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Analysis of the natural activities of radionuclides, heavy metals, and other poisonous elements in lead-free Sn–6.5Zn solders with different alloying elements

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Abstract

Problem statement: Sn–Zn solders are candidate alternatives to Sn–Pb-based solder alloys. With the increasing requirement for lead-free solders, the reliability of successor solders in microelectronics assemblies is in high demand. The elimination of radionuclides, heavy metals, and other poisonous elements in lead-free Sn–6.5Zn solders in the microelectronics industry is a worldwide goal. As a result, it is useful to identify the natural concentrations of radioactive nuclides, heavy metals and other poisonous trace elements (both macro- and micro-element contents), such as Au-196, Th-227, Ag-110M, Fe-59, Zn-65, Rb-89, Rh-106M, Bi-207, Cs-137, Eu-154, Sb-126, Eu-152, Co-56, Co-58, Co-60 and K-40. If this lead-free solder contains high concentrations of natural radioactive nuclides, then workers handling it might be exposed to significant levels of radiation. Therefore, it is important to determine the levels of radioactive nuclides in this solder to protect workers; these levels provide background for the safety rules and precautions that should be applied for those working in this field.

Approach: The levels of natural radionuclides (^{238}U, ^{232}Th, and ^{40}K) and their daughter products contained in Sn–6.5Zn solders have been estimated via gamma-ray spectrometry using a 100% Hyper-Pure Germanium (HPGe) detector.

Results: The mean activities due to radionuclides, heavy metals, and other poisonous elements were measured, and the results are summarised in tables.

Conclusion: The results of this assessment obtained by gamma-ray spectroscopic analysis indicated the presence of high levels of natural radioactivity, heavy metals and other poisonous elements. This result implies that a comprehensive study should be conducted to protect workers from high doses of hazardous substances.

Keywords: Natural radionuclides; Equivalent activity; Annual effective dose; Radiation hazard index; Gamma spectrometer; NAA; Poisonous elements

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1. Introduction

Due to world-wide environmental concerns regarding Pb toxicity, the electronics industry is moving towards the adoption of lead-free solders as substitutes for lead-bearing solders [1,2]. Many promising Sn-rich alloys have been recommended to replace traditional Sn–Pb solders. These lead-free solders commonly have low elastic moduli to accommodate CTE mismatches between the die and substrate, good electrical conductivity, high surface tension in the liquid state to align the parts during assembly, and can be placed via several different techniques. Unfortunately, the incorrect common belief is that lead-free solders have no natural radioactive nuclides, heavy metals, or other poisonous trace elements because they do not contain lead that is, because the lead-free solder is Sn based and Pb is a natural trace impurity in Sn, lead-free solders should not contain any hazardous impurities. However, among these solders, the Sn–Zn system has been considered to be one of the most promising candidates for Pb-free solders due to its lower material cost and low melting point (198 °C), which is close to that of Sn–Pb (183 °C) [3]. Nevertheless, several problems must be addressed to increase the practical application of Sn–Zn solders in electronic manufacturing, such as the poor wettability, easy oxidation and some reliability issues [4,5]. Unfortunately, solders also contain low levels of radioactive isotopes that emit various forms of gamma-ray radiation. Because the solders in a wafer bump are very close to the active area of the chip, the gamma-ray radiation can deposit enough energy in a memory cell on the chip to erase the stored information; in addition, the radiation can affect the workers in this field because human beings are always exposed to natural radiations from their surroundings. An established fact is that over 60 radionuclides can be found in the natural environment. Natural radioactivity is common in the rocks and soil that comprise our planet, in water and oceans, and in our building materials and homes [6]. Therefore, the assessment of the gamma radiation dose from natural sources is of particular importance as natural radiation is the largest contributor to the external dose of the world population [7,8]. This natural exposure implies that a comprehensive study should be conducted to determine the reasons for the high levels of radionuclei, heavy metals and other poisonous elements in the lead free solder alloy samples.

