

Measurement of Radionuclides in Reactor Coolant Water by Ion Chromatography and On-line/Off-line Scintillation Counting

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INTRODUCTION

Ion chromatography with on-line and off-line scintillation counting was utilized for analysis of reactor coolant water. In this technique, ionic radionuclides in an aqueous solution are sorbed onto an ion exchange preconcentration column. By proper selection and sequencing of chemical eluents, the radioactive ions are moved onto an ion exchange separation column where they are separated based on charge density (approximately by element). Following elution from the separation column, the radioactivity is quantified either on-line with a flow-cell scintillation counter or off-line by liquid scintillation counting. The analysis technique has the potential of rapid characterization for radionuclides that decay by electron capture, beta- and alpha-particle emission. The technique is an alternative to the conventional use of scaling factors in the analysis of "non-gamma-ray" emitting radionuclides in reactor coolant water since the technique is simple enough to run on a routine basis. This paper illustrates the use of the technique on the analysis of primary coolant water from a pressurized water reactor.

CALIBRATION

A NIST-traceable solution that contained the radionuclides and concentrations listed in Table 1 was used to characterize the ion chromatography and radiation detection systems. Figure 1 illustrates a typical on-line chromatogram that was obtained by analyzing 0.5 ml of the standard solution. The peak retention time was used to identify the radioactive element that eluted, and the peak area was used to characterize the detection efficiency of that radioactive species. The detection efficiency is listed in Table 1 and plotted as a function of beta end-point energy in Figure 2.

RESULTS and DISCUSSIONS

A one liter sample of primary reactor coolant water from Unit 1 of the Diablo Canyon Nuclear power station was collected on February 20, 1997 and analyzed by gamma-ray spectroscopy on March 11, 1997 by station personnel. Upon receipt at Clemson University (April 7, 1997) a gamma-ray spectrometric analysis was performed and compared to the analysis done by Diablo Canyon personnel (Table 2). Except for ^{113}Sn , ^{131}I and ^{133}Xe , the analyses were consistent with one another. Following the gamma-ray analysis, the sample was wet ashed in preparation for loading into the ion chromatography system. Figure 3 displays the chromatogram obtained by the on-line scintillation detection system for an equivalent of 50 ml of reactor coolant water. The identities of the cobalt and iron peaks were inferred from the elution time and confirmed by gamma-ray spectroscopy. The identity of the manganese peak was determined by gamma-ray spectroscopy. The radionuclide concentrations for the on-line analysis were based on the absolute detection efficiency data presented in Table 1 and Figure 2. For cobalt and iron, the concentrations were determined by assuming that all the activity was due to ^{58}Co and ^{55}Fe , respectively, since these were the predominant isotopes. The on-line analyses are seen to show good agreement with the gamma-ray analyses.

The effluent from the on-line detection system was collected in 0.5 ml fractions and counted for 10 minutes in a ¹Wallac 1415 alpha/beta discriminating liquid scintillation counter. The net count rate obtained in the whole beta window is plotted as a function of the elution time in Figure 4. The off-line chromatogram contains considerably more peaks than the on-line version because of the lower detection limit of the off-line radiation detection system. The identity of the cobalt and iron (as ^{59}Fe) peaks was again inferred from the elution time and confirmed by gamma-ray spectroscopy. The identities of manganese and beryllium peaks were determined by gamma-ray spectroscopy. The identities of the nickel, strontium and iron (as ^{55}Fe) peaks were inferred from the elution time and verified by electron spectroscopy using the liquid scintillation counter. Additionally, decay curves were obtained for the 19 and 21.5 (strontium) minute fractions (Figure 5). The 19 minute fraction has at least two decay components, $t_{1/2} < 18$ d and an undetermined long component which has a half-life longer than

¹ EG&G Wallac, Inc.

0.5 months. The 21.5 minute (strontium) fraction decayed with $t_{1/2} \sim 68$ d implying that approximately 75% of the initial activity in the sample was ^{89}Sr and 25% was ^{90}Sr . Figure 6 is the net electron spectrum of the long decay component of the 19 minute fraction. The peaks at 88 and 388 keV indicate the presence of electron emissions in the sample. No gamma- or x-rays were identified above background. The identities of the radioactive components in the 19 minute fraction are unknown at this time.

