Food Chemistry 116 (2009) 555–560

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Absolute determination of soluble potassium in tea infusion by gamma-ray spectroscopy

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ARTICLE INFO

Article history:
Received 19 June 2008
Received in revised form 2 January 2009
Accepted 1 March 2009

PACS:
82.80.Ej
83.80.Ya

Keywords:
Potassium-40
Gamma-ray spectroscopy
Black tea
K content

ABSTRACT

Potassium content in tea brew was determined by gamma-ray spectroscopy, using the 1461 keV gamma-ray from ^{40}K, the naturally occurring radioactive isotope of potassium. We measured radiation with a shielded HPGe detector from individual test samples of tea leaves, before and after infusion preparation, and from commercial instant tea powder. The correction factor for the gamma-ray self-absorption in the extended source was determined with the help of Monte-Carlo simulations. This gamma-ray spectroscopy technique enabled the absolute determination of potassium content with a relative uncertainty smaller than 4%, at the one standard deviation confidence level, showing the feasibility of this method. An experiment to evaluate a possible systematic uncertainty due to K distribution heterogeneity in the sample was performed, with the result that the corresponding relative standard deviation is smaller than 2% at 95% confidence level.

1. Introduction

Potassium is present in a wide variety of foods and is an essential natural element of our diet. Potassium concentration is determined by several methodologies: precipitation reactions; flame atomic absorption spectroscopy (Philiber & Darracq, 1971) ICP-AES (inductively coupled plasma-atomic emission spectroscopy) (Li, Yu, Li, & Li, 2006); ion-selective electrode (Fritz & Schenk, 1987; Mendham, Denney, Barnes, & Thomas, 2002), and neutron activation analysis (TRS-273, Yamashita, Saiki, Vasconcellos, & Sertie, 1987; Yamashita et al., 2005). However, some of these methods depend on hypotheses about the chemical composition of the samples, which can lead to inaccurate results.

The radioactive decay of ^{40}K, a naturally occurring isotope of K with 0.0117% abundance (Böhlke et al., 2005), can be used to determine the potassium content in tea brew samples by gamma-ray spectroscopy, in a procedure similar to that applied to tea leaves by Harb (2007). However, we did not find in the available literature any report on this particular application of ^{40}K natural radioactivity measurement, and searched for experimental conditions appropriate for reliable results.

The measurements of the ^{40}K radiation were carried out with a high purity germanium (HPGe) photon detector. Since the gamma-rays from ^{40}K occurs also in the background spectrum (Ejnisman & Pascholati, 1994), special care was taken to account for it. The small gamma-ray specific activity of natural potassium required that relatively large amounts of material had to be measured near the detector. The efficiency calibration was obtained from the measurement of a reference material (KCl), and the consequent gamma-ray self-absorption determined from Monte-Carlo simulation, which was validated by special measurements, in a procedure that can be applied to any extended source.

The method allowed the determination of the water-soluble potassium content in black tea leaves and also in tea drink from instant tea powder. The amount of potassium in tea brew was measured with a relative uncertainty smaller than 4%, at the one standard deviation confidence level. A simple experiment was performed to test the hypothesis of homogeneous distribution of potassium in the sample. The methodology described here is independent of hypotheses on the samples' chemical composition and can be used with other infusions.

2. Experimental method

The experiment consisted in the observation of the 1461 keV gamma-rays from the radioactive decay of ^{40}K with a shielded

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doi:10.1016/j.foodchem.2009.03.005

photon detector. In the case of herbal tea samples, the amount of K in tea drink was deduced from radiation measurements of tea leaves before and after infusion, while in the case of instant tea powder, a single measurement of the sample was sufficient. The gamma-ray yield per unit mass from natural ^{40}K isotope was obtained from pure KCl placed in a box similar to those used for the tea samples, taking into account the gamma-ray self-absorption.

