J Radioanal Nucl Chem (2012) 294:435–438
DOI 10.1007/s10967-012-1824-9

Determination of concentration of iodine in grass and cow milk by NAA methods using reactor neutrons

P. V. Geetha · N. Karunakara · Ujwal Prabhu · P. M. Ravi · J. Sudhakar · Nicy Ajith · K. K. Swain · R. Acharya · A. V. R. Reddy

Received: 18 April 2012 / Published online: 24 May 2012

Abstract Instrumental and preconcentration methods of neutron activation analysis (NAA) have been standardized for the determination of concentration of iodine in grass and cow milk samples, respectively. To study the transfer of iodine from grass to milk, known quantity of grass spiked with potassium iodide solution was fed to a cow. The spiked grass samples and milk samples, obtained from the cow after the ingestion of spiked grass, were collected. Iodine was separated from the milk samples chemically using Dowex 1X8 anion exchange resin. Spiked grass and ion exchange resin samples were neutron irradiated and radioactive assay was carried out using a 45 % relative efficiency HPGe detector coupled to an 8k channel analyzer. Iodine concentrations in spiked grass samples were found to be in the range of 1,487–2,002 mg kg^{-1}. Concentration of iodine in milk after 12 h of feeding the cow with spiked grass was 871 ± 56 μg L^{-1} which was reduced to 334 ± 32 μg L^{-1} after 48 h.

Keywords Iodine · Grass · Milk · Neutron activation analysis · Reactor neutron irradiation · Pneumatic carrier facility

P. V. Geetha (✉)
Nuclear Power Corporation Of India Limited, Anushaktinagar, Mumbai 400 094, India
e-mail: pvgeetha@npcil.co.in

N. Karunakara · U. Prabhu
University Science Instrumentation Centre, Mangalore University, Karnataka, India

P. M. Ravi · J. Sudhakar
Health Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

N. Ajith · K. K. Swain · A. V. R. Reddy
Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

R. Acharya
Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Introduction

The operation of nuclear reactors results in low level radioactive effluents. These effluents are treated adequately and then released to the environment in a controlled manner, under strict compliance of discharge criteria set by IAEA [1]. Among many fission products, radioiodine (^{131}I; 8.02d) is one of the radionuclides likely to get released into the atmosphere in case of a reactor accident, though chances of such an accident are very remote due to stringent engineering safety features [2, 3]. During the short initial phase of release of radioactivity, ^{131}I is rapidly transferred to milk through grass → cow → cow milk pathway, leading to significant radiation dose to thyroid for those consuming milk, especially infant and children [4]. Same pathway is considered for impact assessment due to radio-iodine with regulated normal release. Transfer factors are important for quick evaluation of environmental contamination, during both normal and abnormal operational phases of a nuclear facility. These factors play an important role in modeling and understanding the migration of radionuclides through various environmental compartments. Transfer factor of iodine from grass to milk is defined as the ratio of iodine concentration (nCi L^{-1}) in milk obtained at equilibrium for a constant rate of intake of iodine (nCi d^{-1}) [5]. It is reported that the intake to milk transfer coefficient for cow does not seem to depend on the

chemical form of ^{131}I however physical form of ^{131}I may influence the transfer coefficient [5].

Iodine is an important trace element for human beings as it is required for normal thyroid functioning. Deficiency or excess intake of iodine leads to disorders commonly referred to as iodine disorders. Therefore, accurate data of total iodine concentrations in food and food products including milk are of considerable scientific interest [6]. Determination of concentrations of iodine species as well as total iodine has been carried out using wet-chemical analytical techniques like spectrophotometry [7], gas chromatography-mass spectrometry (GCMS) [8], ion chromatography [9], high performance liquid chromatography (HPLC) [10] and inductively coupled plasma-mass spectrometry (ICP-MS) [11]. Since iodine is a volatile element, analysis of sample without sample dissolution is preferred. In this respect, neutron activation analysis (NAA) using reactor neutrons is one of the best techniques for iodine determination due to its favorable nuclear properties that result in high sensitivity, and thus its applicability for trace elements [12, 13]. Here, total iodine is determined by measuring radioactivity due to ^{128}I (25 min, 442.9 keV), which is the activation product of ^{127}I. Epithermal neutron activation analysis has also been applied for the determination of very low concentrations of iodine in biological materials containing high levels of Al, Br, Cl, K, Mn, and Na [14]. NAA hyphenated with chemical separation methods has been used for iodine determination [6, 15, 16]. Low concentrations of iodine can be determined by preconcentration NAA (PNAA), in which matrix effect on the iodine determination is minimized [15].

