Rapid Determination of Radioiodine in Reactor Coolant

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Received June 18, 1980

Radiodine in the reactor coolant is one of the indicators of failed fuel in the reactor. An improved method for radioiodine determination is required in order to reduce the analysis time and the radiation exposure for the radiochemist of a power station. For this reason, a new, rapid determination method with ion exchange paper was developed in the laboratory and examined at a power station for practical use.

The important features of the proposal are as follows:
(1) Recovery of radioiodine in the PWR reactor coolant including boric acid was 98%.
(2) The half-lives of radioiodines derived from the decay curve were nearly agreed with the reported values.
(3) Accuracy of this method was approximately equal to that of the conventional precipitation method.
(4) This method reduced the analysis time to 1/6~1/9 of that of the conventional method.
(5) It took only 2 h to obtain the result after sampling, because interference of $^{135m}$Xe and $^{135}$Xe, daughter nuclides of $^{131}$I, could be eliminated.

KEYWORDS: radioiodine, failed fuel indicator, PWR type reactors, reactor coolants, ion exchange paper, chemical analysis, water, accuracy, comparative evaluations

I. INTRODUCTION

From the viewpoint of safety control of fuel rods in the nuclear power station, it is very important to develop a method for rapid detection of fuel rod failure. This method employed in operating reactors can be divided into two parts, namely, determining the failure position and estimating the degree of the failure. These detection methods are actually employed in research reactors(1). No precise failure detection method is now available for the operating light-water-cooled power reactor because additional work for the reactor to employ this method can be hardly carried out. The estimation procedure for the degree of a failure, with the ratio of short-lived iodine to long-lived iodine contained in the primary coolant of reactor(2) has been proposed and carried out. In this method, the radioiodines are extracted from the primary coolant by chemical isolation, and precipitated as silver iodide. The radioactivity of each radioiodine is measured by an NaI(Tl) or a Ge(Li) detector(3). Two to three hours are required under radiation for preparing counting samples, and it takes 2~7 days to complete the measurement. Therefore, an improved method is required to save the time of operation, both sample preparation and measurement, and radiation exposure for a radiochemist.

This paper describes a radioiodine isolation method with ion exchange paper, and the applicability of the method to the primary coolant of operating reactors

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II. EXPERIMENTAL

1. Sample Preparation

A primary coolant sample (3 ml) was diluted with distilled water to 50 ml as a sample solution. The solution was poured to the anion exchange paper by using the device shown in Fig. 1. Two anion exchange papers were fixed in the position shown in the figure. The feeding rate of the sample solution to the papers was at 5 ml/min. The papers were then rinsed with 20 ml of distilled water to wash out impurities remained on the papers. Gelman 47 mm dia. (SB6407) paper was employed as the anion exchange paper in this method.

After the radioiodine was trapped, the anion exchange papers were fixed on a Petri dish and covered with a mylar film to keep a constant form for radiation counting.

2. Radiation Counting

Quanta system with a Ge(Li) detector, was used for counting radioactivities. Employed channel numbers were 2048, and the gain was adjusted to 1 ch/keV. The counting time was changed from 300 to 2,000 s depending on the radioactivity concentration level.

To identify each radioiodine, typical peaks of radioiodines were adopted; that is to say, 364 and 1,260 keV for $^{131}$I and $^{135}$I, respectively. However, for $^{133}$I, 530 keV peak was adopted in this paper instead of 874 keV peak. This improvement was made because nuclides other than iodine might be present in the sample of this method compared with the previous precipitation method. The peak area was calculated by the photopeak area calculation method.

III. RESULTS AND DISCUSSION

1. Fundamental Studies on Anion Exchange Paper Method

(1) Gamma-ray Detection Efficiency

Iodine-$^{131}$, $^{60}$Co, $^{137}$Cs and $^{54}$Mn of known concentration, approved by the Electrotechnical Laboratory in Japan, were absorbed by a filter paper of 47 mm dia. and used as a standard radiation source. The filter paper was put in the same geometrical condition as that of a sample to be measured.

The detection efficiencies of both the anion exchange and the conventional precipitation methods are shown in Fig. 2. Radioiodine detection efficiencies were derived from efficiency curves shown in the figure. The results are shown Table 1.

