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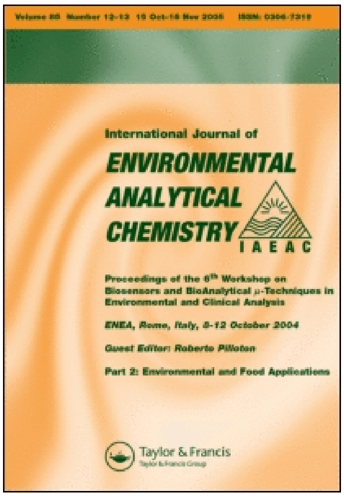

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Kishor R. Shah[a]; Royston H. Filby[a]; Albert I. Davis[a]
[a] Nuclear Radiation Center, Washington State University, Pullman, Washington, U.S.A.

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Determination of Trace Elements in Tea and Coffee by Neutron Activation Analysis

KISHOR R. SHAH, ROYSTON H. FILBY, and ALBERT I. DAVIS
Nuclear Radiation Center, Washington State University,
Pullman, Washington 99163, U.S.A.

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Thermal neutron activation analysis, a high-resolution Ge(Li) gamma-ray spectrometer, and an IBM 360/67 digital computer were used to determine the concentration of Na, K, Sc, Cr, Mn, Fe, Co, Cu, Zn, Se, Br, Rb, Sb, Cs, and Hg in ground coffee and tea. This nondestructive multielement technique requires neither pre- nor postirradiation chemistry and eliminates problems of reagent contamination. The method is simple, precise and sensitive to 15 elements. Interferences from fast neutron (n,p) and (n,α) reactions are small and, if necessary, corrections may be applied easily. This technique can be applied to percolated tea and coffee.

INTRODUCTION

Tea and coffee are the world's most popular stimulant beverages, and there are many reasons for their wide popularity. Both tea and coffee have excellent flavor and can be enjoyed all year around. Apart from being true stimulants, tea and coffee can be considered as foods with some nutritional value, and addition of milk and sugar to these beverages increases this nutritional value. The chemistry and biochemistry of tea and coffee and their manufacturing processes have been studied in some detail,[1–3] and research in this field is continuing. Very little effort has been made to date to study the trace element chemistry of tea and coffee. It is evident from studies in other fields, such as plant physiology, animal science, etc., that certain trace elements are vitally important for plant and animal life cycles. Elements such as iron, copper, manganese, zinc, iodine, and cobalt have been shown to be nutritionally essential for the higher forms of animal life.[4] Similarly, iron, copper, manganese, zinc, boron, silicon, and molybdenum are regarded as essential elements for the life of higher plants. These elements act as catalysts in many biochemical reactions in plants and animals. A knowledge of the significance of trace elements in animal physiology has accumulated in the last 40 years. With the development of newer, more reliable and accurate methods for the determination of very low concentrations (in the range of parts per million to parts per billion) of these elements, their role in plant and animal life is better understood. A considerable amount of work is being done on the physiological effects of elements such as zinc, copper, iron, cobalt, nickel, molybdenum, manganese, selenium, etc.[4,5] It has been shown that both insufficient and excess amounts of these elements may be hazardous to a particular organism.[6] The functions of many other elements, such as bromine, rubidium, and cesium are unknown even though they are always present in the concentration range of 1–40 ppm in plant tissue. In addition to these elements, aluminum, arsenic, barium, strontium, etc., are often present in plant and animal tissue.

Some trace elements are important also from the point of view of their possible adverse effects on biological systems. Heavy metal poisoning from elements such as lead, cadmium, mercury and others is well known. Apart from mercury and lead other elements present in food products and the environment may be dangerous to human life. Because of the complex toxicology of trace elements and lack of knowledge of their role, the scientific data are scarce. The forms in which these elements are present are also important factors in their toxic and nutritional effects. It is also possible that some trace elements (e.g. Mn in tea) may have a role in flavor or taste.