One common approach to improve the properties and reliability of lead-free solders is to identify and eliminate the radionuclides, heavy metals, and other poisonous elements in lead-free solders in the microelectronics industry. Therefore, the goals of this work re to identify and determine the concentration of natural radioactivity due to uranium, thorium, potassium, heavy metals, and other poisonous elements in Sn–6.5Zn lead-free solders doped with different alloying elements and to measure the surface radiation dose rate, the radium equivalent activity and the radiation hazard index (Table 1). The absorption of these elements, including toxic ones, is higher in infants than older children and adults [6]. These toxic substances have a severe and rapid impact on the central nervous system of newly born children. Finally, the determination of the elements present in tin ore samples is performed using the XRF-technique.

Table 1
The natural radionuclides, their gamma lines used and their intensities.

Parent nuclide	Daughter nuclide	γ-Ray energy (keV)	Abundance (%)
226Ra	214Bi	1120.28	14.9
	214Bi	1764.52	16.07
232Th	228Ac	911.16	29.0
	208Tl	2614.7	36.0
40 K	–	1460	10.67

2. Materials and methods

Commercially pure elements of Sn, Zn, Bi and Cu were used to produce the solder alloys in this study. The composition of the solder alloys considered in this study were Sn–6.5Zn, Sn–6.5Zn–1.5 wt.% Cu and Sn–6.5Zn–3.0 wt.% Bi alloys. The process of melting was performed in a vacuum arc furnace under the protection of a high purity argon atmosphere at 800 °C for approximately 1 h. To obtain a homogeneous composition within the ingots, the alloy samples were remelted three times to produce rod-like specimens with a diameter of approximately 1.5 cm. The solder alloys were mounted into clean containers and then measured for 10,480 s. The energy and intensity of the various gamma-ray lines were measured using a system based on a Canberra coaxial High-Purity Germanium detector (HPGe) Fig. 1 with a relative efficiency of 100%. The energy resolution was 2.1 keV full-width at half

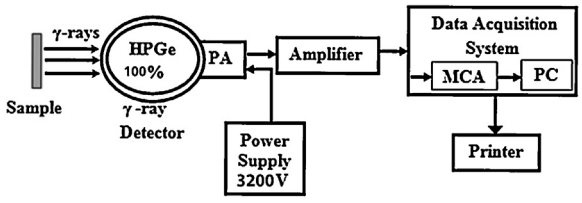

Fig. 1. Blocked diagram of HPGe γ-ray spectrometer system.

maximum (FWHM) for the 1332 keV gamma-ray line of ^{60}Co. A cylindrical lead shield with a 5-cm thickness, which contains an inner concentric cylinder of Cu with a thickness of 10 mm, was used to shield the detector and to reduce the effects of the background. The detector was cooled to liquid nitrogen temperatures and coupled to a PC-based 8K multichannel analyser (8192 Ch) and an ADC with Genie 2000 for data acquisition and analysis. The calibration of the detector was performed by using standard point sources ^{60}Co (1173.2 and 1332.5 keV), ^{133}Ba (356.1 keV), ^{137}Cs (661.9 keV) and ^{22}Na (1368.6 keV) in addition to ^{226}Ra (186.2 keV). The spectra of samples were perfectly analysed using a special PC Genie 2000. Analysis software was used to analyse and calculate the concentrations of U, Th, K and their decay products. These elements were gold (Au-196), thorium (Th-227), silver (Ag-110M), iron (Fe-59), zinc (Zn-65), rubidium (Rb-89), rhodium (Rh-106M), bismuth (Bi-207), caesium (Cs-137), europium (Eu-154), antimony (Sb-126), europium (Eu-152), cobalt (Co-56), cobalt (Co-58), cobalt (Co-60) and potassium (K-40).