<table>
<thead>
<tr>
<th>Nuclide (Energy)</th>
<th>Conventional method (25 mm dia., ppt) (%)</th>
<th>Proposed method (47 mm dia., paper) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{131}$I (364 keV)</td>
<td>3.240</td>
<td>1.91</td>
</tr>
<tr>
<td>$^{131}$I (530 keV)</td>
<td>2.17</td>
<td>1.28</td>
</tr>
<tr>
<td>$^{133}$I (1,260 keV)</td>
<td>0.860</td>
<td>0.513</td>
</tr>
</tbody>
</table>
(2) Ion Exchange Capacity and Break-through Point of Anion Exchange Paper

In order to trap the radioiodine in the primary coolant on the ion exchange paper, the ion exchange capacity must be sufficiently large as compared with the iodine concentration in the coolant. If the radioactivity concentration of $^{131}$I, $^{133}$I and $^{135}$I in the primary coolant is assumed as 1 $\mu$Ci/ml each, the chemical concentration will be calculated as $7.20 \times 10^{-11}$ meq/ml. The ion exchange capacity should be greater than the value. For this reason the capacity of the ion exchange paper was determined using a tracer technique.

The capacity was obtained from the ion exchange curve of potassium iodide solution (20 ppm as I tagged with $^{131}$I) as shown in Fig. 3. The ion exchange capacity for each pair of superposed exchange papers was 0.0555 meq, and the break-through capacity under flow velocity of 5 ml/min was 0.0168 meq. This is sufficiently large with respect to the radioiodine concentration in the primary coolant.

(3) Effect of Boron on Ion Exchange Method

Boron is added to the primary coolant of a pressurized water reactor to 100~2,200 ppm in the form of boric acid as a chemical shim substance. This quantity of boron is very great, as compared with the radioiodine quantity. Therefore the effect of boron on ion exchange of radiiodine was examined. Iodine-131 was added to a boric acid solution with boron concentration of 100~2,200 ppm. The effect of boron on ion exchange of iodide was obtained by determining the quantity of $^{131}$I in the effluent after passing through the ion exchange paper. About 1.9% of $^{131}$I passed through the paper irrespective of the boron concentration as shown in Fig. 4. This proved that the recovery of radiiodine in the anion exchange paper was 98%.
2. Practicability for Primary Reactor Coolant Analysis

(1) Iodine Recovery by Anion Exchange Paper

The effect of anion components besides boron on the proposed method was examined by using the primary coolant of an operating pressurized water reactor as the test solution. The iodine recovery using the proposed method was obtained by measuring the ratio of concentration of each radioiodine before and after passing through the ion exchange paper by gravimetric method.

The recovery by the proposed method was 98.1~98.5%, as shown in Table 2. This result agreed well with the results of fundamental studies on boron concentration, described in the previous section. This made it obvious that radioiodine recovery by the proposed method was not affected by any substances except boron. Therefore, the correction coefficient for the measured value of radioiodine concentration is 1.02 in this method.

(2) Effect of Xenon on Iodine Determination

Figure 5 shows γ-ray spectra of proposed and conventional methods taken 14 h after

![Fig. 5 γ-Spectra by Ge(Li) detector in proposed and conventional methods](image-url)
sampling. The peak of $^{135}\text{Xe}$ of $250\text{ keV}$ in the conventional method appears larger than that obtained by the proposed method. Iodine-135 produces $^{135m}\text{Xe}$ (27%) and $^{135}\text{Xe}$ (73%)\(^{(6)}\). The $^{135m}\text{Xe}$ emits $\gamma$ radiation of $527\text{ keV}$\(^{(7)}\) which affects $^{131}\text{I}$ ($530\text{ keV}$) determination, while $^{135}\text{Xe}$ emits $\gamma$ radiation of $359\text{ keV}$ which affects $^{131}\text{I}$ ($364\text{ keV}$) determination. Decay analysis of $250\text{ keV} \gamma$-ray of $^{135}\text{Xe}$ in the sample of the conventional method indicated that observed decay curve agreed with that calculated by the data of conventional method as shown in **Fig. 6**. In the conventional method, $^{135}\text{Xe}$ and $^{135m}\text{Xe}$ remained in the silver iodide precipitate and emitted $\gamma$ radiation. Small deviations from the calculated curve may be caused by differences in the time required for sample preparation. In the proposed method, the radioactivity concentration of $^{135}\text{Xe}$ is one or more order lower than that in the conventional method, and is different from the calculated curve. It may be speculated that the Xe generated as a daughter nuclide was not held in the ion exchange paper but was released from the samples.

