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MULTIELEMENT ANALYSIS OF FOODS BY NEUTRON CAPTURE PROMPT γ-RAY ACTIVATION ANALYSIS

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A method is described for the determination of H, B, Cl, K, Na, S, Ca, and Cd in foods using in-beam neutron capture prompt γ-ray activation analysis. Special calibration procedures were necessary because of matrix-related thermal neutron scattering-induced sensitivity and background enhancements. Detection limits and sensitivities are presented for best-case and worst-case irradiation conditions. The method was applied to multielement analysis of 41 foods and to B, Cl, and K analysis of 13 orange juice produts in conjunction with analysis by inductively coupled plasma atomic emission spectrometry. The purpose of the latter application was to study B losses during acid digestion.

Introduction

In-beam neutron capture prompt γ-ray activation analysis (PGAA) can be used to determine H, B, Cl, K, Na, S, Ca, and Cd in many foods. Thermal neutron scattering matrix effects, resulting primarily from the presence of H, significantly affect PGAA element sensitivities and background count rates[1-3]. Since H concentrations are relatively high and variable in foods, special calibration methods must be employed to ensure analytical accuracy. In this study, procedures were developed to account for scattering effects while minimizing detection limits (DLs). To test the capabilities of the method, 41 foods, including fruits, vegetables, beverages, and miscellaneous products from the U. S. Food and Drug Administration's Total Diet Study[4,5], were analyzed. Standard Reference Materials (SRMs) from the National Institute of Standards and Technology (NIST) were analyzed as controls. Inductively coupled plasma atomic emission spectrometry (ICP) fortification studies showed B recoveries of only 84 ± 11% for 36 orange juice products after $HNO_3/HClO_4/H_2SO_4$/Kjeldahl digestion. The nondestructive nature of PGAA made it an ideal technique to check these findings; a separate set of 13 orange juice products was analyzed for B by both methods. K was also determined by both methods as a control element, since digestion losses were not likely for this element.

Experimental

PGAA measurements were performed at the NIST 20-megawatt research reactor in Gaithersburg, Maryland (USA). The PGAA facility, developed jointly by NIST and the University of Maryland, has a thermal neutron beam with a fluence rate of 3.3×10^8 $cm^{-2} \cdot s^{-1}$ and detection system consisting of a 27% efficient (relative to NaI) Ge detector surrounded by a 30 x 35-cm

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NaI(Tl) anti-Compton shield. Detailed descriptions of the methods of monitoring, the detection system, analyzer, peak-fitting codes, and neutron fluence rate are described elsewhere[3,6]. Customized personal computer spreadsheets were developed for final data reduction, including calculation of pulse pileup corrections, backgrounds and sensitivities (both as a function of H count rate), nuclide interference corrections, fluence rate and counting geometry normalizations, final concentrations, and detection and quantitation limits. Pulse pileup characterization was accomplished by measuring the count rate of the in-beam Ti foil as a function of system deadtime, which was varied by placing a ^{137}Cs source at various locations relative to the Ge detector.

Analytical portions of the controls, standards, and foods (2.0 g each) were transferred by pipette or Ni-plated spatula to Teflon bags fabricated in our laboratory. The bags were sealed in such a way that each analytical portion was confined to a 2.4 x 2.4-cm square region. This resulted in a "pillow-shaped" target, with a central thickness of 0.5 cm, that effectively subtended the beam and γ-ray collimation (both approximately 2.5-cm dia) while eliminating shape-related neutron scattering effects. A 2.4 x 2.4-cm Ti foil monitor was counted frequently (usually once a day) as a measure of fluence rate and target-positioning variations. Typically, the Ti monitor showed a count rate standard deviation of about 1.5% within a reactor fuel cycle and less than 0.5% day-to-day.

Primary standard solutions were prepared from the following salts: NIST SRM 999 KCl, Mallinckrodt ACS specification H_3BO_3 and Na_2SO_4, and SPEX TMI-10 purity NaCl, KNO_3, and $CaCO_3$. Standard solutions for S and Cd were prepared using NIST SRMs 3154 and 3108 standard spectrometric solutions, respectively. For H standards, 18-megohm deionized water was used. Standard analytical portions were prepared to measure each element's sensitivity behavior as a function of H (2223-keV γ-ray) count rate in counts•s^{-1} (CPS). The H count rate (pulse pileup adjusted) was found to range from about 340 to 400 CPS for 2.0-g portions of most foods. For each element, two standards having 2223-keV count rates of about 400 and 340 CPS (corresponding to H concentrations of about 11 and 9%, respectively) were prepared. The first for each was a 2.0-mL aliquot of standard solution and the second was 1.5 mL of standard solution absorbed in 0.5 g Whatman 541 filter paper (about 6% H). For B, to ensure that linearity holds at lower H count rates, a third standard (about 8% H) was prepared as a slurry of 1.5 mL of standard solution mixed with 0.5 g of high purity graphite, yielding a 2223-keV count rate of ~260 CPS. The calibration for B is shown in Fig. 1. Blanks prepared with deionized H_2O instead of standard solutions were analyzed for the three matrices. The 2.0-mL deionized H_2O and graphite slurry blanks also served as H standards. For the analytical controls, 0.75 g portions of NIST SRMs 1570 Spinach, 1571 Orchard Leaves, and 1549 Milk Powder were slurried with 1.25 mL of deionized water to yield H count rates of about 300-320 CPS.

