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Analysis of radioactive strontium-90 in food by Čerenkov liquid scintillation counting

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ABSTRACT

A simple liquid scintillation counting method using DGA/TRU resins for removal of matrix/radiometric interferences, Čerenkov counting for measuring ^{90}Y, and EDXRF for quantifying Y recovery was validated for analyzing ^{90}Sr in various foods. Analysis of samples containing energetic β emitters required using TRU resin to avoid false detection and positive bias. Additional 34% increase in Y recovery was obtained by stirring the resin while eluting Y with $H_2C_2O_4$. The method showed acceptable accuracy (± 10%), precision (10%), and detectability (~0.09 Bq kg^{-1}).

1. Introduction

Strontium-90 (^{90}Sr, $T_{1/2}$ = 28.79 years, E_{max} = 0.55 MeV) (ENSDF, 2016) poses long lasting radiation risk to humans once released into the environment due to its long physical and biological half-lives. Considering food consumption as the major pathway for human exposure to ^{90}Sr, routine monitoring of ^{90}Sr in foods, such as the Total Diet Study and Radionuclides in Food programs implemented by U.S. Food and Drug Administration (FDA), is necessary for ensuring food safety and protecting public health. The radiochemical method currently used by FDA for testing ^{90}Sr in hundreds of food samples involves using fuming nitric acid, hydrofluoric acid, and liquid extraction, which is not only hazardous and labor intensive but also tedious and time consuming. In the early phase of a nuclear or radiological incident, analysis of ^{90}Sr is complicated by the presence of ^{89}Sr ($T_{1/2}$ = 50.56 days, E_{max} = 1.50 MeV) (ENSDF, 2016) and ^{91}Y ($T_{1/2}$ = 58.51 days, E_{max} = 1.54 MeV) (ENSDF, 2016) as beta energies among ^{89}Sr, ^{90}Sr, ^{90}Y, and ^{91}Y are difficult to resolve. However, this complication is averted in routine ^{90}Sr analysis given that ^{89}Sr and ^{91}Y decayed to background levels at the time several years after the incident. Numerous new approaches from using novel radiochemical separations to applying different detection techniques have been reported to improve and simplify ^{90}Sr analysis. Rao et al. (2000) reported analysis of ^{90}Sr in environmental and dietary samples using various matrix-driven co-precipitation schemes followed by Čerenkov counting of ^{90}Y. Maxwell and Culligan (2008) developed a rapid 8-h method for detection of ^{90}Sr in milk by applying Sr resin and gas proportional counting. Sadi et al. (2015) presented a study on analysis of ^{90}Sr and ^{226}Ra in urine using Sr resin for matrix removal, high performance ion chromatographic (HPIC) system for isolation of ^{90}Sr/^{226}Ra, and liquid scintillation counting. A comprehensive methodological review on determination of Sr isotopes by Vajda and Kim (2010) concluded that limitations in radiochemical separation and instrument detection persist for the analysis of low-level Sr isotopes in large-size samples with complex matrices despite of methodological advancements. As most of the published methods aimed to analyze certain types of samples, it is necessary to develop a simpler and more robust method for food safety compliance programs that test over hundreds of different types of foods and beverages annually. In this context, a general-purpose radioanalytical procedure applicable for routine analysis of ^{90}Sr in a wide variety of foods is presented. The method uses Eichrom's DGA and TRU resins for removal of matrix and radiometric interferences, energy dispersive X-ray fluorescence (EDXRF) analyzer for Y recovery determination, Čerenkov counting of ^{90}Y for achieving low background, and fewer chemicals for minimizing hazardous waste production and operation cost. The method performance characteristics including robustness, detectability, accuracy, precision, and uncertainty are evaluated based on statistical analysis of experimental results.

