Agnieszka Kurpiewska
Centre for Forensic Sciences, University of Warsaw
ORCID: 0000-0001-6887-145X
prof. dr hab. Tomasz Matulewicz
Faculty of Physics, University of Warsaw
ORCID: 0000-0003-2098-1216
Przemysław Sękowski
Faculty of Physics, University of Warsaw
ORCID: 0000-0003-3322-4951

DETERMINATION OF POTASSIUM IN FOOD SAMPLES BY HIGH-RESOLUTION GAMMA SPECTROSCOPY

Summary
High-resolution gamma radiation spectroscopy (using the HPGe detector) was used to study the potassium content by recording 1461 keV gamma radiation from the radioactive decay of the ^{40}K isotope (about 0.012% of the isotopic composition of potassium in the Earth's crust). The measurements may be realised on samples in hermetically sealed containers and are sensitive to the presence of potassium only. The detector was placed in thick lead shields, which improved the sensitivity of the method. The measured intensity of 1461 keV radiation from samples containing KCl solution of various concentrations from 0.002 to 0.1 mole/litre was used to obtain the calibration line. The sensitivity of the method was determined as 0.7 mmol/litre, which corresponds to ^{40}K activity of 0.9 Bq/litre. A study of the potassium content in 5 ketchup samples was carried out, confirming a similar potassium content in the samples differing in the production date and the degree of spiciness. About twice the potassium content was found in the "premium" product – probably more tomatoes were used in its production per kilogram of product. Apart from changes in the intensity of 1461 keV radiation, no increase in the intensity of gamma radiation compared to the background was found for any of the ketchup samples.
Keywords: high-resolution gamma spectroscopy, isotope 40K, food samples (ketchup)

Introduction

Potassium is an important element for vital processes, so its content in food is important for the correct dietary structure. Potassium testing is a common part of blood and urine morphology tests, leading to diagnostic clues. Hypokalemia in COVID-19 patients as part of the body's electrolyte imbalance is considered a source of serious health complications[1]. The potassium content of the vitreous body of the eyeball shows correlations with PMI (*postmortem interval*)[2] and can therefore be used in forensic investigations. The determination of potassium content in medical samples at a typical level of a few mmol/litre is carried out by chemical methods. A frequently used method is the use of ion-selective membrane electrodes, which change their potential depending on the concentration (activity) of ions in solution. Sensitivity as low as 0.01 mmol/litre is then achieved, but the presence of 'interfering' ions (Na^+, Cs^+, Rb^+, $NH4^+$) can affect the accuracy of the measurements.

An alternative method for determining the potassium content of samples is high-resolution gamma-ray spectroscopy, using the decay of the radioactive potassium isotope ^{40}K. This method is very selective in detecting the presence of potassium, as it is insensitive to all other elements, including those listed as 'interfering'. Its advantage is that the sample can be tested in a hermetically sealed container without having to open it for testing. This means that the measurement takes place without contact with the contents of the sample being tested, so no allegation of adulteration can be made. The following section will present the basics of the method, sensitivity, range of applicability, and an example used to measure a food sample (different types of ketchup). The results presented in the paper are described in more detail in the master's thesis[3].

Determination of potassium content by gamma-ray spectroscopy

Potassium and its isotopes

Potassium is a chemical element that has two stable isotopes: ^{39}K and ^{41}K. The lighter one is more prevalent in nature (93.3%) compared to the heavier one (6.7%). For research using gamma radiation, the radioactive isotope ^{40}K, which has a very long half-life of $T_{1/2}$ = 1,248 billion years, is important. This means that since the formation of the Earth (about 4.6 billion years), only less than 8% of its original content remains, but on the time scale of our civilisation, its presence can be considered constant and is $f_{40K} = (1{,}1668 \pm 8)10 - 4$ relative to the total number of potassium atoms[4]. This low content of ~ 0.012% combined with the long half-life means that the

[1] G. Alfano, A. Ferrari, F. Fontana *et al., Hypokalemia in patients with COVID-19,* "Clinical and Experimental Nephrology" 2012, no. 25, pp. 401–409, https://doi.org/10.1007/s10157-020-01996-4 (accessed 1.12.2022).

[2] S.N. Foster, P.R. Smith, M. Biggs, G.N. Rutty, F.E. Hollingbury, S.R. Morley, *Determining the time elapsed since death from ocular vitreous potassium levels in fatal road traffic accident victims,* "Archives of Forensic Medicine and Criminology" 2016, vol. 66(2), p. 71–82.

[3] A. Kurpiewska, Master's thesis, Centre for Forensic Science, University of Warsaw, Warsaw 2022.