2.1. Decay schemes, observed radiations and atomic data

The natural isotopes of potassium are ^{39}K, ^{40}K and ^{41}K, with abundances of 93.2581(44)%, 0.0117(1)%, and 6.7302(44)%, respectively (Böhlke et al., 2005). ^{40}K decays to ^{40}Ar by electron capture (EC) and to ^{40}Ca by beta decay (β^-) with probabilities of 10.72% and 89.28%, respectively; the emission probability of the 1460.830 keV gamma ray is 10.67(13)% and the half-life of ^{40}K is $1.277(8) \times 10^9$ y (Cameron & Singh, 2004). The amount of K in KCl samples was determined by stoichiometry, using A_{K} = 39.0983(1) g and A_{KCl} = 74.551(2) g for K atomic and KCl compound molar masses, respectively (Wieser, 2006).

The analysis of the measurements performed to validate the gamma-ray sample self-absorption needed both the number of 1461 keV emitted photons from the KCl reference sample, determined from the data given above, and the number of 1408 keV gamma-rays from an activity-calibrated ^{152}Eu standard source, determined from decay data (Castro et al., 2004).

2.2. Sample preparation

We investigated test samples of black tea leaves from two different brands, named L and A, bought in the market and used without additional treatment, as well as a sample of commercial instant flavored unsweetened tea powder, and used a sample of KCl (>99% pure, ACS reagent grade) for calibration purposes. A single sample of each material was investigated; no replicates were made, since the aim of this work was to find an adequate procedure for the measurement of K in tea infusion by its natural radioactivity. All samples were placed in cylindrical polyethylene boxes with 28.3 mm height, 70.3 mm in diameter, 1.8 mm wall thickness, and 20.40(2) g mass. The samples filled the boxes avoiding any gap between the upper surface of the sample and the box lid, since a gap of 1 mm may affect the detection efficiency up to 3%; hence, the box was filled with the leaves, tapped repeatedly against a hard surface to compact the material, refilled, and the procedure repeated until the box was completely full. The practical procedure to check that the void internal space was acceptable was to turn the box, placing its cylindrical axis in a horizontal direction, and making certain that the void region between the chord and the circumference had a height, measured as the maximum distance in the radial direction, smaller than 2 mm.

Once the ^{40}K activity in a black tea leaves sample was measured by gamma-ray spectroscopy, we prepared the tea infusion as directed on the packet, i.e. 200 mL of boiling water for each 2 g of black tea. After a waiting time of 5 min, the tea leaves were recovered through filtration to be desiccated and the tea infusion was discarded.

Sample L used leaves were scattered over Al foil in a petri dish in a relative humidity controlled room (50% relative humidity at 22 °C) for two days to become dry. Sample A was dried over Al foil in a petri dish placed in an oven at $\sim$60 °C during four hours. Once dried, the used leaves were weighed, packaged and the remaining ^{40}K activity in each sample was measured. To complete the K mass balance along the process, the filter used for sample A was dried following a procedure similar to that used for sample L, weighed, folded, placed in a polyethylene box with the dimensions given above, and its gamma-ray activity was measured. Net sample masses are shown in Table 1, where the uncertainties correspond to one standard deviation and are given between parentheses in units of the least significant digit of the value, as will be used throughout this paper.

Table 1
Column 1 identify the samples, with their masses and 1461 keV gamma-ray peak areas in columns 2 and 3, respectively, and measurement times in the last column; numbers between parentheses are the standard deviations, due only to counting statistics, in units of the values' least significant digit. The sample labeled "empty box" correspond to an empty polyethylene box measurement for background determination. All values come from single measurements, but for the check sample, counted 9 times for the reproducibility test, where the ranges of masses and peak areas are displayed.

Sample	Mass (g)	Peak area	Time (h)
KCl	97.0(1)	146929(386)	20
Tea before (L)	37.5(1)	2287(51)	20
Tea before (A)	40.6(1)	3166(59)	20
Tea after (L)	23.4(1)	497(27)	20
Tea after (A)	24.2(1)	569(29)	20
Instant tea powder	58.6(1)	4142(67)	20
Check sample	31.9–33.6	2056–2204	20
Empty box (bg)	20.40(2)	1255(48)	80
Filter before (A)	4.57(1)	1486(50)	80
Filter after (A)	4.99(1)	1766(53)	80

The procedure applied for the commercial instant tea powder was much simpler, since all its content is drunk by the consumer. Therefore, the sample consisted in a box completely full of the dry powder, and a single radiation measurement was sufficient for determining the K content.

