Chapter 12
Analyzing Food Samples—Radionuclides

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Introduction

The United States Food and Drug Administration (US FDA) started its first total diet study (TDS) in 1961 as a program to monitor for radioactive contamination of foods [1]. Since then, it has become a program that determines levels of various contaminants and nutrients in foods, which are purchased throughout the US and prepared as they would be normally consumed. The radiological component of the TDS program provides a basis for realistic evaluations of the dietary exposures of the analyzed radioisotopes by the US population. It also establishes a baseline of analyzed radioisotopes in the US population's dietary intake. If it is designed and planned appropriately, the program can also serve as an effective tool for ensuring the nation's food safety and food defense.

Sample Collections and Analyses

General TDS samples are prepared four times a year and each time the samples are collected from different geographic regions of the US. The radiological component of the TDS involves analyzing radioisotopes in the samples from two of the four sample collections. Currently, the radiological TDS program requires US FDA's Winchester Engineering and Analytical Center (WEAC) to conduct gamma-ray analysis and analysis for strontium 90 (Sr-90), a beta-particle-emitting radioisotope.

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Gamma-Ray Analysis of the TDS Samples

This section briefly describes how gamma-ray analysis has been conducted at WEAC [2]. Basically, the food samples are prepared and then gamma-ray emitting radioisotopes in samples are analyzed using high-purity germanium spectrometers. Given varieties of densities among various food matrices, attenuation of the measured activities due to food density is corrected. The procedure also corrects counting losses due to cascade summing.

Sample Preparation

Samples are obtained and secured according to appropriate sample handling procedures. Samples are also maintained in accordance with labeled instructions for preservation and storage. When no labeling or instruction for storage is indicated, the analyst is expected to take appropriate measures to maintain the quality of the food until the time of compositing. These measures may involve refrigeration and freezing. Typical sample preparation involves thawing the sample if necessary, maintaining the food at refrigerated temperature if necessary, and avoiding delay between compositing and counting to minimize uncertainties due to composite layer separation and settling.

The inedible portion of the sample should be removed from all portions that will be used for analysis. Any utensils used in the sample preparation are to be clean, and cannot be used again for another sample until they have been cleaned per standard procedures. The edible portions of sample are combined according to procedures, usually using a food processor or blender to create a homogenous composite. A standard container holding approximately 400 ml of sample is used for hosting sample and counting.

Sample Analysis

Once a geometry is chosen, the composited sample is homogenized, packed into the chosen geometry container and weighed. The identification and the mass of the sample are recorded. The sample is then placed on a gamma-ray detector for counting for a certain time interval depending upon the program requirement. Gamma-ray spectrometers are configured to accumulate counts from gamma-ray emissions of 50–2,000 keV. The gamma-ray counts collected by the detector produce a spectrum which allows an application software provided by the equipment supplier to identify various spectral lines and to compare and correlate those spectral lines with responsible gamma-ray emitting radioisotopes using a selected radionuclide library. If a spectral line is detected within the user defined energy tolerance range, a match will be declared. If more than one spectral line is identified within the energy tolerance range, the closest match is chosen.

The following equation is used to calculate the activity concentration of a radionuclide in the sample:

$$A_d = \frac{P}{q \times \varepsilon_d \times b \times E_l} \times e^{\lambda T_s}$$

The efficiency value, ε_d, is a variable dependent on a sample density.

The equation used to calculate the density correction factor is shown below:

$$dcf = \frac{\varepsilon_u}{\varepsilon_d}$$

The minimum detectable activity concentration (MDC) is calculated using the following equation utilized by the application software:

$$MDC = \frac{\left(2.71 + 4.65 \times \sqrt{B}\right)}{q \times \varepsilon_u \times b \times E_l} \times e^{\lambda T_s}$$

Here, the MDC value is prior to the density correction. The result obtained is further processed by taking into account of matrix density effect for MDC.

The Limit of Quantification in activity concentration (LOQ) is calculated using the following equation:

$$LOQ = \frac{50\left\{1 + \left[1 + \frac{B}{12.5}\right]^{\frac{1}{2}}\right\}}{q \times \varepsilon_d \times b \times E_l} \times e^{\lambda T_s}$$

where,

A_d = *Activity concentration (Bq/kg) corrected for sample density*
q = *Sample quantity (kg)*
d = *Sample packing density (kg/l); d = q/V*
V = *container fill volume; V = 400 ml or 0.4 l*
ε_u = *Uncorrected counting efficiency*
ε_d = *Density adjusted counting efficiency; the uncorrected counting efficiency/dcf*
b = *gamma-ray abundance*
E_l = *Elapsed live time (seconds)*
Λ = *decay constant* ($ln2/T_{1/2}$); *seconds*$^{-1}$
$T_{1/2}$ = *half-life of radionuclide; seconds*
T_s = *sample date – acquisition date; seconds*
P = *Net Peak Area introduced by a sample after subtraction of environmental background*
dcf = density correction factor