Smith *et al.*[7] have determined the potassium concentration of tea by flame photometry. Jervis *et al.*[8] have determined the concentration of mercury in different foods including tea and coffee by neutron activation analysis. The presence of high concentrations of manganese in tea is well known. A lack of abundance data on many trace elements in tea and coffee, e.g. rubidium, chromium, etc., led to this preliminary two-phase study of the trace element chemistry of ground tea and coffee. One important aspect is to determine the amounts of trace elements contributed to human daily intake by coffee or tea. The first phase of this project dealt with the development of techniques for the determination of 15 trace elements. The second phase which is in progress at this time deals with the leaching of elements from ground coffee and tea after percolation. The usefulness of neutron activation analysis as an analytical tool is well known. Shah *et al.*[9] have discussed the advantages of instrumental multi-elemental neutron activation analysis over conventional chemical

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techniques such as emission spectroscopy, X-ray fluorescence, atomic absorption, etc. This multielemental technique is sensitive for many elements of interest. It does not require any pre- or postirradiation chemistry on samples, and hence avoids any chemical contamination. The technique is reliable and precise. Neutron activation analysis has been applied to many different kinds of matrices such as biological materials,[10] petroleum products,[9,11] and geochemical materials.[13] The prime object of this research is to explore the use of instrumental neutron activation analysis, high-resolution Ge(Li) spectrometry and IBM 360/67 computer data reduction for the determination of Na, K, Sc, Cr, Mn, Fe, Co, Cu, Zn, Se, Br, Rb, Sb, Cs, and Hg in tea and coffee.

APPARATUS

The Washington State University 1 MW TRIGA Mark III-fueled water moderated research reactor was used for all irradiations. A thermal neutron flux of 8×10^{12} neutrons/cm^{2}sec was used. The gamma-ray spectrometer system used consisted of an ORTEC true coaxial (Ge(Li) detector (active volume of 47.7 cm^3), ORTEC 118A preamplifier, Tennelec TC202 BLR amplifier, and a Nuclear Data Model 2200 multichannel analyzer coupled to a Kennedy 1400R magnetic tape 7-track unit. Systems specifications were 2.9 keV resolution (FWHM) measured at the ^{60}Co 1333 keV line, peak to Compton ratio of 19:1 at 1333 keV, and 8.9% relative efficiency compared to 3″ × 3″ NaI(Tl) at 1333 keV and 25 cm. An IBM 360/67 computer was used for data reduction.

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PROCEDURE

Tea and coffee samples (1–3 g) were weighed into polyethylene bags which were then heat-sealed. The samples were transferred to 2-dram snap-top polyethylene vials which had been soaked in double-distilled nitric acid for 24 hours followed by washing with double-distilled water and acetone. This procedure was necessary to remove any surface contamination from the vials. The preirradiation processing was performed in a clean-air hood (Agnew-Higgins Model 43) to minimize the contamination from airborne dust. The vials were heat-sealed. A standard Kale[14] was used as a standard for Na, K, Sc, Cr, Mn, Fe, Co, Zn, Br, Rb, Sb, and Cs. Three other standards containing known amounts of Se, Hg, and Cu (prepared from "Specpure" HgO, SeO_2, and CuO) were also used. The samples and standards were placed on a "rotator" assembly and irradiated to an integrated flux of 2.8×10^{17} neutrons/cm^2. The use of the rotator which rotated around its vertical axis during

