Improvements in food analysis by thermal neutron capture prompt gamma-ray spectrometry

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The thermal neutron prompt gamma-ray activation analysis (PGAA) facility, operated by the US Food and Drug Administration and National Institute of Standards and Technology Center for Neutron Research, has been redesigned to lower background radiation levels and improved analytical capabilities. Analysis of 22 element standards and food and botanical certified reference materials revealed significant sensitivity increases and lower limits of detection for H, B, C, N, Na, Al, P, S, Cl, K, Ca, Fe, and Cd. Mass fractions for these elements, as well as Mg, Al, Si, Ti, Mn, Fe, Cu, I, Zn, Sm, and Cd, were determined for 6 dietary supplements.

Introduction

A thermal neutron capture prompt gamma-ray activation analysis (PGAA) system, developed by the University of Maryland and the National Institute of Standards and Technology (NIST),1,2 has been in operation since 1978. Located at the NIST Center for Neutron Research (NCNR) in Gaithersburg, MD (USA). The facility is now maintained by NIST’s Nuclear Methods Group and the US Food and Drug Administration’s (FDA’s) Elemental Research Branch. In 1999, a major redesign effort was begun with goals of lowering background radiation levels, making easier the assembly and disassembly of the instrument (which is necessary before and after refueling), and improving element detection capabilities (i.e., achieving higher element sensitivities and lower limits of detection, LODs, as defined by CURRE).3 The new system, whose redesign features are described in detail elsewhere,4 became operational in 2001. A sapphire crystal beam filter was installed in the beam shutter (below floor level), and a new beam stop, upper beam tube, sample chamber, detection system, and support structure were installed.

With the sapphire filter in place, the number of fast neutrons in the beam was reduced by a factor of 5, while the thermal neutron fluence rate decreased by only about 12%. The filter also reduced low-energy (up to about 400 keV) gamma-ray background count rates by up to a factor of 10. A new lithiumated polymer-lined aluminum sample chamber and beam tube assembly replaced components in the old system that were fabricated from paraffin, boron carbide, natural Li2CO3, and 7Li2CO3. The beam path can now be evacuated to reduce the number of background gamma-rays arising from neutron scattering and capture in air and surrounding materials. A higher efficiency Ge detector and bismuth germanate (BGO) scintillator replaced the old Ge and NaI(Tl) Compton suppression system. The overall results of these changes were significant reductions in background count rates for H, B, C, N, Al, Fe, and Pb, elimination of background for Na and I, and improved sensitivities for most elements.

The purpose of this study was to evaluate the analytical capabilities of the new PGAA system for determination of element content of dry foods and dietary supplements. NIST Standard Reference Materials (SRMs) and a selection of commercial mineral, vitamin, and botanical dietary supplements were analyzed. Sensitivities, blanks, and LODs obtained with the new instrument were compared with those of the old PGAA system.

Experimental

PGAA procedures followed in this study are the same as those used in an SRM revalidation study in 1996.5 As described in that work, B, Na, S, Cl, K, and Ca standard portions were prepared from dry compounds (little or no H) and from solutions deposited on 750 mg of cellulose filter material (mass fraction about 6.2% H). Standard portions were pressed into 1.3-cm diameter cylinders and used to calibrate for sensitivity variation as a function of H content6 for these and other elements. Metal foils or pure elements were used as standards for Mg, Al, Si, Ti, Mn, Fe, Cu, and Zn. A 750-mg portion of urea, pressed into a 1.3-cm diameter cylinder, was used as a standard for H, C, and N. Solutions pipetted onto cellulose filter paper were used as standards for Cd, Sm, and Gd, and 1.3-cm diameter cylinders of sodium metaphosphate and potassium iodide were used as standards for P and I, respectively. Standard and test portions were placed in Teflon bags. Empty Teflon bags, paraffin disks, and Be metal portions were analyzed to measure element blanks.

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and blank/background count-rate enhancement\textsuperscript{7} caused by neutrons scattering off the target and into the surrounding materials.

Cylindrical 750-mg portions of NIST SRMs 1577 Bovine Liver, 1568 Rice Flour, and 1547 Peach Leaves were analyzed as representative dry food matrices and as analytical controls. Dry masses were determined according to NIST Certificate instructions. Single tablets of commercially available multiminerals, multivitamin/ multimineral, and bone meal dietary supplements were packaged and analyzed without any treatment. Similarly, two capsules each (packaged together in Teflon bags) of three botanical dietary supplements, horsetail (\textit{equisetum}), kelp (\textit{Ascophyllum nodosum}), and spirulina (a microalgae) were analyzed. When information was available, results were compared to nominal (label) content.