2.3. Gamma-ray spectroscopy – radioactive counting

The gamma-ray measurements were performed with a HPGe type P detector, ORTEC, 35% relative efficiency, 2.2 keV nominal resolution at 1332 keV, shielded by a 10 cm thick lead wall, using live time counting methodology and pulse pile-up rejection. The polyethylene boxes were placed directly on the top of the detector capsule end cap, with box and detector cylindrical symmetry axis in the vertical direction; hence, the sample weight assures the exact vertical position. To warrant horizontal position reproducibility, the polyethylene boxes were fixed by a 2-mm thick PVC tube, with an internal diameter equal to the box and the detector capsule external diameters. The detection system energy calibration was carried out with a ^{152}Eu calibration source.

Table 1 shows the 1461 keV gamma-ray peak areas along with the counting times of the measured gamma-ray spectra of the above mentioned samples. The 80 h long time measurements of filter paper and empty polyethylene box were not required by the method, and were used only to quantify precisely the small amounts of K in filter and tea leaves after infusion. Fig. 1 compares samples spectra in the 1461 keV energy region.

In the spectra of Fig. 1, it can be seen that the peak in the spectrum taken from the tea leaves sample after infusion is smaller than the peak in the spectrum taken before infusion. Also, the peak areas in the spectra from both the tea leaves after infusion and the filter paper are somewhat greater than the peak area in the background radiation spectrum.

Due to the relatively large amount of material in the samples, gamma-ray self-absorption must be taken into account. This effect was evaluated by simulation, and it was validated with the help of some special measurements. An Amersham activity-calibrated ^{152}Eu standard point source was measured over the polyethylene box either empty or filled with KCl compound or tea leaves, in order to provide experimental tests for the simulation program. Only the experimental efficiencies for 1408 keV gamma-rays from ^{152}Eu were considered, and their values must be deduced from the peak areas taking into account the important sum losses at the small

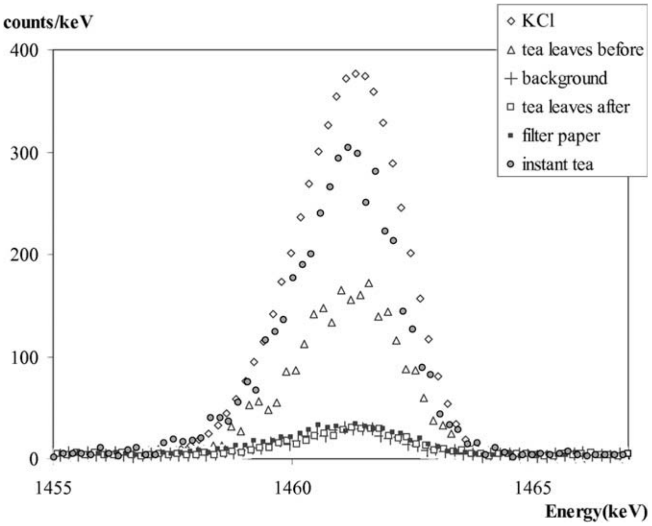

Fig. 1. Gamma-ray spectrum in the 1461 keV energy region from samples of: KCl, open diamonds; tea leaves before and after the tea infusion preparation, open triangle and squares, respectively; instant tea, filled circles; filter paper, black squares, and background (empty box), crosses. All measurements lasted 20 h, with the exception of the KCl sample, 1 h.

source-to-detector distance in this experimental arrangement (Debertin & Helmer, 1988). Both the simulation and its test are discussed in detail in Section 2.5.

2.4. Reproducibility test

A test sample of tea leaves, which we will call *check sample*, was prepared and the measurement of its radioactivity was repeated nine times, aiming for the observation of a possible difference between the peak area variance deduced from the repetitions and the variance calculated from the Poisson statistics characteristic of radioactivity counting experiments (Jenkins, Gould, & Gedcke, 1995).

Check sample preparation was repeated between two consecutive radioactivity measurements, that is, before each measurement run the box was emptied, refilled with the same sample of tea leaves and completed with additional tea leaves when needed, to fill completely the box as explained in Section 2.2; the sample mass varied up to 5% during the full cycle. The check sample mass was measured before and after each run, and the observed mass changes during each measurement run were always smaller than 10 mg. Table 1 shows the minimum and maximum sample mass and number of detected photons.