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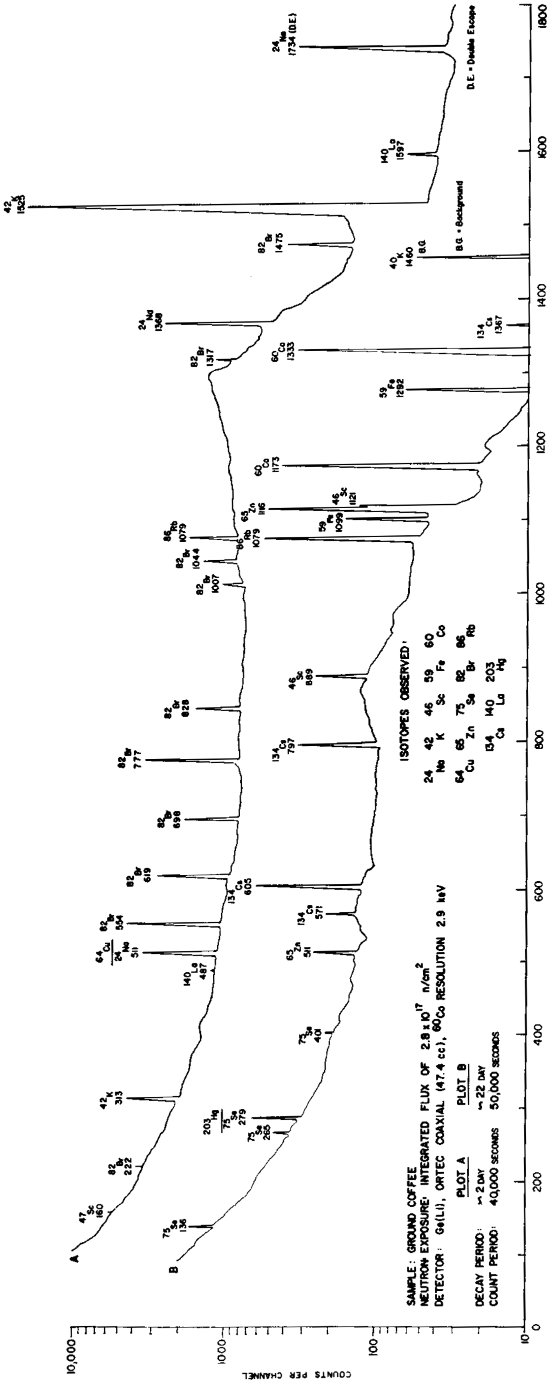

FIGURE 1 Gamma-ray spectra of a coffee sample.

irradiation provided uniform flux distribution across the irradiation position. After irradiation, samples from the polyethylene bags were transferred to 2-dram snap-top vials and unirradiated ground coffee was added to some of the vials to achieve a uniform counting volume. Six hours after irradiation, samples and standards were counted on the Ge(Li) detector under constant geometry conditions for about 4000 seconds for the determination of short-lived radionuclides such as ^{24}Na, ^{42}K, ^{56}Mn, ^{64}Cu and ^{82}Br. The samples were then allowed to decay for about three to four weeks to eliminate activities of ^{24}Na, ^{42}K and reduce bremsstrahlung from ^{32}P. Each sample and corresponding standards were then counted for 40,000 seconds. Figure 1 shows two gamma-ray spectra obtained from a ground coffee sample for two decay periods of two days and twenty-one days.

TABLE I

Nuclear reactions and Properties[15, 16]

Element	Reaction and product	$\sigma_{th} \times f^a$ barns	Half-life	Photon measured keV	Possible interference
Na	$^{23}\mathrm{Na}(n,\gamma)^{24}\mathrm{Na}$	0.53	15.0 h	1368	
K	$^{41}\mathrm{K}(n,\gamma)^{42}\mathrm{K}$	0.08	12.4 h	1525	
Mn	$^{55}\mathrm{Mn}(n,\gamma)^{56}\mathrm{Mn}$	13.30	2.56 h	847	$^{56}\mathrm{Fe}(n,p)$
Sc	$^{45}\mathrm{Sc}(n,\gamma)^{46}\mathrm{Sc}$	13.00	83.9 d	889	
Cr	$^{50}\mathrm{Cr}(n,\gamma)^{51}\mathrm{Cr}$	0.73	27.8 d	320	
Fe	$^{58}\mathrm{Fe}(n,\gamma)^{59}\mathrm{Fe}$	0.0034	45.6 d	1292	$^{62}\mathrm{Ni}(n,\alpha)$
Co	$^{59}\mathrm{Co}(n,\gamma)^{60}\mathrm{Co}$	37.00	5.26 y	1333	$^{60}\mathrm{Ni}(n,p)$
Cu	$^{63}\mathrm{Cu}(n,\gamma)^{64}\mathrm{Cu}$	3.10	12.8 h	511	$\beta+, \gamma > 1022$ keV
Zn	$^{64}\mathrm{Zn}(n,\gamma)^{65}\mathrm{Zn}$	0.23	243.0 d	1116	1120 ^{46}Sc
Se	$^{74}\mathrm{Se}(n,\gamma)^{75}\mathrm{Se}$	0.26	120.0 d	265	
Br	$^{81}\mathrm{Br}(n,\gamma)^{82}\mathrm{Br}$	1.58	35.3 h	777	
Rb	$^{85}\mathrm{Rb}(n,\gamma)^{86}\mathrm{Rb}$	0.72	18.7 d	1079	
Sb	$^{123}\mathrm{Sb}(n,\gamma)^{124}\mathrm{Sb}$	1.41	60.3 d	1691	
Cs	$^{133}\mathrm{Cs}(n,\gamma)^{134}\mathrm{Cs}$	28.00	2.05 y	797	
Hg	$^{202}\mathrm{Hg}(n,\gamma)^{203}\mathrm{Hg}$	1.19	46.9 d	279	280 ^{75}Se