3. Results and discussion

This work presents the analyses of macro- and micro-elements contained in Sn 6.5Zn, Sn–6.5Zn–1.5 wt.% Cu and Sn–6.5Zn–3.0 wt.% Bi alloys. The data are presented in Tables 2–4. Some of the micro-elements are bound in the solder alloy samples, which increases the efficiency of absorption. The iron and potassium contents in the solder samples were found to have an activity between 0.64–1.56 Bq, which is not affected by the environment. The gold contents in solder alloy samples vary between 2.71–6.39 Bq. It appears that the gold contents are not influenced by either the nutriment or the gold intake. The zinc contents in the alloy samples were measured to be between 996.54–1376.35 Bq; it is difficult to specify an average value due to the variations, which are as high as an order of magnitude. Similar to the other micro elements, we analysed the cobalt, bismuth, rhodium, thorium, europium, antimony, caesium, rubidium, silver and zinc contained in the solder samples, as presented in Tables 2–4. The amounts of the latter elements in the solder alloy samples are affected by the pollution in the urban air, that is, the exhaust gas of the motor vehicles, the polluted environment and the number of amalgam fillings. Rossipal and Krachler [10] examined the content of 19 trace elements of three alloy samples. The cobalt, bismuth, rhodium, thorium, europium, antimony, caesium, rubidium, silver and zinc contents were determined. The silver concentration was measured to be 1004 ± 88 counts and the rhodium concentration to be 171 ± 74–253 ± 66 counts. For the three alloy samples, the trace element concentrations of cobalt, bismuth,

Table 2
The average values of the activities due to radioactive nuclei in (1) Sn–6.5Zn.

Isotope	Energy (keV)	Activity (Bq)	Net area
Au-196	75.7	2.71	142 ± 90
Th-227	85.44	24.57	165 ± 85
Ag-110M	657.75	3.42	1004 ± 88
Co-58	810.75	18.12	160 ± 72
Fe-59	1099.22	1.28	182 ± 56
Zn-65	1115.52	996.54	3661 ± 116
Co-60	1173.23	573.59	1523 ± 72
Rb-89	1248.10	0.50	50 ± 22
Fe-59	1291.56	43.58	113 ± 31
Co-60	1332.51	6.54	1548 ± 71
K-40	1460.75	110.81	243 ± 28

Table 3
The average values of the activities due to radioactive nuclei in Sn–6.5Zn–1.5Cu.

Isotope	Energy (keV)	Activity (Bq)	Net area
Au-196	75.70	4.03	165 ± 79
Rh-106M	511.80	53.09	253 ± 66
Bi-207	569.67	0.28	83 ± 61
Cs-137	661.62	1.89	432 ± 99
Eu-154	692.50	30.47	104 ± 57
Sb-126	856.70	0.07	104 ± 57
Fe-59	1099.22	0.64	71 ± 48
Eu-152	1112.07	970.69	2781 ± 80
Co-60	1173.23	488.72	1012 ± 54
Co-56	1238.28	10.46	30 ± 21
Co-60	1332.51	6.93	1205 ± 46
K-40	1460.75	112.26	192 ± 20

Table 4
The average values of the activities due to radioactive nuclei in Sn–6.5Zn–3Bi.

Isotope	Energy (keV)	Activity (Bq)	Net area
Au-196	75.70	6.39	295 ± 83
Th-227	85.44	35.07	207 ± 81
Rh-106M	511.80	0.55	171 ± 74
Cs-137	661.62	4.78	1234 ± 77
Co-58	810.75	18.17	141 ± 68
Fe-59	1099.22	1.56	195 ± 52
Zn-65	1115.52	1376.35	4444 ± 91
Co-60	1173.23	814.17	1900 ± 58
Fe-59	1291.56	1.64	142 ± 26
Co-60	1332.51	10.11	1981 ± 51
K-40	1460.75	14.75	292 ± 26