Standard, SRM, and supplement test portion count rates were corrected for differences in neutron fluence rate by use of Ti monitors\textsuperscript{5} cut to the same shape as the test portions analyzed. Gamma-ray spectrometry was performed during irradiation of the standard and test portions in the beam at a thermal neutron fluence rate of 3.0 \times 10^8 \text{ n cm}^{-2} \text{s}^{-1} for times ranging from 45 minutes to 1.7 days to examine the full range of LODs for these matrices. The Compton-suppression detection system consisted of a Ge detector (40\% efficiency relative to NaI(Tl), 70.6 peak-to-Compton ratio, 2.0 keV resolution at 1333 keV) and a 11-cm \times 11-cm \times 16-cm bismuth germanate (BGO) scintillation detector. Gamma-ray photopeaks used for analyses were (in keV) 2223 (for H), 477 (B), 4945 (C), 10829 (N), 472 and 874 (Na), 1779 (Al, delayed), 4934 (Si), 636 and 1071 (P), 841 and 5420 (S), 787 (Cl, doublet), 770 (K), 1942 (Ca), 6760 (Ti), 212 (Mn), 7631 and 7646 (Fe), 159 (Cu), 115 and 1077 (Zn), 558 (Cd), 134 (I), 439 (Sm), and 182 (Gd). Interference corrections were made for B (Na interference), Mg (P interference from Teflon bag material), and C (Cl interference).

Results and discussion

A comparison of pre- and post-redesign analytical capabilities is shown in Table 1. The same portion of NIST SRM 1568 Rice Flour previously analyzed in the revalidation study\textsuperscript{5} (using the old system) was reanalyzed using the new system. For similar count times (15.5 hours), the mass of each element determined in blanks, element sensitivities (cps/mg), and 3\sigma LODs\textsuperscript{3} (mg/kg, taking into account Compton background, blank, and interferences from other elements) for 14 elements are compared. The Ge detector size, shape, and positioning differences gave rise to significantly different sensitivities with the redesigned system. Above about 300 keV, sensitivities were improved by 3\% to 45\%. Sensitivities for Mn and I decreased because of lower Ge detector efficiency at low energies, and Cd sensitivity decreased because the sapphire filter eliminated most neutrons at Cd resonance energies. Although sensitivities were lower for these three elements, LODs still improved by factors of 2 to 3 because of the reduction in background count rates. Large decreases in blank values were observed for H, B, C, N, Na, Cl, and I. Al blank also decreased, even though the new instrument contained more structural Al. All LODs were lowered by at least a factor of 1.9. With the system evacuated, the most dramatic improvement was for N, with improvement factors of 111 in blank value and 5.6 for the LOD. The 5269 keV line was used in this comparison because the 18029 keV line was not used in the revalidation study. Improvement factors for the 18029 keV photopeak would be even greater.

Results for three NIST SRMs are given in Table 2. Mass fractions and expanded uncertainties (coverage factor=2) determined by PGAA were in good agreement with Certificate and consensus\textsuperscript{8} values with the exception of B in SRM 1577, Bovine Liver. Previous work\textsuperscript{9} on SRM 1577 indicated either non-homogeneity or long-term losses for this element. Matrices of the three SRMs are representative of a variety of dried foods and count times: SRM 1568 with low trace element content and a long count time, SRM 1577 with high Cl content with a shorter count time, and SRM 1515 with relatively high B, K, Ca, Mn, Sm, and Gd content and a long count time. The LOD values for each element are also given, as are LODs for Al, Si, Fe, and I, even though none of these were detected in the SRMs. For all three matrices and count times, LODs for Ca and Cd were similar and most others varied by a factor of 2. LODs for C, Si, P, S, and Fe varied by factors of 3 to 4, while that for Na was a factor of about 6 higher for SRM 1515, because of the interference from the 477 keV (Doppler shifted) B photopeak. Compared to 15-hour counts, LODs for 0.5 to 1-hour counts would be about a factor of 4 higher for a given matrix.

Results for six dietary supplements are given in Tables 3 and 4. In Table 3, findings are given for a single tablet each (1 tablet daily dose, corresponding to the label recommendation) of multivitamin (0.99 g), multivitamin/multimineral (1.60 g), and bone meal (calcium, 1.33 g) supplements. Daily intakes are compared to the label information. Except for B in the multiminerals supplement (0.25 mg/d measured vs. 0.15 mg/d on the label), there was good agreement between the PGAA and label values. In all, 22 different elements were found above LODs in one or more of the three supplements. Results for three botanical dietary supplements are presented in Table 4, along with daily intake ranges calculated from dosages recommended on the labels. A total of 20 different elements were found above the LODs in one or more of these supplements.