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Evaluation of Shiryaev-Roberts procedure for on-line environmental radiation monitoring

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ABSTRACT

Water can become contaminated as a result of a leak from a nuclear facility, such as a waste facility, or from clandestine nuclear activity. Low-level on-line radiation monitoring is needed to detect these events in real time. A Bayesian control chart method, Shiryaev-Roberts (SR) procedure, was compared with classical methods, 3-σ and cumulative sum (CUSUM), for quantifying an accumulating signal from an extractive scintillating resin flow-cell detection system. Solutions containing 0.10–5.0 Bq/L of ^{99}Tc, as $^{99}TcO_4^-$ were pumped through a flow cell packed with extractive scintillating resin used in conjunction with a Beta-RAM Model 5 HPLC detector. While $^{99}TcO_4^-$ accumulated on the resin, time series data were collected. Control chart methods were applied to the data using statistical algorithms developed in MATLAB. SR charts were constructed using Poisson (Poisson SR) and Gaussian (Gaussian SR) probability distributions of count data to estimate the likelihood ratio. Poisson and Gaussian SR charts required less volume of radioactive solution at a fixed concentration to exceed the control limit in most cases than 3-σ and CUSUM control charts, particularly solutions with lower activity. SR is thus the ideal control chart for low-level on-line radiation monitoring. Once the control limit was exceeded, activity concentrations were estimated from the SR control chart using the control chart slope on a semi-logarithmic plot. A linear regression fit was applied to averaged slope data for five activity concentration groupings for Poisson and Gaussian SR control charts. A correlation coefficient (R^2) of 0.77 for Poisson SR and 0.90 for Gaussian SR suggest this method will adequately estimate activity concentration for an unknown solution.

1. Introduction

Conventional methods to detect radionuclides in water involve collecting samples, transporting them to a laboratory, concentrating the analyte of interest, and finally applying detection methods to quantify the radioactivity. This process can take several days to a week to process depending on the radionuclide and desired detection limit, significantly delaying detection of these events. Thus, an on-line radiation monitoring system is necessary that can simultaneously concentrate and detect radionuclides to discover these events in real-time.

One such method is an extractive scintillating resin flow cell coupled to a photomultiplier tube based detection system, which has been developed for alpha- and beta-emitters (DeVol et al., 2000, 2001a, 2001b; Egorov et al., 1999; Seliman et al., 2011, 2013; Duval et al., 2016). In this method, radioactivity selectively accumulates on the sensor as a solution passes through the flow cell while on-line count rate data are simultaneously collected. A stable background count rate with statistical fluctuation is observed when no radioactivity is present on the resin. However, the count rate increases above background in a continuously increasing trend as radioactivity accumulates on the resin. Because it can be difficult to decipher between statistical background fluctuations and ultra low-level radioactivity accumulation on the resin, statistical control charts can be applied to data in real-time to make this distinction.

Control charts are used for process monitoring to quantify whether data points are within control limits. Control limits are established to allow for variability in the system due to statistical fluctuations. Data points inside the control limits are assumed to indicate the system is in-control, while data points outside of the control limits are assumed to indicate the system is out-of-control from changes not inherent in the system. However, statistical fluctuations can cause an out-of-control alarm, or false positive, that occurs with probability α. A false positive will always occur during an infinite run with finite, non-zero control limits. The false positive rate is the frequency that a false alarm occurs when collecting background measurements. Conversely, the system can be out-of-control without an alarm, causing a false negative that occurs with probability β. False negative rate is the number of measurements collected that should have exceeded the control limit, but did not, in a

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given time interval. False positive and false negative probabilities cannot simultaneously be minimized as their probabilities are inversely proportional.

An important measure of control chart performance is the average run length (ARL). The ARL is defined as the average number of data points plotted on the control chart before an out-of-control alarm occurs. The ARL is identified as ARL_0 when a false positive occurs. ARL_0 is theoretically calculated as the inverse of α (Montgomery, 2009). The ARL is identified as ARL_δ when a series of false negative results occur before the control limit is exceeded. ARL_δ is theoretically calculated as the inverse of (1-β) (Montgomery, 2009).

Classical control charts–3-σ, cumulative sum (CUSUM), and exponentially moving average (EWMA)–have been studied for an accumulating signal using an extractive scintillating resin flow cell (Hughes and DeVol, 2008). Bayesian control charts, which rely on Bayes' theorem, were not considered in this prior work. Bayes' theorem updates the current state of knowledge by incorporating new information to the prior state of knowledge using a probabilistic model. Bayesian statistics was first implemented in nuclear science by Little (1982) to differentiate between background and a low-level activity source. Miller et al. built a framework for Bayesian hypothesis testing to detect low-level radioactivity for internal dosimetry and bioassay measurements, though it could have universal use in health physics (Miller et al., 2000, 2008). The U.S. Environmental Protection Agency (EPA) has also revised and updated its estimates for cancer risk coefficients using Bayesian statistics (Pawel, 2013). The success of Bayesian statistics indicates it could be better suited than classical methods for on-line radiation monitoring. A Bayesian control chart method, Shiryaev-Roberts (SR) procedure, will be compared to classical methods, 3-σ and CUSUM, in this work for use in on-line radiation monitoring for an accumulating signal from an extractive scintillating resin flow cell detection system.