2. Experimental

2.1. Chemicals, standards, test samples, and equipment

All chemicals used were ACS certified reagent grade (Fisher Scientific, Inc.) and purified H_2O was produced by Milli-Q® Integral water purification system. Primary ^{90}Sr standard used for spike addition and instrument calibration was purchased from NIST (Gaithersburg, Maryland, USA). Yttrium (Y) element standards used as stable Y carrier

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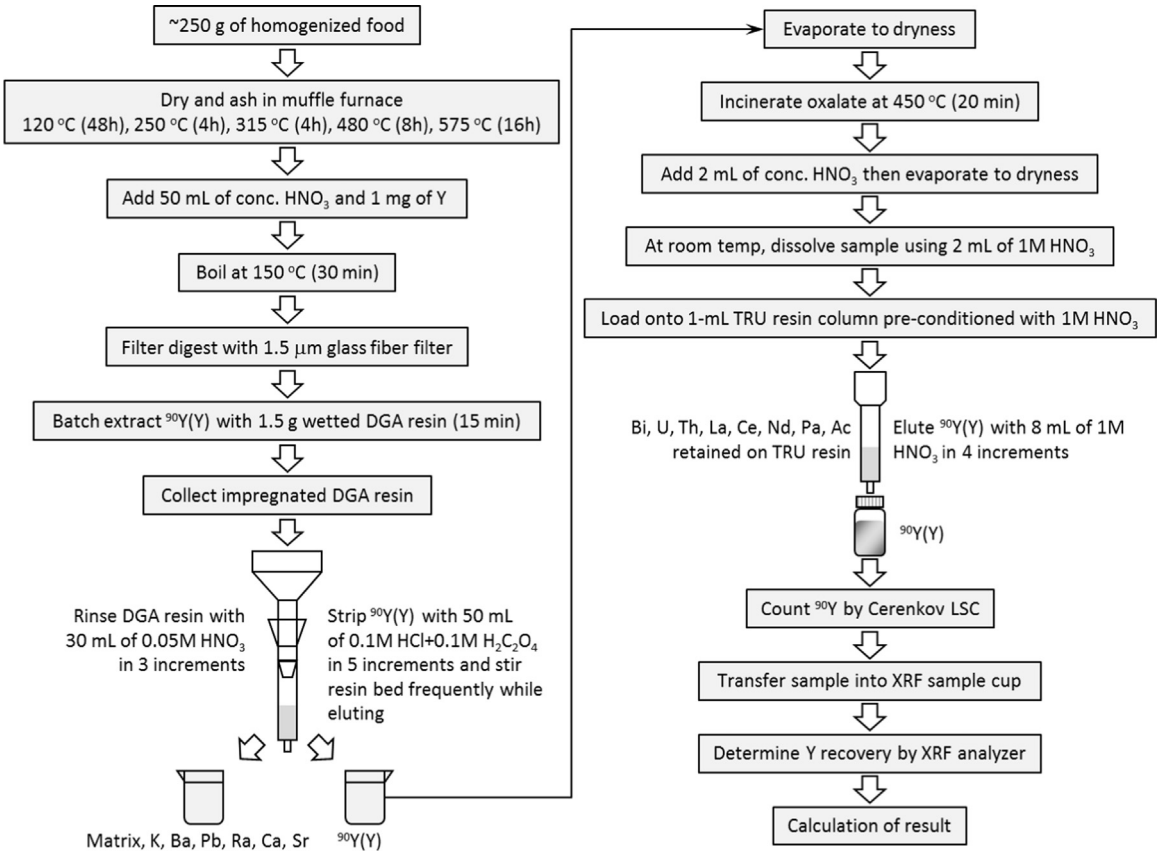

Fig. 1. Radioanalytical procedure used for analysis of ^{90}Sr in foods.

and for calibration of EDXRF were supplied by VHG Labs (Manchester, New Hampshire, USA). DGA resin (*N,N,N′,N′*-tetra-*n*-octyldiglycolamide, Normal, 50–100 μm), TRU resin (CMPO/TBP, 100–150 μm), and Sr resin (4,4′(5′)-di-*t*-butylcyclohexano 18-crown-6, 100–150 μm) were acquired from Eichrom Technologies, Inc. (Darien, Illinois, USA). Test samples were prepared from five food groups including dairy, meat, vegetable, grain, and complex meal followed by addition of a known amount of ^{90}Sr to each sample. Vegetation reference materials containing mixed alpha-, beta-, and gamma-emitting radionuclides certified by ERA (Golden, Colorado, USA) were also used for method development and validation. A Quantulus 1220 liquid scintillation counter (LSC) from PerkinElmer (Waltham, Massachusetts, USA) optimized to provide the highest figure of merit (E^2/B) was used for Čerenkov counting of ^{90}Y. An ARL QUANT'X EDXRF analyzer from Thermo Fisher Scientific (Waltham, Massachusetts, USA) was used for determination of Y recovery.