The number of 1461 keV gamma-ray counts observed in each run was normalised to account for variation in sample mass. The observed peak areas and standard deviations (solely from counting statistics), respectively $C_i(\hat{\sigma}_i)$, for each measurement i in the $N = 9$ check sample counting runs, after normalization, are

$$\{2143(52); 2155(52); 2262(53); 2216(52); 2179(53); 2204(51); 2151(51); 2196(50); 2204(51)\}$$

The statistical analysis of this data is shown in Section 4.2.

2.5. Detection efficiency and gamma-ray self-absorption correction

The relationship between the K content in tea samples and in the reference KCl sample depends on the gamma-ray detection efficiency through the ratio

$$s_{\text{tea}} = \frac{\epsilon_{\text{K(KCl)}}}{\epsilon_{\text{K(tea)}}} \tag{1}$$

where $\epsilon_{\text{K(KCl)}}$ and $\epsilon_{\text{K(tea)}}$ are the efficiencies for the 1461 keV gamma-ray from ^{40}K decay in KCl and tea samples, respectively. Note that s_{tea} would be one if it were not for the difference in photon absorption.

The simulated photon energy deposition from an extended source with the internal dimensions of the boxes used in the radioactive counting by the HPGe detector was obtained with MCNPX code using Tally F:8 (pulse height tally), setting the default electron and detailed photon physics parameters, and using the internal photo-atomic data libraries (MCNPX, 2005). The detector geometry specification included, besides the detector crystal active volume, an empty internal region and dead layers at the crystal surface and contact regions. The dimensions of these regions and crystal length and radius were adjusted in order to fit the experimental efficiencies for the gamma-rays from a calibrated point source (Venturini, Maidana, & Vanin, 2007). Fig. 2 is an illustration of the simulated arrangement.

The radiation absorbing media were defined using the experimental density of each sample and their chemical composition, assuming pure KCl or an average composition for tea: 22% C; 57% H; 19% O, the other 3% consisting mainly of N and K. However, after the simulation, we found that the detailed chemical composition do not affect significantly the absorption of 1461 keV photons, as will be explained in Section 4.1. The efficiency was calculated as the net peak area in the simulated spectrum, since the used pulse height tally already normalises the spectrum to the total number of primary photons followed in the simulation run. Therefore, the efficiency ratio factor of Eq. (1) was given by

$$S_{\text{tea}} = \frac{\epsilon'_{\text{K(KCl)}}}{\epsilon'_{\text{K(tea)}}} \tag{2}$$

where $\epsilon'_{\text{K(KCl)}}$ and $\epsilon'_{\text{K(tea)}}$ are the simulated efficiency values for the 1461 keV gamma-ray from ^{40}K decay in KCl and tea samples, respectively.

The simulations were validated by checking the capability to account for the attenuation of gamma rays by the absorbing materials between the radioactive atoms and the detector, comparing the simulated efficiencies with the experimental results of special measurements using the ^{152}Eu point source as described in the previous section. The simulations used sample sizes, locations, densities, and chemical composition identical to those used in the determination of the self-absorption correction, with the addition of the point radioactive source encapsulated in a plastic slab.

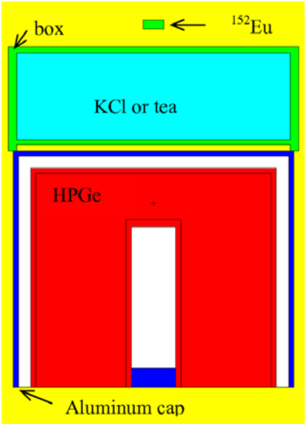

Fig. 2. Cross-section view of the detector and sample, along their symmetry axis, in the simulated arrangement; draw from MCNPX editor.