During the present work, NAA methods have been standardized involving neutron irradiation in pneumatic carrier facility (PCF) to determine iodine concentrations in grass and cow milk matrices.

Experimental

For the current work, a small area of the experimental grass field was identified and grass samples were collected from the field for analysis. Simulated experiments were carried out by spraying known concentration of potassium iodide solution to the grass in small increments for about a week. The grass was then cut and known amount of the same was fed to a cow. Milk samples from the cow were collected in regular intervals (before and after the ingestion of spiked grass with stable iodine). Iodine was separated from milk samples chemically using ion exchange resin as described below. The spiked grass samples were air dried, powdered, homogenized, and subjected to instrumental NAA (INAA). The iodine ingestion to the cow was within the safe limit for cow as reported in the literature [17, 18].

Preconcentration NAA for iodine in milk samples

Total iodine present in the milk was separated employing chemical separation technique reported by Ravi et al. [19]. 100 mL of milk samples were taken in beakers and kept in ice bath. 30 mL of saturated trichloro acetic acid solution was added to each sample and then filtered. To the filtrates, 200 mg of freshly prepared Dowex (1X8) ion exchange resin was added and stirred well for about 2–3 h using shaker. The resin was then filtered off, washed, and air dried. The dried resin samples were weighed and subjected to NAA. Chemical recovery of iodine by this method was ascertained by repeating the procedure using known amount of potassium iodide solution of known concentration (1 mL of 1,000 mg L^{-1} iodine).

Sample preparation and irradiation

Samples of grass and ion exchange resins in the mass range of 50–200 mg were sealed in clean polyethylene sheets. The iodine standards were prepared using AR grade potassium iodide. Aliquots of the standards were transferred using accurately weighed (about 50–200 mg) solutions onto the filter paper discs/resin beads in polyethylene packets and air dried. Reference materials (SRM 1572) in the range of 50–100 mg were also packed for quality control purpose. The samples along with standards were irradiated at PCF of CIRUS reactor, Trombay, Mumbai for 1–5 min. The thermal equivalent neutron flux at PCF of CIRUS reactor is about 10^{13} cm^{-2} s^{-1}. Radioactivity measurement was done during the decay period of 15–60 min. Samples were counted in live-time mode using a 45 % relative efficiency high purity germanium (HPGe) detector coupled to an 8k-channel analyzer. The detector resolution was 1.9 keV at 1,332 keV of ^{60}Co. Peak area under 442.9 keV photo peak of ^{128}I was determined by in-built software of APTEC MCA card.

Calculations

Relative method of NAA was used for determination of concentration of iodine in samples. In this method, mass of an element (m) of interest (in the present work, iodine) was obtained using the relation

$$m_s = m_{std} \times (A_s \times D_{std})/(A_{std} \times D_s) \quad (1)$$

where A is the count rate for sample (s) and standard (std), D ($=e^{-\lambda td}$) is the decay factor, λ is decay constant and t_d is decay time. The mass values obtained are converted to concentration (mg kg^{-1}) by dividing with the sample mass.

Results and discussion

The determined concentration of iodine by INAA in SRM 1572 was found to be 1.91 ± 0.12 mg kg^{-1} with respect to the certified value of 1.84 ± 0.03 mg kg^{-1} (Table 1). The determined concentrations were arrived from analysis of four replicate samples. The percentage of error is 3.8 % with respect to the certified value and the *U*-score at 95 % confidence level is 0.3 reflecting the accuracy of measurement.

The detection limits (L_D) were calculated using Currie's formula [20] as given in Eq. (2).

$$L_D = (2.71 + 3.29\sqrt{C_b})/(t_m \times S \times W) \quad (2)$$

where C_b is the background counts under the peak of sample spectrum, t_m is the measurement time, S is the sensitivity of the element of interest in count rate per μg and W is the sample mass (g). The absolute detection limits for total iodine in grass was found to be 0.1 μg which corresponds to the detection limit of 0.6 mg kg^{-1} in grass by INAA. After chemical separation of iodine on resin from 100 mL of milk sample, the absolute detection limit of 0.1 μg was achieved by PNAA method which correspond to a detection limit of iodine in milk as 1 μg L^{-1}. The detection limit in NAA is affected by Compton background under the peak. In the case of solid grass samples, Compton background is mainly due to gamma rays of ^{56}Mn whereas in the case of milk sample, the background is due to gamma rays of ^{38}Cl (37 min) and ^{80}Br (18 min), activation products of elements/impurities present in the resin.

