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Short Research Article

The radiolysis of [^{14}C]carbon monoxide†

H. EDWIN HARGRAVES, ANDREW G. LASHFORD*, ANTHONY T. REES and BRIAN S. ROUGHLEY
GE Healthcare Limited, Amersham Place, Little Chalfont, Bucks HP7 9NA, UK

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Introduction

Cryogenic distillation of carbon monoxide is a commonly used method of separation for carbon-12 and carbon-13. As part of a continuing program looking at methods of enrichment of isotopes, GE Healthcare has investigated the enrichment of carbon-14 by this method. Cryogenic distillation does not seem to have been used for this purpose previously.

One area of concern is the stability of [^{14}C]carbon monoxide particularly in the liquid state and at high isotopic abundances. GE Healthcare has experience of handling and storage of [^{14}C]carbon monoxide but only in the gaseous state and over relatively short time periods.

Investigation of the literature[1–5] showed several studies on the effects of radiation on carbon monoxide. These suggested radiolysis occurs at a significant rate by Equation (1)

$$4CO \rightarrow CO_2 + C_3O_2 \quad (1)$$

Generally the effects of irradiation will vary widely depending on the nature and source of the radiation.[6] However studies on carbon monoxide show that the rate of radiolysis was largely independent of the nature of the radiation. Investigations of the self-radiolysis of [^{14}C]carbon monoxide are very limited.[7]

Consequently, it was decided to investigate the stability of [^{14}C]carbon monoxide under the conditions to be found in a [^{14}C]carbon monoxide cryogenic distillation system. The preliminary modelling work carried out by GE Healthcare had defined these conditions as:

- High isotopic abundance (~95%, 2.2 TBq/mol).
- In the liquid state.
- At a temperature of approximately 81 K.

Method

[^{14}C]carbon monoxide was synthesised by the reaction of [^{14}C]carbon dioxide with zinc at high temperature.[8] Transfers were achieved by short path cryogenic distillation using liquid helium (4 K) to overcome the high vapour pressure of CO at liquid nitrogen temperatures (77 K). The equipment is shown in Figure 1.

The [^{14}C]carbon monoxide was purified to remove un-reacted [^{14}C]carbon dioxide by distillation at 77K until a low level of residual [^{14}C]carbon dioxide was achieved.

The purified [^{14}C]carbon monoxide was sub-divided into stainless steel pressure tubes (~280 mm × 3 mm i.d.) with an internal volume of 2.7 ml containing approximately 1 mmol such that liquid carbon monoxide would be present at 77 K.

The pressure tubes were stored in liquid nitrogen and samples analysed at 6, 14 and 22 weeks by radio gas chromatography (RGC) and GC/MS.

Results and discussion

The results of the analyses are shown in Table 1.

The percentage transformation due to radiolysis in time t (s) is given by the expression:[6]

$$\left(1 - e^{-kt}\right) \times 100\% \quad (2)$$

where

$$k = F\varepsilon GS \times 6.14 \times 10^{-16} \quad (3)$$

*Correspondence to: Andrew G. Lashford, GE Healthcare Limited, Amersham Place, Little Chalfont, Bucks HP7 9NA, UK.
E-mail: andy.lashford@ge.com

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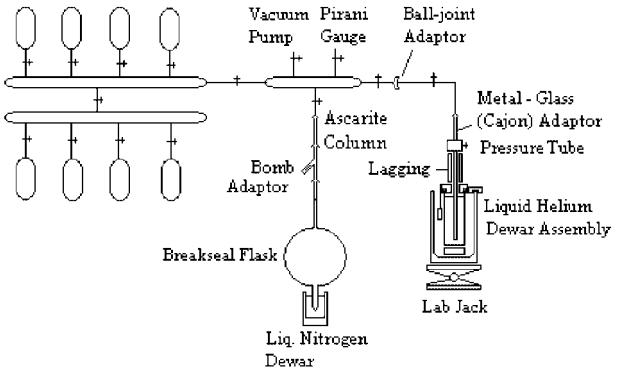

Figure 1 Equipment for the purification and subdivision of ^{14}CO.

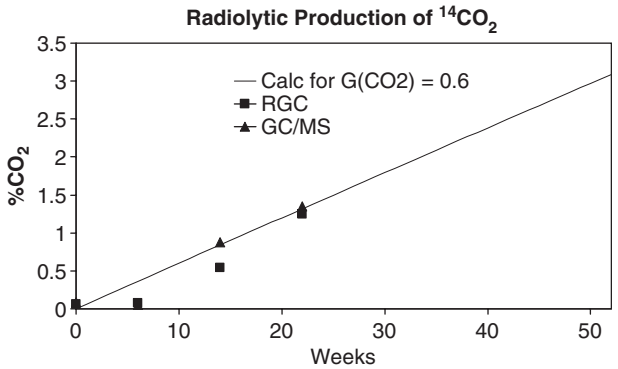

Figure 2 Rate of radiological production of $^{14}CO_2$.

Table 1 Sample analysis Results

Sample number	Analysis time point (weeks)	% $^{14}CO_2$ accumulation	
		RGC	GC/MS
Initial	0	0.06	0.09
1	6	0.08	0.05
2	14	0.54	0.88
3	22	1.25	1.35

Here F is the fraction of the energy absorbed by the compound ($F = 1$ for liquid); ε is the average β energy of ^{14}C in eV (45 000 eV for ^{14}C); G is the susceptibility of the molecule to radiation expressed as molecules transformed per 100 eV absorbed; S is the specific activity of ^{14}C in Ci/mole (62.44 for 100% ^{14}C).

Conclusions

Figure 2 Shows the rate of [^{14}C]carbon dioxide production as measured, and the calculated rate for a value of $G(CO_2)$ of 0.6 which is a typical value found in previous studies carried out with other sources of radiation[1–6]. This corresponds to an initial annual rate of approximately 3%.

The consequences for a [^{14}C]carbon monoxide cryogenic distillation system seem serious. The rate of radiolysis will be highest where the concentration of carbon-14 is highest which will be at the bottom of the distillation column. At this point the column and connecting tubes will be of the smallest diameter.

All products of decomposition from Equation (1) would be solid at the temperature of operation (81 K) and so are liable to block the system. The nature of a cryogenic distillation column dictates that it can take a very long time (1000's of hours) to come to equilibrium and establish the isotope concentration gradients along the columns. However calculations suggest blockage could occur in a matter of weeks. The conclusion must be that cryogenic distillation is an unsuitable method for the enrichment of carbon-14 to high isotopic abundance.

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