**Table 3** shows the effect of Xe on the radioiodine determination. In the conventional method, cooling period of $5\sim30\text{ h}$ is required for radioiodine determination. The maximum contributions were 0.64 and 1.6% for $^{131}\text{I}$ and $^{133}\text{I}$ determination, respectively. The effect of Xe on the proposed method was lowered to less than 0.2% and no cooling period was required.

(3) Quantitative Determination by Half-life Method

Nuclides except radioiodine in the primary coolant may be ion-exchanged or absorbed on the anion exchange paper, and may interfere with determination of radioiodine. We tried to evaluate the extent of interference of the nuclides. Decay analysis for $220\text{ h}$ was carried out for a sample obtained from the primary coolant of an operating power reactor. The decay curve is expressed as a straight line on a semilogarithmic graph as shown in **Fig. 7**. The half-lives obtained are $8.23\text{ d}$, $20.6\text{ h}$ and $6.59\text{ h}$ for $^{131}\text{I}$, $^{133}\text{I}$ and $^{135}\text{I}$, respectively, as shown in **Table 4**, and agreed with the values reported in the literature\(^{(6)}\). This proved that the measurement of radioiodine by the proposed method was not influenced by any other nuclides.

(4) Comparison of Accuracy and Precision between Proposed and Conventional Methods

Accuracy and precision of measurements by the proposed and conventional methods were compared by using the primary coolant of an operating reactor as a test solution. Five samples, from the same test solution, were measured at three different elapsed times. The relationship of accuracy and precision by the change of the time was investigated for the both methods. The value measured by the proposed method was multiplied by the correction coefficient 1.02. Iodine concentration by each method was compared by the concentrations at the sampling time.

The coefficients of variation (C.V.) of all the samples were ranged $2\sim7\%$ as shown in **Table 5**.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Concentration ratio for $^{135}\text{I}$</th>
<th>Effect on measurement (max., %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Conventional method</td>
</tr>
<tr>
<td>$^{131}\text{I}$</td>
<td>0.33</td>
<td>0.64</td>
</tr>
<tr>
<td>$^{133}\text{I}$</td>
<td>1.06</td>
<td>1.6</td>
</tr>
</tbody>
</table>

**Table 3** Effect of Xe on proposed and conventional methods

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Observed value by proposed method</th>
<th>Reported value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{131}\text{I}$</td>
<td>8.23 d</td>
<td>8.05 d</td>
</tr>
<tr>
<td>$^{133}\text{I}$</td>
<td>20.6 h</td>
<td>20.3 h</td>
</tr>
<tr>
<td>$^{135}\text{I}$</td>
<td>6.59 h(^{1})</td>
<td>6.7 h</td>
</tr>
</tbody>
</table>

\(^{1}\) Obtained from decay analysis up to 34 h.
Fig. 6 Determined and calculated values of $^{135}$Xe by cooling period
Calculated under the assumption of no release of $^{135}$Xe from precipitate.
Fig. 7 Relation of cooling period and measured value

Table 5 Comparison of accuracy and precision of proposed and conventional methods

<table>
<thead>
<tr>
<th>Nuclides</th>
<th>Methods</th>
<th>Measured value (in arbitrary unit)</th>
<th>2~6 h</th>
<th>11~14 h</th>
<th>23~27 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{131}I$</td>
<td>PM†</td>
<td>$2.38 \pm 0.07 \times 10^{-2}$ (2.8)</td>
<td>$2.31 \pm 0.07 \times 10^{-2}$ (2.9)</td>
<td>$2.37 \pm 0.08 \times 10^{-2}$ (3.4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CM††</td>
<td>$2.27 \pm 0.10 \times 10^{-2}$ (4.2)</td>
<td>$2.35 \pm 0.09 \times 10^{-2}$ (3.9)</td>
<td>$2.44 \pm 0.06 \times 10^{-2}$ (2.4)</td>
<td></td>
</tr>
<tr>
<td>$^{131}I$</td>
<td>PM</td>
<td>$6.99 \pm 0.18 \times 10^{-2}$ (2.6)</td>
<td>$7.19 \pm 0.30 \times 10^{-2}$ (4.2)</td>
<td>$7.12 \pm 0.25 \times 10^{-2}$ (3.6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CM</td>
<td>$7.13 \pm 0.30 \times 10^{-2}$ (4.2)</td>
<td>$7.36 \pm 0.23 \times 10^{-2}$ (3.3)</td>
<td>$7.41 \pm 0.27 \times 10^{-2}$ (3.6)</td>
<td></td>
</tr>
<tr>
<td>$^{131}I$</td>
<td>PM</td>
<td>$7.37 \pm 0.25 \times 10^{-2}$ (3.4)</td>
<td>$7.12 \pm 0.22 \times 10^{-2}$ (2.2)</td>
<td>$6.80 \pm 0.49 \times 10^{-2}$ (7.3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CM</td>
<td>$6.91 \pm 0.48 \times 10^{-2}$ (7.0)</td>
<td>$7.09 \pm 0.16 \times 10^{-2}$ (2.3)</td>
<td>$7.15 \pm 0.29 \times 10^{-2}$ (4.1)</td>
<td></td>
</tr>
</tbody>
</table>

