Measurement of $^{85}\text{Kr}$ in the environment by liquid scintillation counting

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7. Summary
The concentration of \(^{85}\text{Kr}\) in the environment has been increasing from 1950s by release from nuclear power related facilities in the world. It reaches 1.5 Bq/m\(^3\) level in the northern hemisphere in 2000s. There is no effective sink in the environment except radioactive decay due to Kr is a noble gas.

Kr-85:
- half life 10.76y
- \(\beta\)-decay: 0.67MeV (100%)
- \(\gamma\)-ray: 0.514MeV (0.43%)

Major source:
Nuclear fuel reprocessing plant.

Kr in the atmosphere:
1.14ppm
The purpose of the research is to develop an analytical method which can be applied to determine low level $^{85}$Kr in environmental samples.

We planed to apply the developed method to atmospheric $^{85}$Kr determination and to $^{85}$Kr dating of groundwater.

The concentration of $^{85}$Kr in groundwater is very low due to limited dissolution of Kr in water. The activity of 0.1 Bq/1000L is expected for surface water even if all of the Kr dissolved is recovered. Older groundwater would have lower $^{85}$Kr due to decay.

Then, we need a method with very low detection limit of $^{85}$Kr

- Gamma spectrometry is inappropriate considering small probability of gamma-ray emission. Therefore, beta-ray counting is necessary to achieve low level measurement.
- We decided to use liquid scintillation counting (LSC) because high counting efficiency is expected.
- The most difficult point in LSC is how to enclose Kr in a counting vial.
3. Description of analytical flow

**For atmospheric $^{85}\text{Kr}$ determination**

Atmosphere ($\text{Kr} + ^{85}\text{Kr}$)

- Kr: 1.14 ppm

Collection of Kr from air by charcoal trap at liquid nitrogen temperature

Separation of Kr from other gases by gas chromatography

$^{85}\text{Kr}$ activity measurement by LSC

Specific activity determination

$^{85}\text{Kr}/\text{Kr}$ specific activity is not sensitive to partial sample loss either in sampling or analysis.

**For $^{85}\text{Kr}$ Dating of groundwater**

Solubility of Kr:

- $6-8 \times 10^{-8} \text{ml/g water}$ (0.06-0.08 ml/1000 L)

Recovery of dissolved gas by hollow fiber membrane module and filling into gas container

I will speak on atmospheric $^{85}\text{Kr}$ analysis
4. Analytical system

The system has 3 parts.
Air is collected in charcoal trap at -196°C. N\textsubscript{2}/O\textsubscript{2} were purged with He at -78°C for 2 h. Heated at 200°C, Kr is moved to the charcoal column at -196°C.
Heat the charcoal column with water. Gases are introduced to GC. Kr fraction is taken to the vial with silica gel at -196°C. Scintillator is poured to the vial at -196°C.

Vial is made of synthetic quartz (86ml) Scintillator (PPO/ p-xylene) mp. 13°C Low background LS counter, Aloka LB-5

\(^{85}\text{Kr}\) standard gas (KR85EZSE20, Cerca Lea, France) Counting efficiency: 72.1% (FOM)
Selection of counting vial

No leakage of Kr
Low background

Synthetic quartz vial  Glass vial

![Image of vials]

Graph showing BG (cpm) and Kr-85 (counts) over time (h) for different vials:
- Synthetic quartz (86ml)
- Glass (20ml)
- Teflon (50ml)
- Teflon (20ml)

Legend:
- poly (no piece)
- poly (glass piece)
- poly (synthetic quartz piece)
- poly (natural quartz piece)
5. Application to atmospheric $^{85}\text{Kr}$ determination

500-1000 L air, 62-92% Kr recovery

1.44 to 1.60 Bq m$^{-3}$
Av. 1.54 ± 0.05 Bq m$^{-3}$
Change in $^{85}$Kr in the atmosphere

The increasing rate:
0.029 Bq m$^{-3}$/y

1981: $0.77 \pm 0.03$ Bq m$^{-3}$

2008: $1.54 \pm 0.05$ Bq m$^{-3}$
The detection limit of the present analytical method is calculated with a 95% confidence level \((a = b = 0.05)\) for paired (sample and background) measurements (Currie, 1968).

\[
S_D = 2.71 + 4.65\sigma_B
\]

where \(S_D\) is the detection limit and \(\sigma_B\) is the standard deviation of the background. Using a background count rate of 0.160 cps, a counting time of 2500 min, and counting efficiency of 72.1%, we obtain \(S_D = 0.0015 \text{ Bq}\), which corresponds to the analysis of 1.3 L of air with a 74.6% recovery of Kr. However, the minimum detectable amount of Kr by gas chromatography is about 0.01 mL—this requires a volume of air about 10 times greater than the detection limit of radioactivity.
1. Analytical method of $^{85}$Kr by LSC was develop.
2. The method was successfully applied to determination of atmospheric $^{85}$Kr concentration.
3. The detection limit of 0.0015 Bq is achieved.
4. Application to $^{85}$Kr dating of groundwater is now going on.

Thank you for your kind attention.