3. Relationship between peak area and K content

The deduction of the K content in herbal tea drink from the 1461 keV gamma-ray peak areas in the obtained spectra can be done in a few steps. Since the emitted radiation is proportional to the quantity of potassium in each sample, we deduce from mass balance that the net activity from K in tea drink is related to the quantity

$$\Delta C_{\mathrm{tea}} = C_{\mathrm{before}} - C_{\mathrm{after}} - \Delta C_{\mathrm{filter}} \tag{3}$$

where C_{before} and C_{after} are the peak counting rates in tea leaves before and after infusion, and $\Delta C_{\mathrm{filter}}$ is the difference between the peak counting rates in the filter spectra after and before infusion. This expression assumes that the gamma-ray detection efficiency is the same for tea leaves samples before and after infusion; however, the K content in tea leaves after infusion is not important and the efficiency variation, due to gamma-ray self-absorption increase with sample density, is not sufficiently significant to produce an error of the order of the uncertainty in the final result. The quantitative determination of K in tea brew, $M_{\mathrm{K(tea)}}$, can be obtained by:

$$M_{\mathrm{K(tea)}} = \frac{\Delta C_{\mathrm{tea}}}{C'_{\mathrm{KCl}}} \cdot S_{\mathrm{tea}} \cdot M_{\mathrm{K(KCl)}} \tag{4}$$

where ΔC_{tea} is given by formula (3), S_{tea} is the self-absorption efficiency correction factor given by formula (2) for tea leaves, C'_{KCl} is the 1461 keV peak counting rate in KCl spectra after background subtraction, and $M_{\mathrm{K(KCl)}}$ represents the mass of potassium in KCl compound reference material, deduced from the KCl mass in the reference sample, M_{KCl}, and the atomic masses from Section 2.1, by

$$M_{\mathrm{K(KCl)}} = \frac{A_{\mathrm{K}}}{A_{\mathrm{KCl}}} M_{\mathrm{KCl}} \tag{5}$$

In the case of instant tea, the amount of K, $M_{\mathrm{K(inst)}}$, can be obtained by:

$$M_{\mathrm{K(inst)}} = \frac{C_{\mathrm{inst}} - C_{\mathrm{bg}}}{C'_{\mathrm{KCl}}} \cdot S_{\mathrm{inst}} \cdot M_{\mathrm{K(KCl)}} \tag{6}$$

where C_{inst} and C_{bg} are the 1461 keV gamma-ray counting rates in the instant tea and background spectra, respectively, and S_{inst} is the self-absorption correction factor given by formula (2) substituting instant tea for tea. A similar formula with C_{inst} replaced by C_{before} gives the amount of K in tea leaves (the raw material), and were used to determine the ^{40}K activity, as will be discussed in Section 4.3.

4. Results and discussion

4.1. Efficiency validation

Table 2 shows simulated efficiencies for 1461 and 1408 keV gamma rays, as well as experimental efficiencies whenever available. The efficiency for the 1461 keV gamma ray in an extended source with density equal to air cannot be experimentally measured, but it was simulated to show the importance of self-absorption effects in the samples, which can reach 8% for the denser sample, KCl. The difference in the 1461 keV gamma-ray detection efficiency in tea and KCl sources is mainly due to the different sample densities; the chemical composition almost does not affect the absorption of photons of about 1 MeV, contrary to what happens for photons of lower and greater energies, because the gamma-ray absorption coefficient is almost independent of atomic number in this energy region.

Table 2
Simulated and experimental detection efficiencies for 1461 keV (^{40}K) and 1408 keV (^{152}Eu) gamma rays. All K sources are extended, filling the entire box, while the ^{152}Eu is always the same point source, in a thin plastic slab placed over the box. Numbers between parentheses are the standard deviations in units of the values' least significant digit.

Sample	Efficiency	
	Simulated	Experimental
K in air	0.01298(2)	
K in KCl	0.01205(2)	0.01218(22)
K in tea leaves	0.01257(2)	
K in instant tea powder	0.01254(2)	
Eu on empty box	0.00759(10)	0.0076(7)
Eu on tea sample	0.00709(9)	0.0068(6)
Eu on KCl sample	0.00647(9)	0.0061(6)

Table 3
Ratios of the efficiency values appearing in the Table 2. The uncertainties in ratios of efficiencies for 1408 keV gamma-rays, given in parentheses, were recalculated to exclude common uncertainties from ^{152}Eu source activity and gamma-ray emission probability, and correspond to one standard deviation.

