

## DETERMINATION OF $^{14}\text{C}$ IN GRAB SAMPLES OF STACK AIR FROM NUCLEAR POWER PLANTS

Ivo Světlík<sup>1,2</sup> • Petr Rulík<sup>3</sup> • Václav Michálek<sup>3</sup> • Lenka Tomášková<sup>1</sup> • Jiří Mizera<sup>1</sup>

**ABSTRACT.** At present, the most significant artificial sources of radiocarbon in the environment are effluents from nuclear energy facilities, even though they represent a minor contribution in comparison with the natural production of  $^{14}\text{C}$ . Nevertheless,  $^{14}\text{C}$  is a major contributor to the collective effective dose from all radionuclides released by nuclear power plants (NPP) with light-water pressurized reactors (LWPR) during normal operation. This paper aims to develop a  $^{14}\text{C}$  determination method for grab samples from NPPs' stack air. This method enables separate determination of  $^{14}\text{CO}_2$  and  $^{14}\text{C}$  in combustible compounds. Treated samples are counted by LSC with an indication of interferences. Our results of  $^{14}\text{C}$  activity concentrations in stack air grab samples are compared with results of  $^{14}\text{C}$  determinations performed by the NPP's laboratory, which utilizes monthly/weekly accumulated samples.

### INTRODUCTION

Currently, the most significant artificial sources of radiocarbon in the environment are effluents from nuclear energy facilities, even though they represent a minor contribution in comparison with natural  $^{14}\text{C}$  production. Nevertheless,  $^{14}\text{C}$  is a major contributor to the collective effective dose from all radionuclides released by nuclear power plants (NPP) with light-water pressurized reactors (LWPR) during normal operation (UNSCEAR 2000), as reported in Table 1 for 1990–1994. The Czech Republic has 2 LWPR-equipped NPPs, Temelin and Dukovany, with installed power outputs of  $2 \times 1000$  MW and  $4 \times 440$  MW, respectively.

Table 1 Normalized collective effective dose from radionuclides released from nuclear reactors, 1990–1994, airborne effluents (UNSCEAR 2000).

Reactor type <sup>a</sup>	Electrical energy generated (%)	Collective effective dose per unit of electrical energy generated (man Sv [Gwa] <sup>-1</sup> )			
		Radioactive noble gasses	$^3\text{H}$	$^{14}\text{C}^b$	$^{131}\text{I}$
LWPR	65.04	0.003	0.005	0.059	0.0001
BWR	21.95	0.15	0.002	0.14	0.0002
GCR	3.65	1.44	0.010	0.38	0.0004
HWR	5.04	0.23	1.4	0.43	0.0001
LWGR	4.09	0.19	0.05	0.35	0.002
FBR	0.24	0.042	0.10	0.032	0.0009

<sup>a</sup>LWPR – light-water pressurized reactor; BWR – boiling water reactor; GCR – gas-cooled reactor; HWR – heavy-water reactor; LWGR – light-water, graphite-moderated reactor; FBR – fast breeder reactor.

<sup>b</sup>Local and regional components only.

$^{14}\text{C}$  from the NPP's gas outlet can be captured from the surroundings or dissipated in the atmosphere, depending on the form of  $^{14}\text{C}$ . The most stable chemical forms are hydrocarbons with prevailing  $^{14}\text{CH}_4$  (Kunz 1985), which is not significantly captured in the NPP vicinity and contributes to the increase of the  $^{14}\text{C}$  activity level on a regional and/or global scale (Eisma et al. 1995). The

<sup>1</sup>Department of Radiation Dosimetry, Nuclear Physics Institute AS CR, Na Truhlářce 39/64, 180 86 Prague, Czech Republic.

<sup>2</sup>Corresponding author. Email: svetlik@ujf.cas.cz.

<sup>3</sup>National Radiation Protection Institute, Šrobárova 48, 10000 Prague, Czech Republic.

biota in the vicinity of NPPs takes in  $^{14}\text{CO}_2$  especially during calm weather, rainfall, haze, or atmospheric inversion.  $^{14}\text{C}$  in the form of  $\text{CO}_2$  is assimilated by plant photosynthesis and then transferred into the food chain. The abundance of  $^{14}\text{CO}_2$  in airborne effluents from LWPRs varies between 5 and 43% (Kunz 1985; Uchirin et al. 1992; EPRI 1995; Smith et al. 2002; Pintér and Molnár 1997; Molnár et al. 2005).