Background count rates for H, B, Na, and Cl (contained in the detection apparatus and shielding) were also affected by the scattering characteristics of the analytical portion[3,7]. For this study Teflon bags, empty and with 1.0-, 1.5-, and 2.0-mL aliquots of deionized water, were analyzed to obtain background count rates as functions of the H 2223-keV count rates as shown for B in Fig. 2. H background count rates were related to the total H count rate indirectly by H/Al count rate ratios determined for nonhydrogenous calibration standards as described in another study[7].

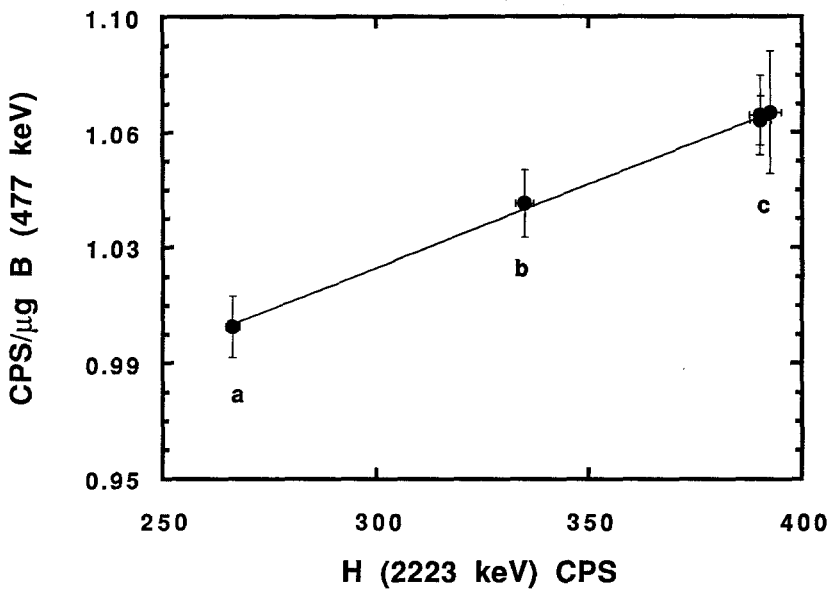

Fig. 1. B sensitivity (S_B, CPS/μg) as a function of H count rate (A_H, CPS). Linear regression analysis yields the fit: $S_B = 0.8554 + 0.0005435 \cdot A_H$ ($R^2 = 0.998$). (**a**, 1.5 mL of standard solution with 0.5 g of graphite; **b**, 1.5 mL of standard solution with 0.5-g Whatman filter; **c**, 2.0 mL of standard solution.)

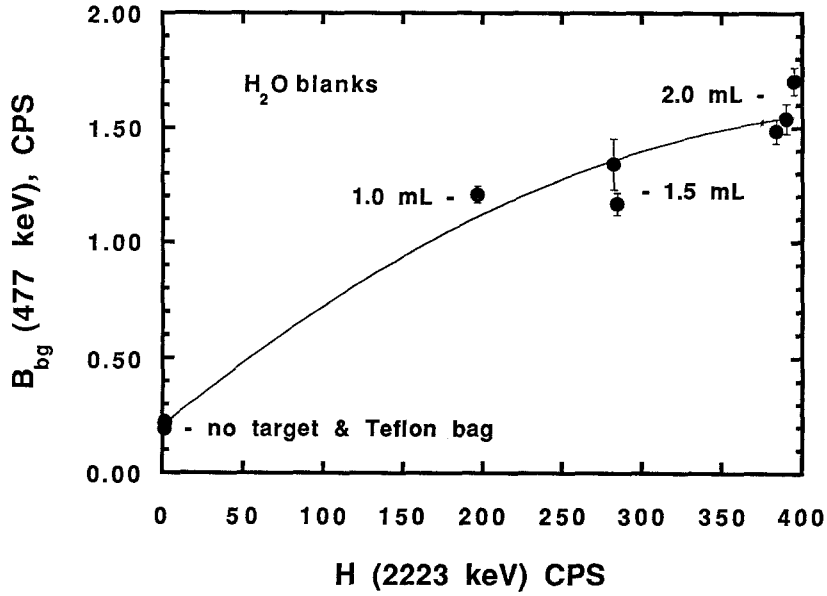

Fig. 2. B background count rate (B_{bg}) as a function of H count rate (A_H). Polynomial fit yields $B_{bg} = 0.205 + 0.00578 \cdot A_H - 6.021 \cdot 10^{-6} \cdot A_H^2$ ($R^2 = 0.997$). Combined data from three fuel cycles. Three data points labeled "no target" represent a Teflon bag blank, one run with no target in the sample holder, and one run with no sample holder.