Figure 1 shows a typical gamma ray spectrum of a neutron irradiated spiked grass sample by INAA (t_i = 5 min, t_d = 15 min, t_m = 500 s) and Fig. 2 shows a typical gamma ray spectrum of a neutron irradiated resin sample after separation from milk using PNAA (t_i = 5 min, t_d = 15 min, t_m = 500 s).

The results of iodine concentration in iodide spiked grass samples and milk samples are presented in Tables 1 and 2, respectively. Iodine concentration was found to be below detection limit (<0.6 mg kg^{-1}) in control grass (without spiking) sample. In the present study, grass to cow

Table 1 Total iodine concentrations in grass samples (N = 4) by INAA

Type of sample	Concentration (mg kg^{-1} dry weight basis)
Spiked grass-1	1,487 ± 78
Spiked grass-2	2,002 ± 116
NIST SRM1572 (citrus leaves)	1.91 ± 0.12 (1.84 ± 0.03)

Concentration value in *bracket* is the certified value of iodine concentration in SRM 1572

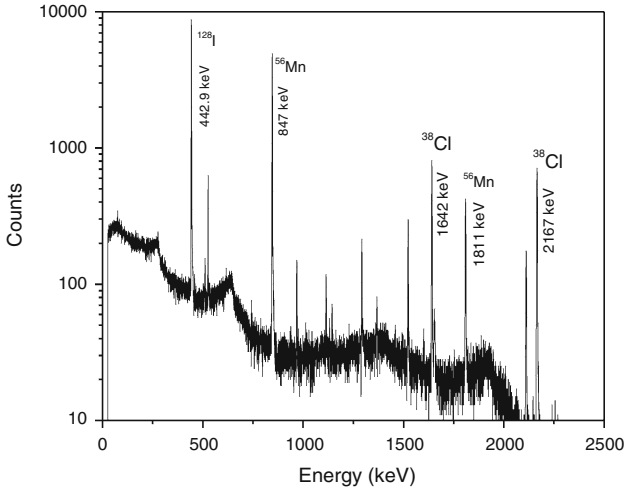

Fig. 1 Typical gamma ray spectrum of a neutron irradiated spiked grass sample by INAA (t_i = 5 min, t_d = 15 min, t_m = 500 s)

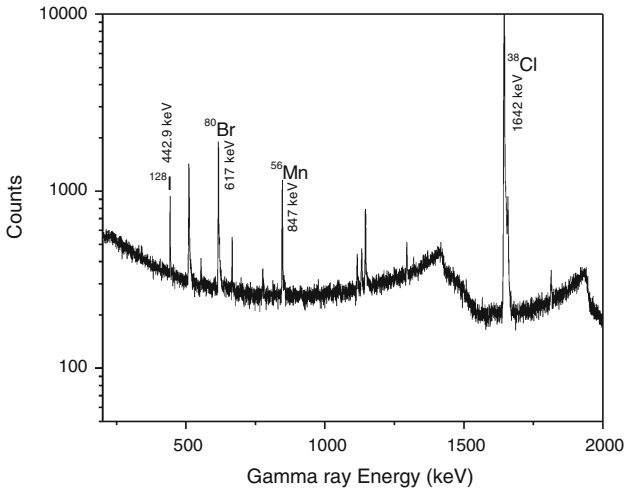

Fig. 2 Typical gamma ray spectrum of a neutron irradiated resin sample after separation from milk using PNAA (t_i = 5 min, t_d = 15 min, t_m = 500 s)

transfer factors determined are comparable with IAEA values [21]. From Table 2, it is observed that concentration of iodine in milk after 12 h of feeding the cow with spiked grass was 871 ± 56 μg L^{-1} which was reduced to 334 ± 32 μg L^{-1} after 48 h. It was also observed that iodine concentration was maximum after 12 h of intake of spiked grass by the cow. Similar observations were reported by National Cancer Institute during their experimental study on transfer of ^{131}I from deposition on the ground to fresh cow's milk to assess the dose received by pubic following Nevada atmospheric bomb test [5]. The study clearly demonstrated the capability of NAA methods for the determination of iodine in milk and grass samples using high flux pneumatic carrier neutron irradiation facility. Further study is being carried out for finding