Samples	Efficiency ratio	
	Simulated, *S*	Experimental, *s*
Eu on tea/Eu	0.934(17)	0.900(20)
Eu on KCl/Eu	0.852(16)	0.820(23)
K in KCl/Eu	1.59(2)	1.60(9)
K in KCl/K in tea	0.959(2)	
K in KCl/K in instant tea	0.961(2)	

The uncertainties in the experimental efficiencies at 1408 keV are, for the most part, due to the uncertainty in the activity of the ^{152}Eu standard source; therefore, ratios of efficiencies determined with the same source are more precise, as can be seen in Table 3, and are mainly due to the uncertainty in point source positioning (~0.5 mm) close to the detector. The good agreement between experimental and simulated efficiency ratios for the 1408 keV gamma rays using either tea or KCl as absorber shows that the gamma-ray intensity attenuation in these samples was correctly evaluated by the simulation program. Moreover, the good agreement between experimental and simulated efficiency ratio for 1461 keV gamma rays from the extended K source and 1408 keV gamma rays from the ^{152}Eu point source shows that the source extension is being correctly accounted by the simulation.

It is worth to note that the concentration, given by Eq. (4), depends only on efficiency ratios defined in Eq. (1), because the K content in tea was related to the amount of K in KCl reference sample measured in the same geometry. Therefore, we did not adjust the detector parameters to match exactly the experimental efficiency curve, which takes a lot of work not needed by the method, but choose detector parameters that gave absolute efficiencies reasonably close to the experimental values to assure that the simulation was realistic. The efficiency ratio (formulas (1), (2)) affects the result by about 4% (see formula (4) and (3)), which is of the same order of magnitude of the standard deviation of the result; hence, the relative statistical uncertainty in the simulated efficiency ratio would impact the result uncertainty only if it was much bigger than estimated.

The possibility of measuring the aqueous filtered solution of tea brew was considered. The sample volume corresponding to the tea leaves mass used in this work amounts to about 4 L, which requires a Marinelli beaker (Hill, Hine, & Marinelli, 1950; Park & Jeon, 1995) 21 cm in diameter and 13 cm in height with a central hole of 8 cm in diameter and 7 cm in height, approximately, destined to embrace the HPGe detector capsule. In this experimental arrangement, the 1461 keV gamma-ray detection efficiency decreases with respect to the box-over-capsule geometry employed, due to the increase both in detector-source distance and self-absorption, reducing the efficiency by a factor of about 1/3. Since the relative precision in source activity depends basically on the inverse of the square root of the number of detected photons from the sample rich in K, as will be seen in Section 4.3, a measurement of precision equivalent to that obtained with the tea leaves source would take about one week. This long counting time would also require some sample shaking mechanism to warrant solution homogeneity.

4.2. Systematic uncertainties

In radioactivity counting experiments, the number of counts in each channel follows a Poisson probability function, then the sum of counts in many channels also follows Poisson statistics; since the average number of counts is large, a normal probability function with variance equal to the mean value is a very good approximation for the number of counts probability function (Jenkins et al., 1995). These characteristics resulted in the very similar peak-area standard deviation estimates in the different measurement runs reported in Section 2.4, and we can adopt $\hat{\sigma} = 52$ as a very good approximation of the (true) peak-area standard deviation due to counting statistics in the reproducibility test, $\hat{\sigma}_0$. This value must be compared to the external standard deviation, defined as

$$\sigma = \frac{1}{N-1}\sqrt{\sum(C_i - \overline{C})^2} = 38 \tag{7}$$

where $\overline{C} = 2190$ is the unweighted mean. Since $\hat{\sigma}_0$ is a lower bound on the standard deviation because the counting random fluctuation is unavoidable and $\sigma < \hat{\sigma}$, we do not need to perform a formal Fisher F-test to state that there is no reason to believe that the observed standard deviation is different from that due solely to Poisson counting statistics.