[a] Product of the isotopic fraction f, and thermal neutron cross-section, σ (in barns).

Table I shows pertinent nuclear data of nuclear reactions used and nuclides measured in this study.[15,16] The gamma-ray full-energy peaks used for each nuclide and possible interferences from either other nuclear reactions or overlapping gamma rays are also tabulated. Figure 2 shows a gamma-ray spectrum obtained from a tea sample after a decay period of two days. Figure 3 shows the gamma-ray spectrum of the same tea sample after a decay period of 21 days. Gamma-ray spectra were recorded on magnetic tape for data processing. The computer program developed at Washington State

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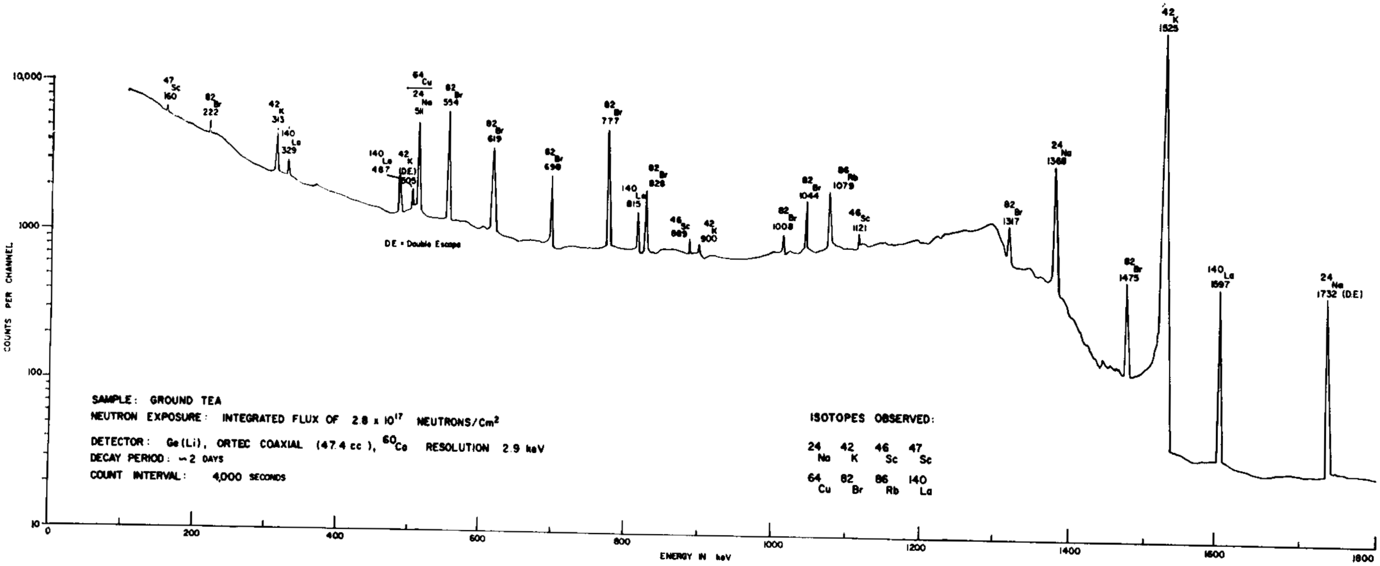

FIGURE 2 Gamma-ray spectra of a tea sample.