[4] M.O. Naumenko, K. Mezger, T.F. Nëgler, I.M. Villa, *High precision determination of the terrestrial ^{40}K abundance,* "Geochimica and Cosmochimica Acta" 2013, no. 122, p. 352.

dose of radioactivity from this source is very low[5], but the radioactivity is measurable (e.g. ^{40}K activity has been determined in medicinal and natural mineral waters[6]).

The radioactive isotope ^{40}K decays in several ways[7], but the only decay relevant to the method of gamma-ray spectroscopy is the electron capture (EC, *electron capture*) process to the first excited state of the ^{40}Ar nucleus decays very quickly (time on the order of picoseconds) to the ground state with the emission of gamma radiation with an energy of 1460.849 keV. The detection of gamma radiation of this energy (further recorded as 1461 keV) is precisely the basis for identifying the presence of potassium in a sample.

Gamma-ray spectroscopy

Recording gamma radiation with an energy of 1461 keV requires either scintillation or semiconductor detectors. Despite clear improvements in their energy-resolving capacity due to the introduction of new materials, the former is more than an order of magnitude behind semiconductor detectors such as the germanium detector with a typical energy-resolving capacity of 2 keV for an irradiation energy of 1332 keV. A Canberra HPGe detector with a nominal capacity of 40% (model GC4020-7500S) was used in the study.

Importance of reduced background levels

Potassium is a widespread element in nature (it makes up about 2.5 per cent of the Earth's crust by weight), so testing samples with a natural content of potassium is hampered by radiation from around the germanium detector. To reduce the level of this background, the germanium detector was placed in a cylindrical lead shield with a wall thickness of 10 cm, made of low-activity lead. The system is installed in the basement of the Faculty of Physics building at the University of Warsaw. To reduce the impact of potassium radiation on the room's walls, an additional shield of lead bricks (5 cm thick) was built against the underground walls nearest the detector. With this shielding, the intensity of gamma radiation reaching the detector was significantly reduced. Compared to when the detector was unshielded, the intensity of radiation events corresponding to an energy of 1461 keV decreased from 2.7 counts per 1000 seconds (CPTS, counts per thousand seconds) to 0.0085 CPTS, a factor of 318. Due to the decrease in the background level, for a finite measurement time, the standard deviation of the obtained experimental result decreases.

---

[5] P. Moskal, S. Jowzaee, *Promieniowanie naturalne z Ziemi i z Kosmosu,* "FOTON" 2012, no. 117, pp. 4–20.

[6] K.A. Pachocki, K. Wieprzowski, Z. Różycki, M. Bekas, T. Latour, *Promieniotwórczość naturalna potasu ^{40}K w wodach leczniczych i naturalnych wodach mineralnych oraz ocena dawek,* "Roczniki Państwowego Zakładu Higieny" 2011, vol. 62(1), p. 19–25.

[7] International Atomic Energy Agency, https://www-nds.iaea.org/relnsd/vcharthtml/VChartHTML.html (accessed 1.12.2022).

Determination of method sensitivity

The reference level in the measurements carried out is the number of registrations of 1461 keV radiation corresponding to the measurement situation without the test sample. This unavoidable background is due to environmental radiation, which the lead absorbers could not absorb. It is also important to bear in mind the radiation reaching the detector from the side of the liquid nitrogen container, which is essential for this type of detector to function properly.

The test samples were placed in Marinelli's dedicated 1,000 cm^3 containers. These containers are used as the standard for food testing[8]. As radiation from outside will also be absorbed in the sample material, a radiation intensity of 1461 keV was used as a reference level for the situation when the Marinelli container was filled with distilled water. It amounted to

$$A_0 = 0{,}00696 \pm 0{,}00022 \text{ CPTS.} \qquad (1)$$

To calibrate the experimental system, a potassium salt solution of hydrochloric acid KCl[9] (molar mass 74.55 g) was prepared at three concentrations: 0.1 mole/litre, 0.01 mole/litre, and 0.002 mole/litre. The radioactive activity of the ^{40}K in a sample containing a 0.1 mol/liter solution calculated as $A = 0{,}1 \times N_A \times f_{40K} \times ln2/T_{1/2}$ is 123.7 Bq (N_A is the Avogadro number, other parameters are defined above). Gamma--ray emission decays with an energy of 1461 keV accounting for 10.66% of the total activity calculated above. The measurements resulted in gamma-ray spectra in which a signal corresponding to an energy of 1461 keV is clearly present. The intensity of this radiation was corrected for the level of background radiation determined for a container filled with distilled water (Tab. 1). The uncertainty in the radiation intensity values obtained is essentially statistical in nature. This is due to the probabilistic nature of subatomic processes. The key factor in these considerations is the number of recorded cases (*N*), the uncertainty of which is an elemental function ($\sqrt{N}$)[10]. The number of recorded cases increases in proportion to the measurement time. As far as uncertainty is concerned, it is a root function; increasing the measurement time reduces the standard deviation of the obtained measurement result. The resulting uncertainties relate to measurements lasting approximately 24 hours. It is worth noting that the relative accuracy deteriorates from a fraction of a per cent for the highest KCl concentration in the solution tested to several per cent for the lowest concentration.