This paper aims to develop a method of  $^{14}\text{C}$  determination for NPPs' stack air in order to determine an independent grab sample control. Experiments connected with the method development started in 2001. In the following years, grab sampling was performed at Czech NPPs. This method enables us to distinguish between  $^{14}\text{CO}_2$  and  $^{14}\text{C}$  in combustible compounds, similar to the continual sampling routines in NPPs.

### **SAMPLING**

Grab samplings were performed in the Temelin NPP for both reactors, HVB1 and HVB2. For HVB1, 2 samplings were done in 2002, 4 in 2003, and 3 in 2004; sampling for HVB2 started in 2004 (4 samplings). Stack air samples were collected into high-pressure stainless bombs (~200 atm). The apparent sampling time did not exceed 30 min.

### **SAMPLE TREATMENT**

All samples were stored for at least 1 month to reduce the activity of short-lived radionuclides. In the laboratory, a gas sample was transferred into a low-pressure gas storage bag equipped with 2 inlet/outlet tubings on opposite sides. The gas was passed through a gas-meter and traps with humidifying and washing solution (1%  $\text{H}_3\text{PO}_4$ ), sorption solution (3M NaOH), and a condensation flask with 1%  $\text{H}_3\text{PO}_4$  cooled solution (+5 °C), to avoid water vapor condensation in other parts of the system. When a sample was transferred into a low-pressure bag, a cycling pump was connected between the condensation flask and the gas storage input. The gas then flowed from the bag's output into the gas-meter input. The pressure inside the gas-meter and flasks was lower than the atmospheric pressure, to avoid leaking of the gas sample. The total volume cycled corresponds to 13 volumes of a gas sample processed to reach a sufficiently high yield (above 98%) of  $\text{CO}_2$  sorption in the NaOH solution. According to the sorption yield experiments, testing a single sample passage through a trap with NaOH (i.e. 1 sorption cycle), the yield was 33–36%, depending on the gas flow rate. Thus, long-term cycling allows us to achieve a high yield with negligible  $^{14}\text{CO}_2$  residue in the gas. To determine  $^{14}\text{C}$  in combustible compounds, a catalyst (CuO, heated to 700 °C) in a quartz tube was inserted between the cycling bag output and the gas-meter input.

The solution with the  $^{14}\text{C}$  sample was sequentially stripped by nitrogen (5.0 purity) to remove the residual radioactive noble gasses. After sample processing, the low-pressure gas storage bag was depleted and twice flushed out with nitrogen.

Consequently, from the sample solution (apparent mass ~50 g) 8 g were repeatedly recovered into a 20-mL glass vial to prepare duplicate samples for measurement. The pH in the vials was gently reduced by diluted  $\text{H}_2\text{SO}_4$  dosed from a capillary tube onto the bottom while stirring, to avoid surface acidification resulting in  $\text{CO}_2$  escape. To minimize chemiluminescence interferences, the final pH value was adjusted to 9.3, indicated by thymolftalein (solution color changed from blue to colorless). A background sample was prepared from 3M NaOH using the same routine after fossil  $\text{CO}_2$  addition. Finally, 5 g of the sample solution was mixed with 15 mL of Hionic-Fluor (PerkinElmer, USA) scintillation cocktail in a 20-mL low-potassium glass vial. The yield of the sample treatment

was determined at random by the standard addition of a  $^{14}\text{C}$ -labeled sodium carbonate solution into a fraction of the sample solution subsequently processed by the routine described above.

To check the accuracy of the routine, barium carbonate was precipitated from a fraction of randomly selected samples. After the addition of a sodium carbonate carrier with a small controlled amount of  $^{14}\text{C}$ , the precipitate was washed and dried, and 1 g was treated in an ultrasound bath with 7 mL of water. The yield from precipitation and washing was 97%. Finally, the carbonate sample was homogenized with 12 mL of an InstaGel (Packard Instrument Co., USA) cocktail.

### SAMPLE MEASUREMENT

All samples including blanks and standards were counted for 60 min by a Tri-Carb 1050 or 3170 TR/SL in normal mode. Measurement of each sample series was repeated in 2-week intervals, 3 times at minimum. For carbonate solution counting, a counting window derived from the optimized one was utilized, with the lower edge above the maximum energy of tritium beta emission. Counting efficiency was determined individually, usually by standard addition (0.05 g of carbonate solution spiked with a known activity of  $^{14}\text{C}$ ) into the sample after the third counting.