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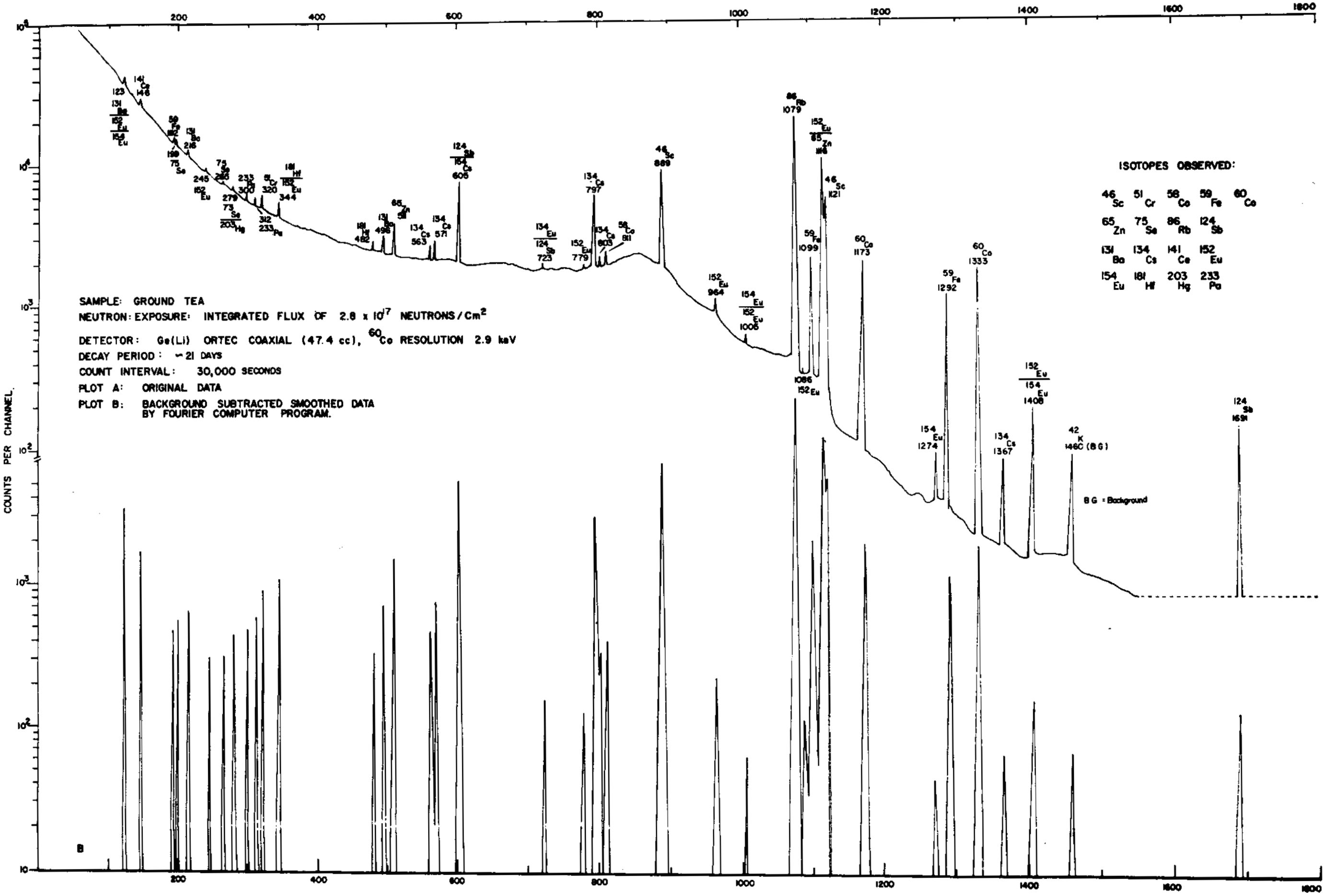

FIGURE 3 Gamma-ray spectra and smoothed background subtracted data for a coffee sample.

University for gamma-ray spectral analysis was based on a capture gamma-ray program.[17] In this computer program the spectral data were smoothed using Fourier transform method. A computed baseline was subtracted and peak areas were calculated by Gaussian fitting for each peak. Any peak yielding more than 25% counting statistics error was discarded. The decay constants for different radionuclides with their corresponding energies were stored in a computer library. After applying appropriate decay correction, activities of samples were compared to that of corresponding standards to calculate the concentration of each element.