SUMMARY

The objective of this project was to illustrate the use of ion chromatography and on-line/off-line scintillation counting for the measurement of non-gamma-ray emitting radionuclides in reactor coolant water. The work was successful in that the measured radionuclide concentrations are consistent with expectations based on scaling factors. The technique represents a promising alternative to the use of scaling factors for reactor coolant water analyses.

Table 1. Detection efficiencies for the radionuclides in the standard. (N=5)

Radionuclide	Radiation	Energy (keV)	Concentration in Standard (Bq/ml) (on Sept. 22, 1995)	Detection Efficiency
^{55}Fe	X-rays	6.4	292.6	0.15 ± 0.04
^{63}Ni	β^-	66.9	298.5	0.15 ± 0.01
^{147}Pm	β^-	224	286.2	0.71 ± 0.13
^{90}Sr	β^-	546	291.8	0.96 ± 0.06
^{90}Y	β^-	2281	291.8	1.21 ± 0.11

Table 2. Summary of the gamma-ray and non-gamma-ray analyses of the Diablo Canyon reactor coolant water. The data have been decay corrected to March 11, 1997.

Isotope	$t_{1/2}$	Diablo Canyon ($\mu\text{Ci/ml}$) - γ	Diablo Canyon ($\mu\text{Ci/ml}$) - Scaling ¹	Clemson U ($\mu\text{Ci/ml}$) - γ	Clemson U ($\mu\text{Ci/ml}$) On-line	Clemson U ($\mu\text{Ci/ml}$) Off-line (LSC)
^7Be	53.3 d	2.15×10^{-4}	-	3.35×10^{-4}	-	2.8×10^{-5}
^{14}C	5715 a	-	2.11×10^{-6}	-	-	-
^{54}Mn	312.1 d	2.63×10^{-5}	-	3.68×10^{-5}	2.5×10^{-5}	3.0×10^{-5}
^{55}Fe	2.73 a	-	1.74×10^{-4}	-	8.2×10^{-5}	1.7×10^{-4}
^{59}Fe	44.51 d	2.96×10^{-6}	-	6.05×10^{-6}	-	-
^{57}Co	271.8 d	-	-	5.44×10^{-6}	-	-
^{58}Co	70.9 d	1.15×10^{-4}	-	4.40×10^{-4}	1.1×10^{-4}	1.9×10^{-4}
^{60}Co	5.3 a	3.54×10^{-5}	-	4.85×10^{-5}	-	-
^{59}Ni	7.6×10^4 a	-	1.53×10^{-7}	-	-	-
^{63}Ni	100 a	-	1.48×10^{-5}	-	-	8.1×10^{-6}
^{89}Sr	50.5 d	-	3.70×10^{-6}	-	-	2.7×10^{-6}
^{90}Sr	28.8 a	-	1.39×10^{-8}	-	-	-
^{95}Zr	64.0 d	-	-	2.25×10^{-4}	-	-
^{95}Nb	35.0 d	-	-	4.03×10^{-4}	-	-
^{99}Tc	2.1×10^5 a	-	2.96×10^{-11}	-	-	-
^{113}Sn	115.1 d	2.77×10^{-6}	-	2.08×10^{-5}	-	-
^{125}Sb	2.8 a	-	-	8.34×10^{-6}	-	-
^{129}I	1.6×10^7 a	-	6.94×10^{-15}	-	-	-
^{131}I	8.0 d	1.45×10^{-5}	-	-	-	-
^{133}Xe	5.2 d	3.17×10^{-5}	-	-	-	-
^{134}Cs	2.1 a	-	-	1.63×10^{-6}	-	-
^{137}Cs	30.1 a	-	-	1.82×10^{-6}	-	-
*Pu	-	-	9.50×10^{-8}	-	-	-
^{241}Am	432.7 a	-	5.05×10^{-10}	-	-	-
**Cm	-	-	2.25×10^{-6}	-	-	-