After each measurement, the spectra were checked in the region above the maximum energy of  $^{14}\text{C}$  beta emission. Resulting count rates in parallel samples were compared; if a significant discrepancy was observed, a new sample solution treatment for LSC was performed. Such a case happened only 3 times during the entire experimental campaign. After the third measurement, count rates from each sample measurement with their combined uncertainties were compared. Significant differences in the results obtained could indicate the presence of interfering radionuclides with shorter half-lives and/or the instability of the sample scintillation mixture.

Precipitate samples were measured for 60 min in a full  $^{14}\text{C}$  counting window (channels 1–90), and quenching corrections depending on the tSIE parameter were consequently performed.

Table 2 Parameters of  $^{14}\text{C}$  determination in carbonate solution and carbonate precipitate.

Typical processed volume of stack air	150–350 L
Sample cycling yield (on the base of residual activity determination)	>98%
Typical sample mass ( $^{14}\text{C}$ converted to carbonate in solution)	40–50 g
Yield of the sample solution treatment (reduction of pH)	95.0–96.5%
Counting efficiency (solution)	32.5–34.0%
Background (solution)	6.5 cpm
Yield of barium carbonate precipitation	97%
Counting efficiency (precipitate) <sup>a</sup>	94–98%
Background (precipitate)	8.5 cpm

<sup>a</sup>Within the range of tSIE values 200–175.

In 2001, the laboratory was equipped with a Tri-Carb 1050; hence, the experimental results in Table 2 relate to this instrument. Later measurements of barium precipitate were performed on a Tri-Carb 3170 TR/LL purchased in 2004. For yield tracing and calibration ( $^{14}\text{C}$ -labeled sodium carbonate solution), radioactive standards were utilized of type ER 25, produced by the Czech Metrology Institute-Inspectorate for Ionizing Radiation, Prague.

## RESULTS

Figure 1 illustrates results of the grab sampling of stack air from the reactor HVB1 in NPP Temelin, and its comparison with data from the continual sampling performed by the NPP's laboratory.

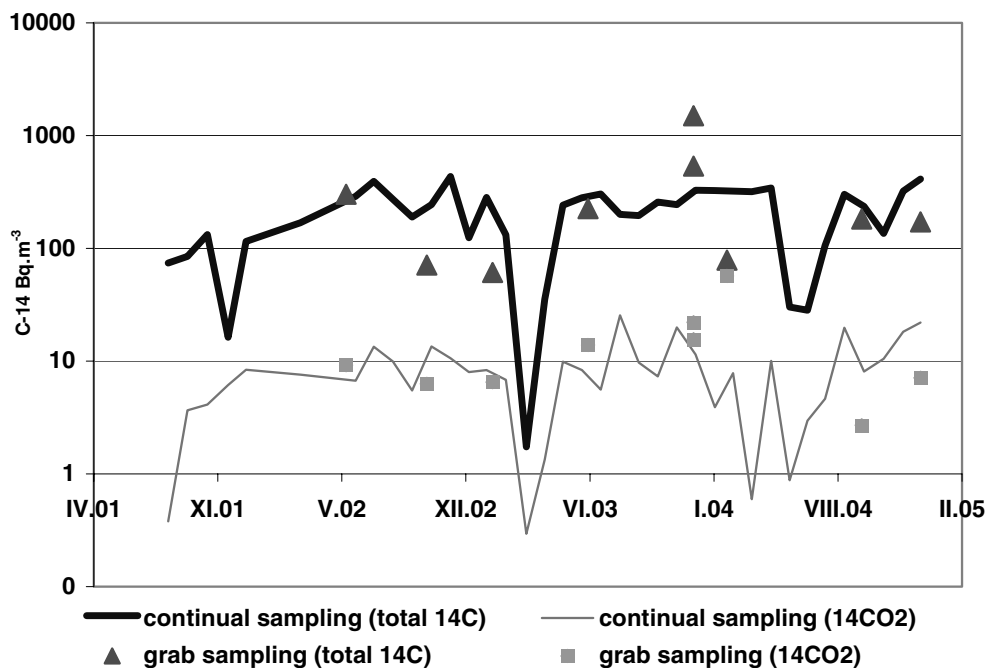


Figure 1 A comparison of <sup>14</sup>C activities (Bq/m<sup>3</sup>) determined in stack air from continual and grab sampling in NPP Temelin, reactor HVB1.