2.2. Method Procedure, Instrument Calibrations, and Calculations

A procedure shown in Fig. 1 was used to extract (removal of sample matrix), isolate (elimination of interfering radionuclides), and analyze (quench-free and Čerenkov energy-threshold counting) ^{90}Y from ~250 g of food sample. The average time for processing a batch of 8 counting samples was found to be ~7 h. The purified ^{90}Y in 10 mL of 1 M HNO_3 was counted using 20 mL low-diffusion/anti-static polyethylene LSC vial and then was transferred into a XRF sample cup assembly (Cat. No. 2131, Chemplex Industries, Inc.) for quantifying Y recovery. Čerenkov counting efficiency was determined using purified ^{90}Y, which was obtained by loading 0.5 mL of 3 M HNO_3 containing a known activity of ^{90}Sr(^{90}Y) and 1 mg of stable Y onto a preconditioned 2 mL Sr resin column and then eluting the column with 7 mL of 3 M HNO_3. The activity for the purified ^{90}Y was corrected with respect to stable Y recovery. Calibration of EDXRF spectrometer was performed using a set of Y element standards prepared in 1 M HNO_3 at concentrations of 25, 50, 75, 100, 125, and 150 μg g^{-1}.

The net sample ^{90}Sr activity concentration (C_{Sr}) and uncertainty (U_{CSr}) estimated at 95% confidence level were calculated as follows.

$$\mathbf{C_{Sr}} = \frac{\mathbf{A_s} - \mathbf{A_{mb}}}{\mathbf{W_s}}$$

$$\mathbf{A_s} = \frac{\mathbf{R_s}}{\mathbf{E_y} \times \mathbf{Y_s} \times \mathbf{60}} \times \mathbf{e}^{\lambda_Y \times (T_2 - T_1)}$$

$$\mathbf{A_{mb}} = \frac{\mathbf{R_{mb}}}{\mathbf{E_y} \times \mathbf{Y_{mb}} \times \mathbf{60}} \times \mathbf{e}^{\lambda_Y \times (T_3 - T_1)}$$

$$\mathbf{U_{C_{Sr}}} = \mathbf{2} \times \mathbf{C_{Sr}} \times \sqrt{\left(\frac{\mathbf{u_{R_s}}}{\mathbf{R_s}}\right)^2 + \left(\frac{\mathbf{u_{R_{mb}}}}{\mathbf{R_{mb}}}\right)^2 + \left(\frac{\mathbf{u_{E_Y}}}{\mathbf{E_Y}}\right)^2 + \left(\frac{\mathbf{u_{Y_s}}}{\mathbf{Y_s}}\right)^2 + \left(\frac{\mathbf{u_{Y_{mb}}}}{\mathbf{Y_{mb}}}\right)^2 + \left(\frac{\mathbf{u_{W_s}}}{\mathbf{W_s}}\right)^2}$$

where, A_s and A_{mb} are the activities measured in sample and method blank in Bq, W_s is sample weight in kg, R_s and R_{mb} are sample and method blank count rates in cpm, E_Y is ^{90}Y Čerenkov counting efficiency in fraction, Y_s and Y_{mb} are sample and method blank Y recoveries in fraction, λ_{Sr} and λ_Y are ^{90}Sr and ^{90}Y decay constants in day^{-1}, T_1, T_2, and T_3 are the times at ^{90}Sr/^{90}Y separation, sample ^{90}Y mid-count, and method blank ^{90}Y mid-count, and u_{Rs}, u_{Rmb}, u_{Ey}, u_{Ys}, u_{Ymb}, and u_{Ws} are the uncertainties corresponding to their measured quantities in one sigma.

3. Results and discussions

3.1. Effects of matrix and high energy beta radionuclides

With using 1 mg of Y carrier for analyzing ~250 g of foods,