* Primarily ^{241}Pu

** Primarily ^{242}Cm

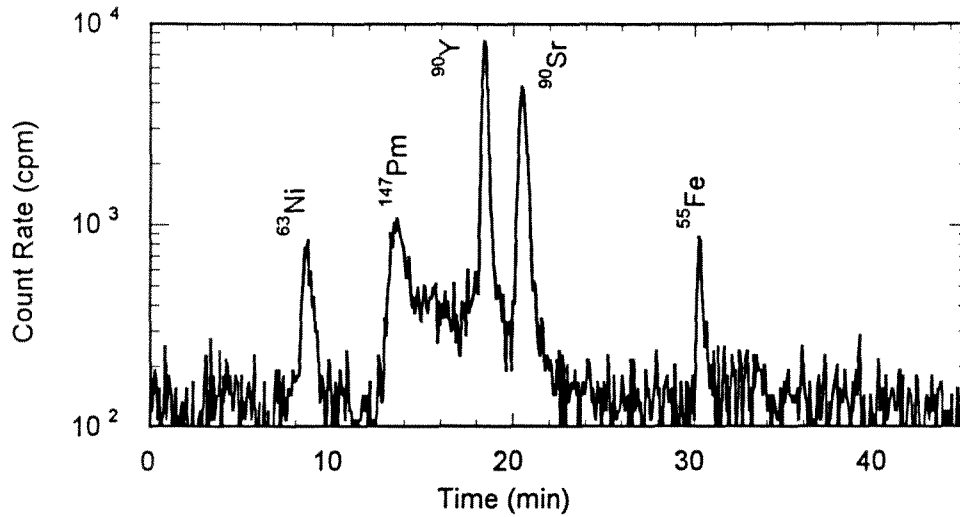


Figure 1. On-line chromatogram obtained using 0.5 ml of the standard solution.

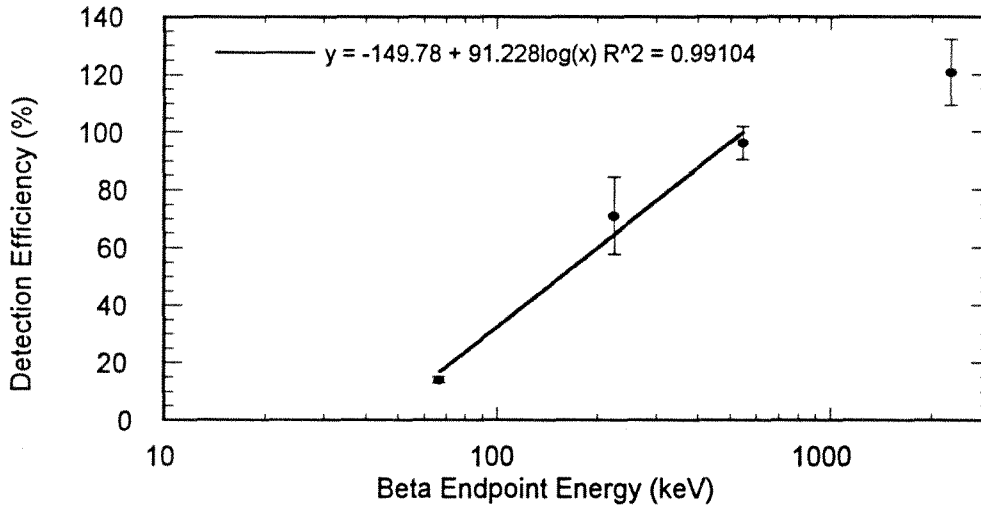


Figure 2. Beta absolute detection efficiency of the on-line flow-cell detector versus the beta endpoint energy.