The ^{64}Cu determination was made using the 511 keV positron annihilation peak. The ^{24}Na contribution was subtracted after multiplying the ^{24}Na 1369 keV peak area by a normalizing factor (511 keV peak area/1369 keV peak area). This factor was calculated from pure ^{24}Na spectrum using the same counting geometry. The 279 keV peak, used for Hg determination, is due to the presence of two gamma rays, 279.2 keV ^{203}Hg and 279.5 keV ^{75}Se. The concentration of ^{75}Se was determined using 265 keV ^{75}Se peak area. The 279 keV/265 keV peak area ratio (correction factor) was determined experimentally using a gamma-ray spectrum obtained from pure ^{75}Se under the counting geometry that was used for the samples. The ^{75}Se contribution was then subtracted from 279 keV total peak area for each sample. The ^{203}Hg concentration was determined using the corrected 279 keV peak area.

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RESULT AND DISCUSSION

Table II shows the concentration of Na, K, Mn, Br, Cu, Cs, Rb, Sc, Fe, Zn, Co, Hg, and Se in ground coffee (A, B, C, G, and I), instant coffee (D, E, F, and H), and a tea sample. For all samples the values reported are to three significant figures and are single determinations except for sample C. Relative standard deviations were calculated in the standard manner from counting statistics. The calculated relative standard deviation is less than 5% for Rb, Sc, Co, Fe, Zn, Br, Na, Mn, and K values and less than 10% for Cs and Cu. In the case of Cr and Sb, the lack of a sufficient number of counts from neutron-induced radionuclides of the respective elements was responsible for the relatively large standard deviation (less than 18%). In the case of Se and Hg, the high Compton background (due to ^{32}P) and low activities of ^{75}Se and ^{203}Hg are responsible for the relatively large variations (less than 30% for Se). The large uncertainty in the Hg concentration is also due to the 279.5 keV ^{75}Se peak subtraction. Table III shows elemental concentrations of five replicate analyses of a coffee sample (sample C). The relative standard deviations calculated from the replicate analyses are less than 10% for all elements except for sodium. This demonstrates that the method is precise

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TABLE II

Trace element concentration (ppm) in coffee and tea

Element	Coffee A	Coffee B	Coffee C	Coffee D	Coffee E	Coffee F	Coffee G	Coffee H	Coffee I	Tea
Sodium	7.51±0.40	21.00±0.79	11.36±1.86	55.61±0.82	115.20±2.86	204.60±4.94	4.72±0.35	22.31±0.82	14.17±0.66	19.42±0.96
Potassium[a]	1.73±0.03	1.70±0.03	2.13±0.05	4.04±0.07	3.78±0.07	4.53±0.08	1.63±0.03	2.32±0.05	1.71±0.03	1.68±0.03
Scandium[b]	2.57±0.10	1.21±0.06	0.75±0.06	1.12±0.09	<0.40	0.76±0.08	2.61±0.11	<0.50	1.67±0.07	1.32±0.42
Chromium[b]	<40.0	<40.0	<40.0	<40.0	<40.0	<40.0	<40.0	<40.0	<40.0	177.00±22.5
Manganese	29.58±0.77	30.73±0.83	26.52±0.68	21.77±0.53	27.44±0.69	37.43±0.90	33.74±0.72	15.43±0.67	19.42±0.72	259.30±4.20
Iron	36.70±1.73	32.70±1.50	33.31±10.8	58.50±2.83	50.43±3.20	66.70±3.04	36.34±1.87	55.36±2.45	31.17±1.41	80.20±3.60
Cobalt[b]	46.22±2.29	38.23±1.90	100.50±7.80	130.20±6.23	17.17±8.55	58.96±2.96	39.74±2.08	84.72±4.04	48.75±2.33	78.10±3.85
Copper	18.00±0.84	16.80±0.66	15.52±0.41	6.08±0.42	6.08±0.44	6.42±0.52	17.70±0.81	10.30±0.70	17.60±1.11	27.70±1.42
Zinc	4.81±0.09	5.13±0.09	6.79±0.33	4.06±0.10	3.30±0.13	5.61±0.02	4.00±0.09	3.68±0.07	3.36±0.07	19.80±0.28
Selenium[b]	167.00±35.60	91.20±20.5	203.70±22.5	70.30±17.21	170.10±38.0	31.32±8.67	28.00±6.90	4.00±1.23	130.80±28.1	115.90±27.4
Bromine	4.50±0.11	1.25±0.05	1.40±0.07	3.38±0.14	7.89±0.21	8.20±0.21	3.38±0.08	3.74±0.08	8.10±0.18	3.86±0.10
Rubidium	30.75±0.39	24.40±0.32	43.62±1.97	69.76±0.88	66.62±0.97	86.25±1.06	31.90±0.04	81.14±0.97	30.13±0.38	67.80±0.86
Antimony[b]	<6.00	<7.00	5.54±1.00	<6.00	<6.00	15.80±2.60	<7.00	<10.00	7.28±1.24	46.51±6.25
Cesium[b]	84.45±5.60	24.03±1.79	47.88±3.30	88.75±6.10	143.90±10.0	149.70±9.91	126.10±8.33	239.00±15.50	57.16±3.80	116.50±7.85
Mercury[b]	26.42±5.51	19.75±4.77	32.00±6.30	<12.00	15.79±9.90	14.51±8.74	22.60±6.07	<7.00	31.13±5.64	19.68±6.90