[8] N. Lavi, Z.B. Alfassi, *Development and application of Marinelli beaker standards for monitoring radioactivity in dairy-products by gamma-ray spectrometry,* "Applied Radiation and Isotopes" 2004, vol. 61(6), p. 1437–1441.

[9] The purity declared by the manufacturer is 99%.

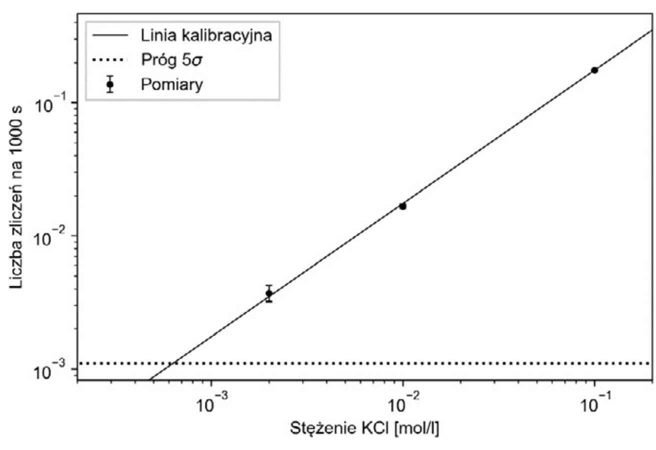
[10] R. Nowak, *Statistics for Physicists,* Wydawnictwo Naukowe PWN, Warsaw 2002, example 7.3.4.

Tab. 1. Radiant intensity 1461 keV, corrected for background level of the distilled water container, for litre containers with KCl solution

KCl concentration mole/litre (S_K)	Radiant intensity 1461 keV (CPTS) $A–A_0$
0.1	0.1747 ± 0.0014
0.01	0.01689 ± 0.00057
0.002	0.00372 ± 0.00052

Source: own research.

Fig. 1. Measured recorded radiation level of 1461 keV per 1000 seconds for samples containing aqueous KCl solution. The solid line shows a linear fit to the experimental data. The horizontal dotted line corresponds to the detection limit adopted as five standard deviations for the measurement with distilled water



Source: own research.

The results shown in Table 1 indicate that the number of counts of 1461 keV radiation is proportional to the concentration of KCl in the sample

$$A - A_0\ [\text{CPTS}] = (1{,}744 \pm 0{,}022) \times S_K\ [\text{mole/litre}] \qquad (2)$$

The resulting fit reproduces the observed relationship well (Fig. 1) 1461 keV radiation intensity from KCl content. Taking five standard deviations of the A_0, magnitude as the threshold for accurate detection, the sensitivity of the method can be determined as 7×10^{-4} mole/litre, which corresponds to 0.9 Bq/litre of the radioactive activity of the ^{40}K isotope. This means a detection rate of approximately 30 mg of potassium dissolved in a litre of water (1 tablet of potassium used in therapy dissolved in more than 10 litres of water).

Testing of ketchup samples

As an example of food analysis for potassium content (and to check for other radioactivity), five-litre samples of ketchup produced by three companies were tested. Ketchup was chosen as a product for which tomatoes containing significant amounts of potassium are used. For comparison, products from the same company (B) differing in the date of manufacture were examined, as well as comparing the mild and spicy versions of Company C. The results are shown in Table 2. The last column of Table 2 gives the potassium content calculated according to the calibration formula (2), taking into account the quotient of the molar mass of potassium to the molar mass of KCl. Analysing the potassium contents obtained, it can be concluded that:

a) no difference was observed in samples differing in date of manufacture,

b) no difference was noticed in the spicy and mild versions,

c) the "premium" product contains about twice as much potassium as standard products, so it was probably made from a greater weight of tomatoes per kilo of ketchup.