Table 3 presents <sup>14</sup>C activities determined in grab samples using both carbonate solution processing and carbonate precipitation procedures. Activities of total <sup>14</sup>C ( $\Sigma$ ) were calculated from the determination of <sup>14</sup>C in combustible compounds and <sup>14</sup>CO<sub>2</sub>.

Table 3 A comparison of <sup>14</sup>C activities determined in HVB1 samples, Bq/m<sup>3</sup>. Reported combined uncertainties correspond to ~68% probability.

Sampling date	Carbonate solution		Carbonate precipitate	
	$\Sigma$ <sup>14</sup> C	<sup>14</sup> CO <sub>2</sub>	$\Sigma$ <sup>14</sup> C	<sup>14</sup> CO <sub>2</sub>
4.II.2004	78.5 ± 3.7	56.9 ± 1.8	82.2 ± 5.0	52.6 ± 3.4
8.IX.2004	181.7 ± 4.7	2.7 ± 0.8	174.2 ± 8.9	3.6 ± 1.1
12.XII.2004	172.1 ± 4.3	7.1 ± 1.4	172.0 ± 7.3	5.5 ± 1.2

Results obtained by both methods agree well within the uncertainty margins. The relatively greater uncertainties associated with the carbonate precipitation method are due to only a minor part of the precipitate being measured during carbonate processing.

The average activities were calculated from data from the NPP Temelin laboratory (i.e. continual sampling data of total <sup>14</sup>C and <sup>14</sup>CO<sub>2</sub> for HVB1 and HVB2). The abundance of <sup>14</sup>CO<sub>2</sub> was calculated from the averages. Data presented in Table 4 allow a comparison of the grab sampling with the aver-

age values for continual sampling in HVB1 and HVB2 from May 2002 to December 2004 and February to December 2004, respectively. The grab sampling averages were calculated from the values determined by the carbonate solution counting. Combined uncertainties of determination did not exceed 15% for activities above 10 Bq/m<sup>3</sup>.

Table 4 Observed average activities in stack air grab samples from HVB1 and HVB2 compared with results of the continual sampling in the given time periods.

Sampling	$\Sigma$ $^{14}\text{C}$ (Bq/m <sup>3</sup> )	$^{14}\text{CO}_2$ (Bq/m <sup>3</sup> )	$^{14}\text{CO}_2$ (%)
Grab, HVB1	348 (169 <sup>a</sup> )	15.6 (7.6 <sup>a</sup> )	4.5 (4.5 <sup>a</sup> )
Continual, HVB1 (V/02–XII/04)	234	9.3	4.0
Grab, HVB2	186	6.8	3.6
Continual, HVB2 (II/04–XII/04)	289	6.9	2.4

<sup>a</sup>Data reported in parentheses were calculated after discarding outlying values (couple): total  $^{14}\text{C}$ , twice sampled 12.XII.2003, 1-hr interval;  $^{14}\text{CO}_2$ , sampled 4.II.2004.

Short-time pulses of  $^{14}\text{C}$  activity may have been the reason for the higher average activity found in the grab samples from HVB1 (see Figure 1). Such a pulse was observed on 12.XII.2003, and could be connected with some routines of servicing operation. At that time, the stack air was sampled twice, in 1-hr intervals. The observed activity of  $^{14}\text{C}$  combustible compounds decreased from 1482 to 520 Bq/m<sup>3</sup> during 1 hr, without a sharp change of  $^{14}\text{CO}_2$  activity (from 22.1 to 15.6 Bq/m<sup>3</sup>). Continual sample cumulating<sup>1</sup>, performed by the NPP, includes these short-lived  $^{14}\text{C}$  pulses. During the grab sampling, there is only a small probability for short-lived pulse detection, as is made obvious by the average activities in HVB1 after discarding the outlying values (72% of total  $^{14}\text{C}$ , 82% of  $^{14}\text{CO}_2$ ). The average total  $^{14}\text{C}$  activity in HVB2 (but only from 4 results) can probably confirm this effect as well (64% of total  $^{14}\text{C}$ ). However, the observed average activity of  $^{14}\text{CO}_2$  is closer to the continual sampling results from HVB2.