[a] Potassium values are in percent.

[b] These values are in ppb.

TABLE III

Replicate determination of elements in coffee (ppm)

	Cesium[a]	Bromine	Sodium	Potassium[b]	Copper	Iron	Rubidium	Scandium[a]	Cobalt[a]	Zinc	Selenium[a]	Mercury[a]
1	47.000	1.482	9.497	2.202	15.484	33.600	43.61	0.702	106.70	7.009	182.1	33.7
2	51.170	1.380	14.320	2.101	15.479	28.110	42.69	0.771	90.99	6.529	202.3	39.4
3	43.660	1.450	10.940	2.085	15.232	35.670	41.82	0.695	97.23	6.482	235.0	24.3
4	49.670	1.324	11.810	2.099	15.176	35.840	46.37	0.819	107.20	7.124	195.0	30.5
5	42.110	1.335	10.220	2.156	16.207	33.880	—	—	—	—	—	—
Mean	47.875	1.394	11.357	2.129	15.516	33.305	43.62	0.747	100.50	6.786	203.7	32.0
Standard deviation	3.290	0.070	1.860	0.049	0.411	3.610	1.97	0.059	7.80	0.327	22.5	6.3
Relative standard deviation (%)	6.800	5.000	16.400	2.300	2.600	10.800	4.50	7.920	7.80	4.800	11.0	19.7

[a] These values are in ppb.

[b] Potassium values are in percent.

and reliable. The larger variation in Na values is due principally to sample No. 2. This wide variation could be due to inhomogeneity of the sample with respect to Na.

A possible source of error in the results is reactions initiated by fast neutrons which are present in the neutron flux in the nuclear reactor. The fast reactions such as (n,p) or (n,α) that produce ^{24}Na, ^{42}K, ^{82}Br, ^{46}Sc, ^{65}Zn, ^{75}Se, ^{203}Hg, ^{126}Sb, and ^{51}Cr are unimportant due to the low effective fission spectrum cross-sections for these reactions, and very low concentrations of the interfering elements. The contribution of ^{64}Zn(n,p)^{64}Cu reaction to the copper content has been calculated using the fission-neutron cross-section data of Rochlin.[18] This interference was found to be less than 0.5%. Hence, the copper concentrations are not corrected for this interference. The fast neutron reactions ^{60}Ni(n,p)^{60}Co and ^{62}Ni(n,α)^{59}Fe may interfere with the cobalt and iron determination for tea. Since the ratio of Ni/Fe in tea is low (approx. 0.01), the interference was determined experimentally to be less than 0.3%.

The sensitivity of this instrumental technique varies for each element, and depends upon sample composition. A second part to this paper will examine this possibility in greater detail.

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CONCLUSION

Nondestructive neutron activation analysis allows the simultaneous determination of 15 trace elements in tea and coffee. The method is precise, sensitive and simple. Absence of any chemistry on samples reduces contamination. The fast neutron reactions interferences are found to be very small and can be neglected. A computer program developed for gamma-ray spectrum analysis increases the speed and accuracy of the method. This technique can easily be applied to percolated tea and coffee.

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