Results

A summary of details and capabilities of the PGAA procedure is presented in Table 1. The photopeak energies are given for the γ-rays most useful for food analysis, along with sensitivities and any background or interference lines that were encountered. DLs according to Currie[8] were calculated for two extreme cases. For a given count time, Compton background due to high Cl levels is the most frequent cause of increased DLs. Accordingly, the worst case encountered was a short (4 h) count of high-Cl salad dressing, for which DLs are approximately 4 to 6 times higher than for a long count (22 h) of low-Cl 2% lowfat milk. Quantitation limits were about 3 times greater than the DLs. Also given are the number of foods for which each element was above the DL and the corresponding concentration ranges observed above the DL. Except for the results for Cl, the findings for two controls, NIST SRMs 1570 Spinach and 1571 Orchard Leaves (Table 2), show good agreement with certified, information, and literature values. The validity of the Cl findings is not discounted, however, because instrumental neutron activation analyses of these SRMs in our laboratory also yield higher values, and the PGAA Cl concentration found for another control, SRM 1549 Milk Powder (1.10 ± 0.03%, not shown in Table 2), agreed well with the NIST certified value of 1.08 ± 0.01%.

Table 1. Analytical γ-rays, necessary corrections, and detection capabilities of PGAA for foods

			detection limit (μg/g)			
Element, keV	interf's[a]	Sensitivity CPS/μg[b]	low Cl, long count[c]	high Cl, short count[d]	# of foods above DL	concn. range
H, 2223	bg	1.72×10^{-3}	30	80	41	80600 - 114000
B, 477	bg, Na (472), Cl (468)	1.069	0.04	0.19	39	0.12 - 21.5
Cl, 787	bg	2.83×10^{-3}	7	37	41	7 - 32000
Cl, 1164	bg	2.31×10^{-3}	8	37		
Cl, 6111	bg	3.88×10^{-4}	12	160		
K, 770	-	2.65×10^{-4}	60	210	40	127- 7880
Na, 472	bg, B (477)	3.32×10^{-4}	70	300	14	170 - 20300
Na, 874	-	3.39×10^{-5}	350	2060		
S, 841	K (843)	1.14×10^{-4}	140	630	15	104 - 760
S, 5420	-	1.85×10^{-5}	150	2180		
Ca, 1942	-	4.65×10^{-5}	410	2460	9	500 - 1300
Ca, 6420	Ti (6420), Cl (6423)	6.59×10^{-6}	450	4700		
Cd, 558	F (556)	0.322	0.04	0.26	2	0.07 - 0.16

[a] bg: background; element and interfering photopeak energy given for nuclide interferences.
[b] For 2.0-mL standard solution (H 2223-keV count rate ~390 CPS).
[c] 2% lowfat milk, 860 μg Cl/g, 22-h count.
[d] Bottled salad dressing, 3.20% Cl, 4-h count.

B and K findings for the PGAA and ICP analyses of 13 orange juice products are reported in Table 3. PGAA findings (3-h irradiations) are averages for duplicate test portions and the ICP findings are for single test portions. Excellent agreement was found for K (not likely to be lost during acid digestion); for B, however, ICP findings averaged 27% lower than those for PGAA, suggesting that some B had volatilized during digestion. These results are consistent with the the findings for the separate set of 36 orange juice products in the ICP fortification study. Cl was also determined by PGAA in the orange juice test portions. Cl concentrations were found to be 17-88 μg/g, but no comparative ICP analytical data were available for these products.

Table 2. Concentrations (μg/g unless indicated) determined by PGAA for NIST control SRMs

	SRM 1570 Spinach			SRM 1571 Orchard Leaves		
Element	PGAA	NIST	Lit.[9]	PGAA	NIST	Lit.[9]
H (%)	5.45 ± 0.08	-	5.57	5.84 ± 0.08	-	5.84 ± 0.26
B	28.2 ± 0.4	30	27.7 ± 0.6	31.3 ± 0.4	33 ± 3	33 ± 3
Cl (%)	0.775 ± 0.010	-	0.661 ± 0.041	808 ± 13	690	730 ± 40
K (%)	3.69 ± 0.08	3.56 ± 0.03	3.56 ± 0.15	1.51 ± 0.03	1.47 ± 0.03	1.44 ± 0.07
Na	13700 ± 200	-	14200 ± 1000	-	82 ± 6	89 ± 15
S	4180 ± 120	-	4350 ± 470	1760 ± 210	1900	2040 ± 240
Ca (%)	1.31 ± 0.17	1.35 ± 0.03	1.33 ± 0.08	2.02 ± 0.26	2.09 ± 0.03	2.04 ± 0.12
Cd	1.45 ± 0.10	1.5	1.43 ± 0.14	0.10 ± 0.04	0.110 ± 0.010	0.119 ± 0.022