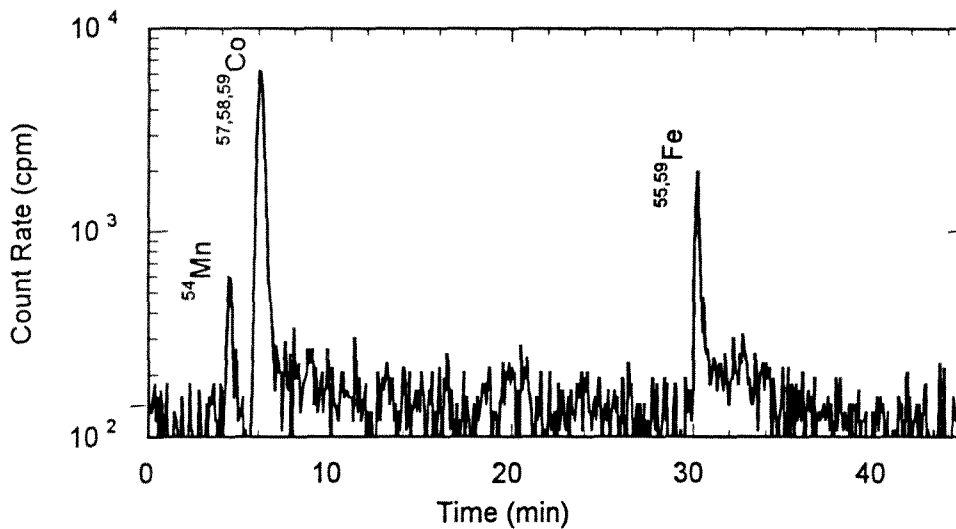


Figure 3. On-line chromatogram from 50 ml equivalent of Diablo Canyon reactor coolant water.

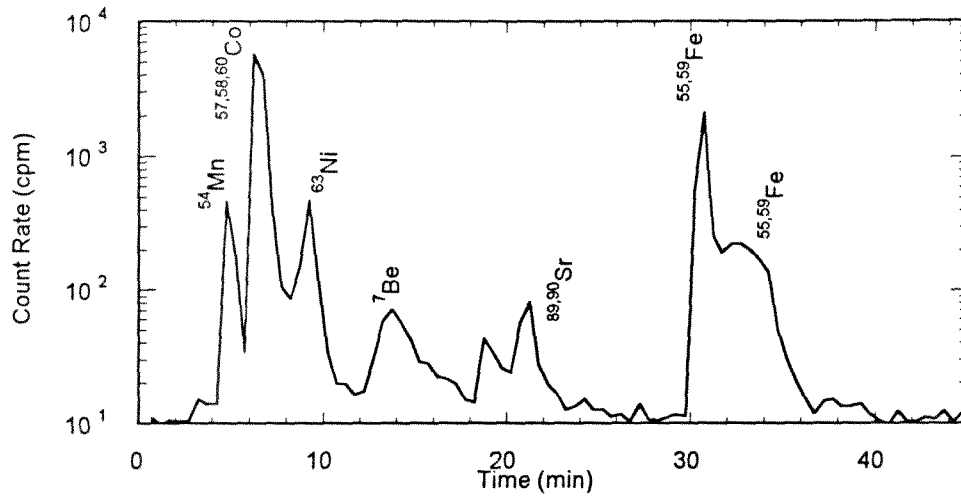


Figure 4. Off-line chromatogram (0.5 ml fractions) of 50 ml equivalent of Diablo Canyon reactor coolant water.

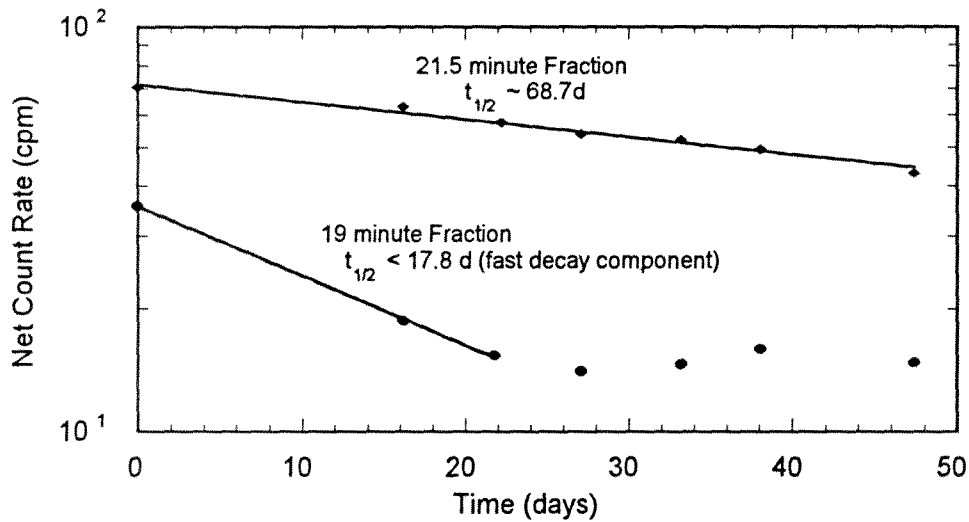


Figure 5. Radiological decay of the 19 and 21.5 minute fractions.