Table 2 Total iodine concentrations in cow milk ($N = 3$) samples by preconcentration-NAA method

Type of sample	Amount of sample (mL)	Concentration ($\mu g\ L^{-1}$)	Remark
Milk-1 (control)	100	2.9 ± 0.3	Fresh milk with out intake of iodide spiked grass.
Milk-2	100	871 ± 56	Samples collected at various intervals starting from 12 h after the intake of iodide spiked grass.
Milk-3	100	503 ± 40	
Milk-4	100	472 ± 34	
Milk-5	100	334 ± 32	

transfer factor of iodine from grass to cow mik with equilibrium environmental conditions.

Conclusions

Two methods of NAA have been optimized for total iodine concentration determination in grass and cow milk. The absolute detection limits achieved by both INAA (grass) and PNAA (milk) methods are 0.1 μg. Use of high flux neutron irradiation at PCF of CIRUS reactor improved the detection limit. The iodine concentration obtained in the milk will be useful for transfer factor studies.

Acknowledgments The authors wish to thank Sri S. G. Ghadge, Executive Director, Reactor Safety & Analysis, NPCIL, Sri M. Kansal, Associate Chief Engineer, NPCIL, Sri V. K. Sharma, Safety Study Section, BARC, for their keen interest and help in this work. Authors thank Dr. R. Verma, Analytical Chemistry Division, BARC, Dr. A. Goswami, Head, Radiochemistry Division, BARC and Dr. P. K. Pujari, Radiochemistry Division, BARC for their support and encouragement. Authors are grateful to Sri B. N. Dileep, Officer-in-Charge, ESL, Kaiga and other staff members of ESL Kaiga for providing the necessary support. We are also thankful to the operation crew of Cirus reactor facility.

References

1. Environmental and source monitoring for purposes of radiation protection, IAEA safety standards RS G-1.8 (2005)
2. The Chernobyl accident, IAEA safety series No:75 INSAG-1 (1986)
3. Preparedness and response for a nuclear or radiological emergencies, IAEA safety standards GS-R-2 (2002)
4. Derived intervention levels for application in controlling radiation doses to the public in the event of a nuclear accident or radiological emergency, IAEA safety series No: 81 (1986)
5. Estimated exposures and thyroid doses received by the American people from Iodine-131 in fallout following Nevada Atmospheric Bomb test, Report of National Cancer Institute/National Institute of Health (1999) Chapter-4, 4.19
6. Bhagat PR, Pandey AK, Acharya R, Nair AGC, Rajurkar NS, Reddy AVR (2007) Talanta 71:1226–1232
7. Niazi SB, Mozammil M (1991) Anal Chim Acta 252:115–119
8. Shin HS, Oh-Shin YS, Kim JH, Ryu JK (1996) J Chromatogr A 732:327–333
9. Kumar SD, Maiti B, Mathur PK (2001) Talanta 53:701–705
10. Schwehr KA, Santschi PH (2003) Anal Chim Acta 482:59–71
11. Larsen EH, Ludwigsen MB (1997) J Anal Atom Spectrom 12:435–439
12. Bhagat PR, Acharya R, Nair AGC, Pandey AK, Rajurkar NS, Reddy AVR (2009) Food Chem 115:706–710
13. Landsberger S, O'Kelly DJ, Braisted J, Panno S (2006) J Radioanal Nucl Chem 269:697–702
14. Acharya R, Chatt A (2009) J Radioanal Nucl Chem 282:991–996
15. Kucera J, Randa Z, Soukal L (2001) J Radioanal Nucl Chem 249:61–65
16. Rao RR, Chatt A (1991) Anal Chem 63:1298–1303
17. Hilmann D, Curtis AR (1980) J Dairy Sci 63:55–63
18. Voigt G, Kiefer P (2007) J Environ Radioact 98:218–227
19. Ravi PM, Iyer MR, Bhat IS, Somasundaram S, Subramaian MS (1988) Bull Radiat Prot 11(1&2):71–74
20. Currie LA (1968) Anal Chem 40:586–593
21. Hand book of parameter values for the prediction of radionuclide transfer in terrestrial and freshwater environments (2010) Technical Report series No: 472, IAEA