† PM: Proposed Method, †† CM: Conventional Method, ( ) : Coefficients of variation (%)
Difference of C. V. based on the cooling period was negligible. Regarding deviation of measured values, no significant difference was found at 5% risk by the "t" test. This proved that accuracy of the proposed method was almost the same as that of the conventional method.

(5) Operating Time Reduction and Labor Saving

Table 6 shows the process and required time for the preparation of counting sample in the proposed and the conventional methods. In the conventional method, sample preparation procedure is complicated, requires skill of the operator, and takes 2~3 h to complete. On the contrary, in the proposed method, the procedure is only passing the test solution through the ion exchange paper at a flow rate of 5 ml/min. The time required for sample preparation is only 20 min, which is 1/6~1/9 shorter than that of the conventional method. The proposed method is simpler and more labor-saving than the conventional method.

Table 6 Comparison of sample preparation of proposed and conventional methods

<table>
<thead>
<tr>
<th>Process and time</th>
<th>Conventional method</th>
<th>Proposed method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1) Sampling (5 min)</td>
<td>(1) Sampling (5 min)</td>
</tr>
<tr>
<td></td>
<td>(2) Adding carrier (5 min)</td>
<td>(2) Pouring to ion exchange paper (10 min)</td>
</tr>
<tr>
<td></td>
<td>(3) Extraction (3 times) (45~70 min)</td>
<td>(3) Inserting counting holder (5 min)</td>
</tr>
<tr>
<td></td>
<td>(4) Prepa. silver iodide (20~45 min)</td>
<td></td>
</tr>
<tr>
<td>Total time</td>
<td>2~3 h</td>
<td>20 min</td>
</tr>
</tbody>
</table>

In the conventional method, 7-day's cooling period is required when an NaI(TI) detector is used, owing to poor resolution of the detector. When the precipitate sample is measured by a Ge(Li) detector, 5~30 h of cooling period is required, until the effect of $^{135m}$Xe and $^{135}$Xe (daughter nuclides of $^{135}$I) disappears. In the proposed method, the effect of Xe was not found, and the measurement of the half-life showed that other $\gamma$ radiation were not superimposed on the measured peaks. Thus, in the proposed method, measurement can be performed immediately after preparing the sample. It takes only 2 h to obtain the result after sampling by this method. It was found that this method saves a considerable amount of time.

IV. CONCLUSIONS

The main results of the research are as follows:

(1) The ion exchange capacity of the ion exchange paper for iodine proved to be sufficient in determining the radioiodine in the primary coolant.
(2) The recovery for radioiodine in the primary coolant of a pressurized water reactor containing 1,000~2,000 ppm of boron was 98%.
(3) From the decay analysis of radioiodine trapped on the ion exchange paper, no influence of other nuclides was observed, and the half-life of each radioiodine agreed closely with the value reported in the literature.
(4) Effect of $^{135}$Xe, on the iodine determination, which is a problem in the conventional method, was negligible, being less than 0.2%. This proved that radiation counting could be started immediately after sampling.
(5) The error of the measurement in this method was 2~7% in terms of coefficients
of variation, which was the same as for the conventional method. No deviations were detected.

(6) The time required for pretreatment was reduced to 20 min. (2~3 h in the conventional method) by simplifying the pretreatment procedure. The proposed method reduced the radiation exposure of a radiochemist in the nuclear power station.

(7) The proposed method required only 2 h to obtain the result after sampling, and it was proved that this method saved a considerable amount of time.

Acknowledgments

We wish to express here our thanks to Mr. T. Kitamura and Mr. I. Mai of the Kansai Electric Power Co. and Dr. T. Ohtsuka, Central Research Institute of Electric Power Industry and the staff of the Radiochemistry Section for encouragement and useful advises.

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