The percentage of  $^{14}\text{CO}_2$  activity, calculated from the grab sampling averages, exceeds that measured by the continual monitoring in HVB1 and HVB2 by 0.5% and 1.2%, respectively. Results obtained in the grab sampling could also have been influenced by the high-pressure sampling and by procedures applied in the processing of relatively small grab samples. Nevertheless, the results from continual and independent grab sampling confirm a relatively small percentage (<5%) of  $^{14}\text{CO}_2$  in the airborne effluents from NPP Temelin.

## CONCLUSION

Several grab samplings of stack air from reactors HVB1 and HVB2 in NPP Temelin were performed. On the basis of  $^{14}\text{C}$  determination in combustible compounds and  $^{14}\text{CO}_2$ , average activities determined in the grab sampling were below average values determined by continual monitoring during the relevant period. The maximum difference (36% of total  $^{14}\text{C}$ ) was found in HVB2. After discarding of outliers, the average values in HVB1 are below the continual sampling for total  $^{14}\text{C}$  and  $^{14}\text{CO}_2$  by 28% and 18%, respectively. These differences can be caused by short-lived pulses of  $^{14}\text{C}$  activity, as observed in samplings repeated with 1-hr intervals on 12.XII.2003.

Since the grab sampling results are affected by short-lived variations of  $^{14}\text{C}$  activity, the data from the continual sampling are more representative for calculation of  $^{14}\text{C}$  releases. For the purpose of an

<sup>1</sup>Samples were cumulated during 1 week or several weeks.

independent control of  $^{14}\text{C}$  amount in the airborne effluents, the grab sampling results can be utilized for a comparison only as a basis for a greater number of samplings performed.

Nevertheless, the resulting abundances of  $^{14}\text{C}$  in the  $\text{CO}_2$  chemical form have been found to be close to the results of the continual sampling. Part of the  $^{14}\text{C}$  in this form is captured by biota in the surrounding environment and is consequently transferred into the food chain. Ingestion of  $^{14}\text{C}$  represents 99% of the collective effective dose from this radionuclide intake (UNSCEAR 2000). Regarding the released quantity of this radionuclide, the abundance of  $^{14}\text{CO}_2$  can be validated without additional data about the volume of stack air released.

## REFERENCES

- Eisma R, Vermeulen AT, van der Borg K. 1995.  $^{14}\text{CH}_4$  emissions from nuclear power plants in northwestern Europe. *Radiocarbon* 37(2):475–83.
- EPRI [Electrical Power Research Institute]. 1995. Characterization of C-14 generated by the nuclear power industry. Report EPRI TR-105715. Palo Alto, California, USA: EPRI.
- Kunz C. 1985. Carbon-14 discharge at three light-water reactors. *Health Physics* 49:25–35.
- Molnár M, Szántó Z, Svingor É, Palcsu L, Futo I, Elekes Z. 2005. Measurement of beta-emitters in the air around the Paks NPP, Hungary. In: Olariu A, Stenström K, Hellborg R, editors. *Proceedings of the International Conference on Applications of High Precision Atomic and Nuclear Methods*. Neptun, Romania, 2–6 September 2002. p 32–8.
- Pintér T, Molnár M. 1997. Radiocarbon in primary water, stack air and waste streams of Paks, Bohunice and Krsko nuclear power plants. In: *Proceedings of the 3rd International Seminar on Primary and Secondary Side Water Chemistry of Nuclear Power Plants*. Paks, 16–20 September 1997.
- Smith G, Merino J, Kerrigan E. 2002. Review of C-14 inventory for the SFR facility. 2002:14 report of the Swedish Radiation Protection Authority. URL: [http://www.ssi.se/ssi\\_rapporter/pdf/ssi\\_rapp\\_2002\\_14.pdf](http://www.ssi.se/ssi_rapporter/pdf/ssi_rapp_2002_14.pdf).
- Uchirin G, Hertelendi E, Volent G, Slavík O, Morávek J, Kobal I, Vokal B. 1998.  $^{14}\text{C}$  measurements at PWR-type nuclear power plants in three middle European countries. *Radiocarbon* 40(1):439–46.
- UNSCEAR [United Nations Scientific Committee on the Effects of Atomic Radiation]. 2000. Exposures from man-made sources of radiation. Report 1, Annex C. 134 p. URL: <http://www.uncsear.org/docs/reports/annexc.pdf>.