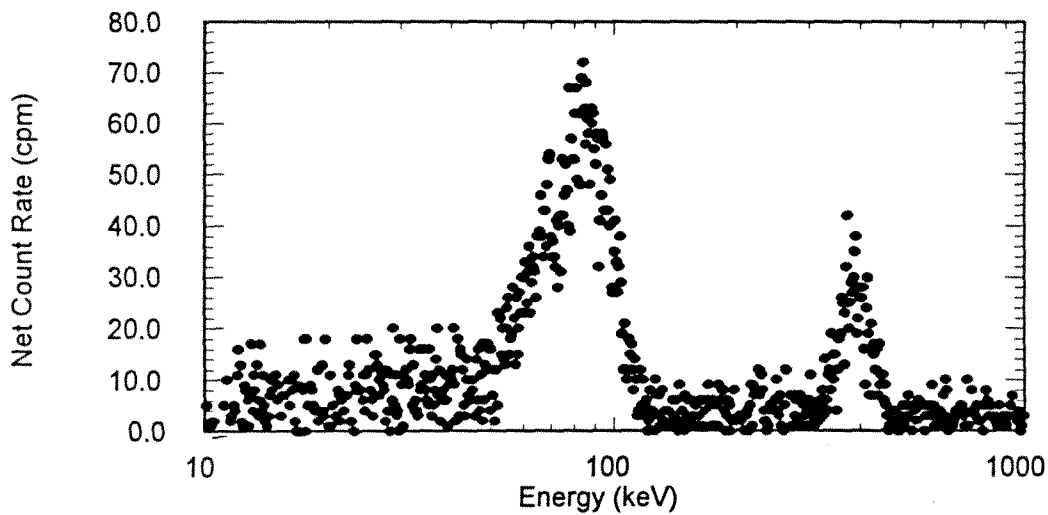


Figure 6. Electron spectrum for the 19 minute fraction.

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REFERENCES

- [1] D. Bradbury, G. R. Elder and M. J. Dunn, "Rapid Analysis of Non-Gamma Radionuclides Using the ANABET System," *Waste Management*, (1990) 327.
- [2] S. H. Reboul and R. A. Fjeld, "A Rapid Method for Determination of Beta-emitting Radionuclides in Aqueous Samples," *Radioactivity & Radiochemistry*, **5**, 3, (1994) 42-49.
- [3] R. A., Fjeld, S. Guha, T. A. DeVol, and J. D. Leyba, "Ion Chromatography and On-line Scintillation Counting for the Analysis of Non-gamma Emitting Radionuclides in Reactor Coolant," *J. Radioanal. and Nucl. Chem.*, **194**, (1995) 51-59.
- [4] S. Guha, J. E. Roane, T. A. DeVol, J. D. Leyba and R. A. Fjeld, "Ion Chromatography Coupled with On-line and Off-line Radiation Detection for the Rapid Analysis of Radionuclides in Reactor Coolant Water." Conference Proceedings, *Waste Management*, (1995).
- [5] O. T. Farmer III, J. H. Reeves, E. J. Wyse, C. J. Clemetson, C. J. Barinaga, M. R. Smith and D. W. Koppenaar, "Analysis of radioactive Waste Samples by Ion Chromatography-beta-ICP-MS," Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations, ASTM STP 1291, R. W. Morrow and J. S. Crain, Eds., American Society of Testing and Materials, West Conshohocken, USA (1995), pp. 38-47.
- [6] S. H. Reboul and R. A. Fjeld. "Resolution of actinides using low hydrophobicity ion exchange columns." *Journal of Chromatography* (in review).