$B = B_{SC} + N_B$; *The background counts used for the MDC and LOQ calculations in the region of the radionuclide key-line energy*
B_{SC} = *The continuum counts in the region of the radionuclide key-line energy in the sample spectrum*
MDC = *Minimum Detectable Activity Concentration*
LOQ = *Limit of Quantification*

Sr-90 Analysis of the TDS Samples

Because of the nature of food matrices, Sr-90 analysis is a lengthy and labor-intensive process. A brief summary of the procedure is described below [3]:

After completion of gamma-ray analysis of a sample, the sample is used for Sr-90 analysis. The sample is ashed first and then digested in nitric acid. The resultant sample solution is mixed with nitric acid equilibrated tributylphosphate in a separatory funnel where yttrium 90 (Y-90) is separated from Sr-90 and the sample matrix. After removal of iron and rare earths by fluoride ion and hydroxide ion precipitations, the purified Y-90 is deposited onto a glass fiber filter as yttrium oxalate and the beta emission from the Y-90 is counted using a low-background internal gas-flow proportional counter. The Sr-90 concentration in a sample is equal to the Y-90 concentration calculated with its respective attenuation-corrected counting efficiency, chemical yield, decay correction factor, and sample weight.

Quality Control of the Sample Analysis

Gamma-Ray Analysis

Gamma counting efficiency is sample specific and must be determined with the same geometry that is used for the sample. Whenever possible, a matrix and geometry specific efficiency should be established. Efficiencies for mixed-gamma standards are determined annually or after a detector is repaired. An efficiency fit is considered acceptable when an analysis of a Laboratory Control Sample (LCS) using the new efficiency file yields results with an uncertainty that overlaps the certified uncertainties for each radionuclide declared in the certificate. This quality control is documented in a quality control logbook.

Prior to sample analysis, a check standard shall be counted and evaluated to demonstrate that the instrument is suitable to collect sample data. During periods of time when no samples are being analyzed, this check must be performed at least weekly. After the standard is counted and passed quality control criterion, the spectrum is analyzed to demonstrate that the instrument is meeting specifications for energy, resolution and efficiency.

Background Checks

The background check spectrum is collected in conjunction with food sample analysis. This check analysis is conducted daily. During periods when no samples are being analyzed, a daily background check must be performed at least weekly. The counting of a daily background should be reported on the function verification/preventative maintenance chart.

Strontium 90

The quality control for analysis of Sr-90 in foods involves insuring instrument quality control and method procedures quality control. For instrument quality control, it basically requires routine instrument calibration, which includes establishing operating voltages for alpha and beta particle counting and corresponding efficiencies; making sure both alpha and beta counting efficiencies meet established criteria. Continuing quality control steps are also implemented, which involves: monitoring background; counting both alpha and beta standard sources and insuring the source activities are within the established quality control boundary; and monitoring the quality control chart trend. The method quality control procedures basically require the analysis of LCS, analysis of method blank sample with each batch of TDS samples. The results of both LCS and method blank samples need to meet established criteria. The quality control criteria, i.e. the warning and control limits, are preestablished according to the corresponding historical data or standard reference value(s) for each quality control element. The laboratory corrective action procedures are followed if there are any quality control violations.

Key Findings

WEAC sample analysis results of past decades indicated that the levels of analyzed radioisotopes in the foods collected for the analysis have been minimal, or notdetected for most samples. In rare cases, trace results were found from certain samples. A non-detected result was assigned if the detected level is below the minimum detected activity (MDA) per kilogram of a sample; trace was assigned if a detected level was above the MDA and below the LOQ of the detection system used for the analysis. It is worth noting, however, that the detected trace levels were far below the FDA's derived intervention levels (DILs). For instance, the DIL for Cs-134 and Cs-137 together is 1,200 Bq/kg, whereas a typical MDA for Cs-134 is at the scale of 1 Bq/kg and the same holds true for Cs-137. The Cs-134 and Cs-137 activity levels in the samples have been below the MDA values. The DIL for Sr-90 is 160 Bq/kg, whereas the MDA values have been mostly below 0.1 Bq/kg. The Sr-90 activities of the samples have been mostly below the MDA values. In rare cases, the Sr-90 activity of certain samples was detected at a level above the MDA.

For instance, the highest Sr-90 activity of 2004 TDS samples was found at 0.28 Bq/kg with the 0.08 Bq/kg MDA value and 0.38 LOQ value. The data collected in the last decade also showed that there have not been variations in the analytical results of the samples collected in different years.

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References

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