Table 3. ICP and PGAA findings (μg/g) and ICP/PGAA ratios for B and K in 13 orange juice products

	Boron			Potassium		
Product #	PGAA	ICP	ICP/PGAA	PGAA	ICP	ICP/PGAA
720	0.57 ± 0.10	0.379	0.66	1306 ± 118	1319	1.01
721	1.01 ± 0.09	0.842	0.83	1678 ± 114	1699	1.01
722	1.15 ± 0.11	0.703	0.61	1386 ± 108	1433	1.03
723	1.10 ± 0.09	0.757	0.69	1385 ± 104	1421	1.03
732	0.95 ± 0.11	0.767	0.81	2035 ± 133	2085	1.03
733	0.94 ± 0.11	0.658	0.70	1530 ± 111	1428	0.93
734	0.75 ± 0.10	0.557	0.74	1640 ± 114	1738	1.06
735	1.24 ± 0.12	0.866	0.70	1264 ± 117	1223	0.97
736	0.86 ± 0.07	0.710	0.82	1496 ± 90	1597	1.07
737	0.97 ± 0.11	0.712	0.74	1297 ± 105	1422	1.10
738	1.08 ± 0.12	0.883	0.82	1315 ± 104	1438	1.09
739	1.08 ± 0.13	0.806	0.74	1314 ± 120	1364	1.04
740	0.74 ± 0.11	0.492	0.67	806 ± 101	822	1.02
Av. ICP/PGAA:			0.73 ± 0.07			1.03 ±0.05

Discussion

In-beam PGAA is an accurate nondestructive method for food analysis, but special sensitivity and background calibration must be performed. For each element, the sensitivity, and, if applicable, background behaviors are affected by thermal neutron scattering caused by the standards, controls, and unknowns. For foods, these behaviors can be calculated as functions of H concentration and, therefore, as functions of H count rate. Use of a constant target shape simplifies the calibration procedure. Neglecting neutron-scattering effects would lead to inaccurate measurements. For example, if only non-hydrogenous standards were used for the analyses in this study, measured concentrations would have been biased high by 15 to 25%. Conversely, if solutions (approximately 11% H) alone were used as standards, the concentrations would have been biased low by as much as 10%. For B, background enhancement characterization is especially important if B-containing materials are used for neutron shielding near the detection system. For our system, neglecting background enhancement would have resulted in a high bias of about 80% at 1 μg B/g and about 3% at 20 μg B/g. For Na determination using the 472-keV line, neglecting background enhancement would have resulted in a high bias of about 20% at a concentration of 2000 μg Na/g. For our system, the Na background comes from the anti-Compton shield.

This PGAA method is advantageous for food-related studies because it is sensitive for elements of nutritional or toxicological interest, and no digestion or drying, with the associated risk of volatilization losses[1], is needed. The analysis also leaves test materials virtually unaltered and available for further studies.

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References

1. D. L. ANDERSON, W. C. CUNNINGHAM, E. A. MACKEY, Biol. Trace Elem. Res., 27 (1990) 616.
2. E. A. MACKEY, G. E. GORDON, R. M. LINDSTROM, D. L. ANDERSON, Anal. Chem., 63 (1991) 288.
3. D. L. ANDERSON, W. C. CUNNINGHAM, E. A. MACKEY, Fresen. Z. Anal. Chem., 338 (1990) 554.
4. J. A. T. PENNINGTON, J. Am. Diet. Assoc., 82 (1983) 166.
5. P. LOMBARDO, Environmental Epidemiology, Lewis Publishers, Inc., Chelsea, MI, USA, 1986.
6. D. L. ANDERSON, M. P. FAILEY, W. H. ZOLLER, W. B. WALTERS, G. E. GORDON, R. M. LINDSTROM, J. Radioanal. Chem., 63 (1981) 97.
7. D. L. ANDERSON, E. A. MACKEY, elsewhere in these Proceedings.
8. L. A. CURRIE, Anal. Chem., 40 (1968) 586.
9. E. S. GLADNEY, B. T. O'MALLEY, I. ROELANDTS, T. E. GILLS, National Bureau of Standards Special Publication NBS SP 260-111, 1987.