We can proceed now to determine an upper limit for the possible additional uncertainty. First, assuming independence between counting statistical fluctuations and efficiency changes from potassium distribution heterogeneity, we define the peak-area variance as

$$\sigma_0 = \sqrt{\hat{\sigma}_0^2 + \epsilon_0^2} \tag{8}$$

where ϵ_0^2 is the variance of all errors that affect the peak area with the exception of counting statistical distribution; hence, ϵ_0 measures the systematic uncertainty that is associated with a single radioactivity counting measurement of a sample. The appropriate statistics to build the confidence interval is not the standard deviation given in Eq. (7), but

$$(N-1)\frac{\sigma^2}{\sigma_0^2} = \sum\frac{(C_i - \overline{C})^2}{\sigma_0^2} \tag{9}$$

which is distributed like χ^2 with $N-1$ degrees of freedom (Kendall & Stuart, 1961). The usual procedure for two-sided variance confidence interval determination (Jenkins et al., 1995) cannot be applied here, since the variance lower limit is already known from first principles (the Poisson statistics in radioactivity counting); hence, we follow the general procedure to build confidence intervals (Kendall & Stuart, 1961) to find an upper limit for ϵ_0. The confidence level α for the sought one-sided interval is the integral P of the χ^2 probability function for $N-1$ degrees of freedom for values *greater* than the critical value χ^2_α, or, using Eq. (9) for the appropriate argument,

$$P\left(\chi^2_\alpha \leqslant \frac{(N-1)\sigma^2}{\sigma_0^2}\right) = \alpha \tag{10}$$

After finding $\chi^2_\alpha, \sigma_\alpha$ can be determined as the extreme value for σ_0, giving

$$\sigma_\alpha = \sqrt{\frac{(N-1)\sigma^2}{\chi^2_\alpha}} \tag{11}$$

Now, using Eq. (8) and approximating $\hat{\sigma}_0$ by $\hat{\sigma}$, a very good approximation as already discussed, we arrive at

$$\epsilon_\alpha = \sqrt{\frac{(N-1)\sigma^2}{\chi^2_\alpha} - \hat{\sigma}^2} \tag{12}$$

which allows the determination of the systematic standard deviation with any confidence level.

The values obtained for σ and $\hat{\sigma}$ in this experiment imply that ϵ_α is null at the 83% confidence level and, at 95% confidence level, is $\epsilon_{95} = 39$, which, when compared to the average peak area, $\overline{C} = 2190$, represents a 2% relative systematic standard deviation, which is smaller than the variance in the final result, as will be seen in the next section. Therefore, the systematic errors are likely negligible and, since the guide to the expression of uncertainty in measurement (GUM, 1995) in section E.1 recommends avoiding conservativeness in expressing uncertainties, we will assume that there is no contribution from systematic errors to the estimated variance.

4.3. Potassium concentration in the samples

The experimental values of K content in tea brew and their uncertainties, according Eqs. (3) and (4), depend on the quantities:

(1) 1461 keV peak areas obtained when measuring the radiation from:
  (a) tea leaves before infusion;
  (b) tea leaves after infusion;
  (c) filter before use;
  (d) filter after use;
  (e) KCl reference sample.
(2) Efficiency self-absorption correction.
(3) Potassium mass in the reference sample.

The results shown in Table 4 were obtained using the peak areas and masses of Table 1, and the ratios of efficiency values from Table 3. The small difference in peak areas between filter paper after and before infusion preparation, $\Delta C_{\text{filter}} = 70(18)$ per 20 h counting, corresponds to less than 3% of the amount of K in sample A, comparable to the relative uncertainty in the final result, also 3%. Therefore, in the case of sample L, we used this value multiplied by 3/4, the ratio of K content in sample L to A: $\Delta C_{\text{filter,L}} = 52(18)$, without reducing the estimated standard deviation to allow for the uncertainties arising from the simplifying hypothesis used.

The variances were calculated with the usual propagation formula (GUM, 1995). The main component of the variance comes from item (1a), amounting to 70% and 74% of the total variance for samples L and A, respectively; hence, the possibility of systematic error in this quantity was investigated, as discussed in Sections

Table 4
Experimental total amount of K in the samples per unity sample mass (column 2), water-soluble K in the infusion per unity sample mass (column 3), mass of K in 200 mL of drink (column 4), and ^{40}K activity per sample mass (last column). Numbers between parentheses are the standard deviations, in units of the values' least significant digit, under the hypotheses shown and discussed in Sections 4.2 and 4.3.

