tau_{1/2} = 0.693/1.54 = 0.45
\]

\[
\frac{R_{\text{std}}}{R_{\text{sam}}} = \frac{W_{\text{std}}(e^{-\lambda T})_{\text{std}}}{W_{\text{sam}}(e^{-\lambda T})_{\text{sam}}}
\]

\[
\frac{7.11 \times 10^3}{1.73 \times 10^3} = \frac{17.5 \times 10^{-6} (e^{-0.45 \times 3.50})_{\text{std}}}{x(e^{-0.45 \times 5.25})_{\text{sam}}}
\]

\[
4.1098 = \frac{17.5 \times 10^{-6} (0.2070)}{x (0.0942)} = \frac{3.846 \times 10^{-5}}{x}
\]

\[
x = \frac{3.846 \times 10^{-5}}{4.1098} = 9.359 \times 10^{-6}
\]

i.e., in the 333 \times 10^{-3} g bullet sample, there were 9.359 \times 10^{-6} g Sb,

i.e., \([\text{Sb}] = 2.810 \times 10^{-5} \text{ g/g} = 28.104 \text{ ppm} \)
6 (c) Draw the edges of a two-dimensional unit cell on the accompanying Escher drawing. **Remember to hand in the sheet with your answer booklet.**

Two types of birds
3 x White birds 1 up
   1 from right above
   1 from left above
1 from right above
1 from left above
3 x Black birds 1 down
   1 from right below
   1 from left below
Unit cell is 8.8 x 8.8 cm 60° angles

(d) A 1 g sample taken from 50 g of the ashes of Bob Egle, one of Graham Young’s victims, was analysed for thallium by atomic absorption as follows.

The 1 g sample was completely digested in 100 mL of acid. The acid solution was diluted to 1 L. Two separate one hundred microlitre (100 μL) aliquots of the sample were each diluted to 1.00 mL after addition of ten microlitres (10 μL) of a 0.010 M solution of TlNO₃ to one of them. The two solutions gave emission signals of 39.8 and 49.6 arbitrary units.

12 Determine the concentration of thallium (in mg/g) in the ashes.

Tl “spike” = 10 x 10⁻⁶ L of 0.010 M solution = (0.010)(10 x 10⁻⁶) = 1 x 10⁻⁷ mole Tl

\[ x \text{ mole Tl gives absorbance of } 39.8 \text{ units} \]
\[ x + (1 \times 10^{-7}) \text{ mole Tl gives absorbance of } 49.6 \text{ units} \]

i.e., 1 x 10⁻⁷ mole Tl gives absorbance of \( (49.6 - 39.8) = 9.8 \) units

since \( x \) mole Tl gives absorbance of \( 39.8 \) units

then, \( x = (1 \times 10^{-7})(39.8)/(9.8) = 4.06 \times 10^{-7} \) mole Tl.
This is in 100 μL of diluted sample
Thus, number of mole Tl in 1 L of diluted sample = \((4.06 \times 10^{-7})(1)/(100 \times 10^{-6}) = 4.06 \times 10^{-3}\) mole

This is the amount from 1 gm of sample

i.e., \([\text{Tl}] = 4.06 \times 10^{-3}\) mole/g = 204.4(\(4.06 \times 10^{-3}\))g/g = 0.8299 g/g = 830 mg/g

Selected Ion Monitoring is used in the analyses of arson residues and in sports drug testing.

(e) Briefly describe the basis for and requirements of analyses using this technique.

Selected Ion Monitoring is used to interpret mass spectrometric data. The abundance and relative intensities of three characteristic (m/e) ions of an analyte are determined to very high precision and matched against those from a genuine sample of the suspect material.

(f) The FID has been described as "almost the universal detector". Briefly describe the operation of the FID and why it is not a universal detector.

The FID mixes the column eluent with air and \(H_2\) and burns the mixture within the detector, producing \(CH\) radicals from the CH moieties in the eluent. Those radicals react with oxygen atoms in the flame generating \(CHO^+\) ions (and electrons) which migrate to a cathodic detector, generating a current which is proportional to the number of CH groups in the molecule being detected. Because the FID relies on the generation of \(CH\) radicals, it detects only analytes with \(CH\) radicals, and so does not detect many inorganics, nor is the current always proportional to the molecular weight of the analyte (e.g., if the analyte contains CO or P functional groups).

(g) Briefly describe the main differences between the techniques of X-Ray Fluorescence and Auger spectroscopy.

(h) The new Australian synchrotron, probably to be built in Victoria, is likely to become an indispensable tool in forensic chemistry. Give two possible uses of synchrotron radiation in forensic chemistry. For each example explain why a synchrotron, rather than a conventional X-ray source, is needed for the analysis.

The main points here are:
- High intensity radiation
- Monochromatic radiation
- Wide spectrum of radiation available

Therefore ability to concentrate enough radiation onto a small area allows spectra (and hence analyses) to be obtained on small samples, or small sections of samples. This part of the answer needs to indicate (briefly) an understanding of how these virtues are achieved (and, in combination with the second part of the answer, why, indeed, they are virtues).

Additional use would be in XANES and EXAFS, which are techniques not practical without synchrotron source.

The rest of the answer needs to demonstrate an understanding of how these features provide advantages to whatever examples have been chosen.

\(\Delta\)ατα:

\(\text{Tl} \ \text{Ατομική οχηματική} = 204.4\)

1 \(\mu\)L = \(10^{-6}\) L