Tab. 2. Characterisation of the ketchup samples and the determined radiation intensity at 1461 keV, corrected in the third column for the A_0 reference level. The last column gives the potassium content per litre of product

Ketchup	Radiation intensity 1461 keV (CPTS)		Potassium content (mmol/litre)
	A	$A–A_0$	
A Premium Spicy	0.01902 ± 0.00040	0.01206 ± 0.00046	3.62 ± 0.15
B mild (2.09.2021)	0.01301 ± 0.00044	0.00605 ± 0.00049	1.82 ± 0.15
B mild (3.11.2021)	0.01230 ± 0.00074	0.00534 ± 0.00077	1.60 ± 0.23
C spicy	0.01182 ± 0.00037	0.00486 ± 0.00043	1.46 ± 0.13
C mild	0.01230 ± 0.00024	0.00534 ± 0.00033	1.61 ± 0.10

Source: own research.

An overall analysis of the gamma-ray spectrum from all the ketchup samples tested did not show any increase in radioactivity above the designated background, with the exception of the investigated activity from the decay of the ^{40}K isotope.

Conclusions

High-resolution gamma-ray spectroscopy was used to study the potassium content by recording gamma rays with an energy of 1461 keV from the radioactive decay of the ^{40}K isotope, which represents approximately 0.012% of the potassium isotopic composition of the Earth's crust. Placing the gamma-ray detector used in thick lead shielding resulted in a significant decrease in the background level, which has a positive effect on the detection threshold over the finite measurement time. By examining the 1461 keV radiation intensity from samples containing KCl solution at different concentrations, a calibration line in the range of 0.002 to 0.1 mole per litre was determined, and the detection threshold was set as 0.7 mmol/litre, corresponding to a ^{40}K activity of 0.9 Bq/litre. A test of the potassium content of five ketchup samples was carried out, finding similar potassium content in samples differing in date of production and degree of spiciness. Approximately twice the potassium content was observed in the 'premium' product – presumably, a greater weight of tomatoes per kilogram of the product was used in its manufacture. Apart from changes in radiation intensity at an energy of 1461 keV, no other change in gamma radiation intensity was detected above the background of the detection system for all ketchup samples tested.

Bibliography

Literature

Alfano G., Ferrari A., Fontana F. *et al., Hypokalemia in patients with COVID-19,* „Clinical and Experimental Nephrology" 2012, nr 25, https://doi.org/10.1007/s10157-020-01996-4 (dostęp 1.12.2022).

Burchart J., Král J., *Izotopowy zapis przeszłości Ziemi,* Wydawnictwo Uniwersytetu Marii Curie-Skłodowskiej, Lublin 2015.

Foster S.N., Smith P.R., Biggs M., Rutty G.N., Hollingbury F.E., Morley S.R., *Ustalanie czasu, jaki upłynął od zgonu, na podstawie poziomu potasu w ciele szklistym oka u ofiar śmiertelnych wypadków drogowych,* „Archiwum Medycyny Sądowej i Kryminologii" 2016, t. 66(2).

Kurpiewska A., praca magisterska, Centrum Nauk Sądowych, Uniwersytet Warszawski, Warszawa 2022.

Lavi N., Alfassi Z.B., *Development and application of Marinelli beaker standards for monitoring radioactivity in dairy-products by gamma-ray spectrometry,* „Applied Radiation and Isotopes" 2004, t. 61(6).

Morf W.E., *The Principles of Ion-Selective Electrodes and of Membrane Transport,* Elsevier, Budapest–Amsterdam 1981.

Moskal P., Jowzaee S., *Promieniowanie naturalne z Ziemi i z Kosmosu,* „FOTON" 2012, nr 117.

Naumenko M.O., Mezger K., Nëgler T.F., Villa I.M., *High precision determination of the terrestrial ^{40}K abundance,* „Geochimica and Cosmochimica Acta" 2013, nr 122.

Nowak R., *Statystyka dla fizyków,* Wydawnictwo Naukowe PWN, Warszawa 2002.

Pachocki K.A., Wieprzowski K., Różycki Z., Bekas M., Latour T., *Promieniotwórczość naturalna potasu ^{40}K w wodach leczniczych i naturalnych wodach mineralnych oraz ocena dawek,* „Roczniki Państwowego Zakładu Higieny" 2011, t. 62(1).

Online sources

Gorzkiewicz K., *Niskotłowy, cyfrowy spektrometr promieniowania gamma z osłoną aktywną w zastosowaniach do badań śladowej radioaktywności,* rozprawa doktorska, Instytut Fizyki Jądrowej PAN, Kraków 2020, http://rifj.ifj.edu.pl/handle/item/326 (dostęp 1.12.2022).

Gilmore G.R., *Practical Gamma-Ray Spectroscopy,* wyd2, J. Wiley & Sons 2008, DOI:10.1002/9780470861981 (dostęp 1.12.2022).

International Atomic Energy Agency, https://www-nds.iaea.org/relnsd/vcharthtml/VChartHTML.html (dostęp 1.12.2022).

Conflict of interest

None

Source of funding

None