Sample	Total K mg/g	Soluble K mg/g	K per cup mg/200 mL	^{40}K activity Bq/kg
Tea (L)	17.5(5)	15.4(5)	30.5(11)	556(15)
Tea (A)	23.4(5)	20.7(6)	41.3(11)	742(16)
Instant tea	21.8(4)	21.8(4)	30.5(6)	691(13)

2.4 and 4.2, and an upper limit for the associated variance was found. Next in importance comes item (1b), which gives rise to about 20% of the total variance, but, as can be calculated from Table 1, more than half of the observed peak area comes from background radiation, which cannot give rise to systematic errors. Moreover, considering that the amount of K inside the tea leaves sample after infusion is small and its distribution should not be much more heterogeneous than in the sample before infusion because the sample filled completely the box, we do not expect important systematic errors from item (1b). In case of items (1c) and (1d), it must be noted that the number of counts from filter paper increased by only 20% after use; therefore, the predominant factor in the variance of ΔC_{filter} are background counts, which cannot be affected by systematic errors. Certainly, there is a systematic error from the irregular mass distribution due to the simple preparation used for counting the radioactivity from the filter paper, which was folded and placed inside a box similar to those used for tea leaves, filling it reasonably well; this systematic error was neglected because the amount of potassium retained in the filter represents less than 3% of the final result. Item (2) contributes to less than 2% of the total variance because the experimental result depends on a efficiency ratio, as explained in (Section 4.1). Finally, the contribution of the uncertainty in item (3) is completely negligible. Therefore, we will adopt the upper limit of the variance of all possible systematic errors relative to the final result as 2% at 95% confidence level.

The amount of K in instant tea was calculated using Eq. (6). In this case, the peak areas in the radiation measurements of tea powder and background contribute to 94% and 3% of the final variance, respectively, and systematic uncertainties are not expected, because the industrial production process results in a quite homogeneous material.

The amount of K given in the Library of United States Department of Agriculture (USDA) for tea drink prepared from tea leaves with distilled water is 42 mg in 200 g of drink (USDA[1], 2008), and in unsweetened instant tea 28 mg in 200 g of drink (USDA[2], 2008) which are in the same range of the values obtained in this work. We can also compare the ^{40}K activity in the leaves calculated from the measured amount of K in our samples with the values in the literature for black tea, 461 Bq/kg (Isasa & Marquina, 1980) and for other kinds of tea leaves (Scheibel & Appoloni, 2007), which are in the range 350–1200 Bq/kg. The application of other analytical techniques to the same tea samples used here would give a very interesting cross-check of the methodologies.

5. Conclusions

The amount of potassium in tea drink from soluble K in tea leaves or instant tea powder was determined by gamma-ray spectroscopy using the radioactivity of ^{40}K, a natural isotope of potassium. In the analysed individual test samples of two brands of tea leaves and one brand of instant tea, we found quantities of potassium similar to reference values and those obtained in other works. Some of the measurements and calculations were required to develop the method and do not need to be repeated for every sample. The amount of soluble K can be determined with a relative accuracy of about 4% at one standard deviation level with a one-day experiment. We performed an experiment to search for heterogeneity in potassium distribution in the tea leaves sample before brewing, which is expected to be the most important cause of systematic errors. The calculated upper limit for the relative standard deviation of the systematic errors is null at about 80% confidence level, and 2% at 95% confidence level. Therefore, in this work, we found appropriate experimental conditions for using the natural radioactivity of potassium to obtain the amount of soluble potassium in tea brew, independently of its chemical form. This method can likely be extended to determine the amount of soluble K in any other herbal infusion.

Acknowledgements

To Rita Tereza dos Santos for help in the preparation of the samples; to CNPq (Conselho Nacional de Pesquisas, Brazil), FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo, Brazil), and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior, Brazil) for partial support. M.U. Rajput thanks the Higher Education Commission and the Physics Research Division, PINSTECH (Pakistan Atomic Energy Commission), Pakistan, for their financial support and permission to perform the research in Universidade de São Paulo.

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