2. Materials and methods

2.1. Detection system

The detection system was an extractive scintillator packed flow cell coupled to a Beta-RAM Model 5 radio-HPLC detector (LabLogic Systems, Inc., Brandon, FL). The flow cell was made of fluorinated ethylene propylene (FEP) tubing (1/16″ inner diameter, 1/8" outer diameter) packed with approximately 50 mg of extractive scintillating resin. The tubing was bent into a U-shape, inserted into the flow cell holder, and installed in the Beta-RAM. The extractive scintillating beads were synthesized by copolymerization of an organic fluor (vinyl-NPO) and methyl styrene via a suspension polymerization process. The beads were subsequently functionalized with methyldioctylamine (MDOA), an anion exchange ligand selective for $^{99}TcO_4^-$, which constituted the dual functionality extractive scintillating resin. Preparation of this resin is described elsewhere (Bliznyuk et al., 2015; Seliman et al., 2015). Small pieces of glass frit were fitted into each flow cell to prevent resin from escaping while still allowing solution to flow through. Solution through a flow cell passing.

Time series data sets were collected in 10-s intervals to establish loading and detection efficiencies. An internal pump of the Beta-RAM passed a 5 mL solution containing 0.01 M HCl and approximately 25 Bq of ^{99}Tc through flow cells at a rate of 0.93 ± 0.01 mL/min. The test solution was preceded and followed by 5 mL 0.01 M HCl to establish average count rates before and after the radioactive solution. These values were used to calculate a net count rate for the detection efficiency. The effluent from the radioactive solution was collected and counted for 30 min using a Quantulus Liquid Scintillation Spectrometer (Perkin Elmer, Inc., Waltham, MA) to quantify the loading efficiency, which had a minimum detectable concentration (MDC) of 7.2 Bq/L based on a detection efficiency of 97%, background count rate of 6.2 ± 0.5 cpm, and volume of 5 mL. The average value of two tests is reported.

Control chart data were collected in a similar fashion as efficiency data. The pre-activity-loaded background count rate for each flow cell was established by pumping at least 100 mL of 0.01 M HCl through the flow cell. Once a stable background count rate was observed, 70–500 mL of solution containing 0.01 M HCl and 0.10–5.0 Bq/L $^{99}TcO_4^-$ was pumped through the flow cell. The test solution was followed by 30 mL of 0.01 M HCl solution. Effluent was not collected because it was below the MDC. The loading efficiency was assumed to be the same as determined above. Upon measurement completion, the time series data were re-binned to 100-s intervals. This time interval provided good counting statistics for detecting an increase in count rate as radioactivity accumulates on the resin and minimized time between data points so that an increase can be detected. Re-binned time series data were then passed through statistical algorithms developed in MATLAB written by the authors. The algorithms calculated 3-σ, CUSUM, and SR statistics, determined the volume of ^{99}Tc solution needed to exceed the control limit, and plotted each statistic versus volume to construct the control charts.

2.2. Control chart design

For 3-σ control charts, count rate data are plotted in real time and each point is compared to control limits three standard deviations, σ, above and below the mean count rate, μ (Kennett and Zacks, 1998; Montgomery, 2009). The system is designated as out-of-control if a data point falls outside of the $\mu + 3\sigma$ limits. This method has $ARL_0 = 741$ and theoretical false positive rate α=0.135% (Montgomery, 2009).

The CUSUM statistic, c_i, is the cumulative difference between the most recent normalized count rate, CR_i, and a reference value, k. The system is designated as out-of-control when the deviation between CR_i and k is greater than the control limit, h (Lucas, 1985). A one-sided upper CUSUM scheme is used in radiation monitoring, because only an increase in deviation is of interest. The upper-CUSUM statistic, c_i^+, is calculated as

$$c_i^+ = \max(0, CR_i - k + c_{i-1}^+) \tag{1}$$

(Montgomery, 2009). An upper CUSUM scheme with parameters $k = 0.5$ and $h = 4.77$ corresponded to ARL_0= 741 ($\alpha = 0.135\%$), which is the same as the 3-σ control chart (Montgomery, 2009).

Derived using Bayes' theorem, the SR statistic, W_m is calculated by

$$W_m = \sum_{i=1}^{m-1} \prod_{j=i+1}^{m} R_j \tag{2}$$

where R_j is the likelihood ratio, the probability of an event occurring divided by the probability of the same event not occurring (Kennett and Zacks, 1998). Multiplying and summing the likelihood ratio in this manner allows the newest data point to update the latest SR statistic such that Bayes' theorem is satisfied. For the case Poisson distributions estimate the likelihood ratio, the SR statistic becomes

$$W_m = \sum_{i=1}^{m-1} \exp\left[-j\delta\sqrt{\mu} + \sum_{j=i+1}^{m} CR_j \log\left(\frac{\mu + \delta\sqrt{\mu}}{\mu}\right)\right] \tag{3}$$

where CR_j is the j^{th} count rate measurement, δ is the size of the shift to be detected, and m is the measurement number. For the case Gaussian distributions estimate the likelihood ratio, the SR statistic becomes

$$W_m = \sum_{i=1}^{m-1} \exp\left[-\frac{n\delta^2(m-i)}{2\sigma^2} + \frac{n\delta}{\sigma^2} \sum_{j=i+1}^{m} (CR_j - \mu)\right] \tag{4}$$

where n is the number of samples collected per data point (Kennett and Zacks, 1998). SR parameters were $\delta = 3$ and $n = 1$. Control limits were established using a computer program written by Kenett and Zacks (Kennett and Zacks, 1998). Five hundred runs of this program for $W_{stop} = 700$ produced ARL_0= 784 ± 57 ($\alpha = 0.13 \pm 0.01\%$) for Poisson SR