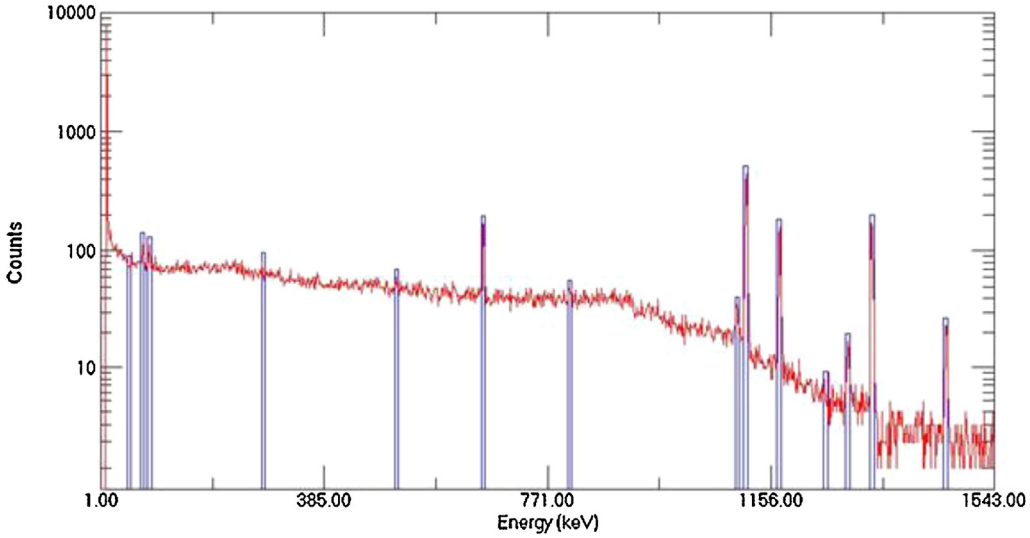

Fig. 2. Portion of Gamma ray spectrum 10,480 s counting illustrates the analysis of Sn–6.5Zn sample.

rhodium, thorium, europium, antimony, caesium, rubidium, silver, zinc, and uranium were obtained and listed in Tables 2–4. The average activity of the three alloy samples was measured to be 3.42 Bq for silver, 24.57 Bq for cerium, 996.54 Bq for zinc, 0.28 Bq for bismuth, 53.09 Bq for rhodium, 30.47 Bq for europium, 488.72 Bq for cobalt, 24.57 Bq for thorium, and 0.07 Bq for antimony.

All of these elements in the solder alloy samples raise important issues for paediatric practice, the practice of public health, and the environmental health research community. Insufficient information exists on the nature and levels of contaminants in solder alloy, and a lack of consistent protocols exist for collecting and analysing the solder samples. There is a gap in information regarding the exact concentrations of those elements. Therefore, the need for risk assessment can be verified as well as the difficult formulation of evidence-based health guidance. The results of this study will make the consideration of contamination in the solder alloys mandatory for environmental risk assessment.

3.1. Natural activity measurement

Activities due to the presence of ^{226}Ra, ^{232}Th and ^{40}K radionuclides have been determined in the samples. As can be observed in Tables 2–4, the measured values of the activity in the samples vary from 21.9 Bq to 9.9 Bq due to ^{232}Th, from 42.77 Bq to 21.43 Bq due to ^{226}Ra, and from 145.33 Bq to 16.22 Bq due to ^{40}K. The results of the activity of this assessment obtained by the gamma-ray spectroscopic analysis Table 2 have indicated the high levels of natural radioactivity, heavy metal and other poisonous elements.

The obtained spectrum of the background gamma radiation was subtracted from the measured gamma ray spectra of the alloy samples. The characteristic gamma-ray emitters are marked above the corresponding peaks. A selected spectrum for solder alloy samples is shown in Figs. 2–4.

To assess the radiological hazard of the solder sample, it is useful to calculate an index called the radium equivalent activity, Ra_{eq}, defined according to the estimation that 1 Bq/kg of ^{226}Ra, 1.43 Bq/kg of ^{232}Th and 0.077 Bq/kg of ^{40}K produce the same γ-ray dose [11]. This index Ra_{eq} is given as:

$$Ra_{eq} = A_{Ra} + 1.43\,A_{Th} + 0.077\,A_K \quad (1)$$

where A_{Ra}, A_{Th} and A_K are the activity concentrations in Bq/kg of ^{226}Ra, ^{232}Th and ^{40}K, respectively. The maximum value of Ra_{eq} in the solder samples must be less than 370 Bq/kg for safe use (UNSCEAR, 1993), i.e., to keep the external dose below 1.5 mSv y^{-1}. The values of Ra_{eq} are below this criterion limit. In alloy samples, the Ra_{eq} activity is within the recommended safety limit when used in industry. The calculated values of the radium equivalent Ra_{eq} for the studied solder samples are presented in Table 5.

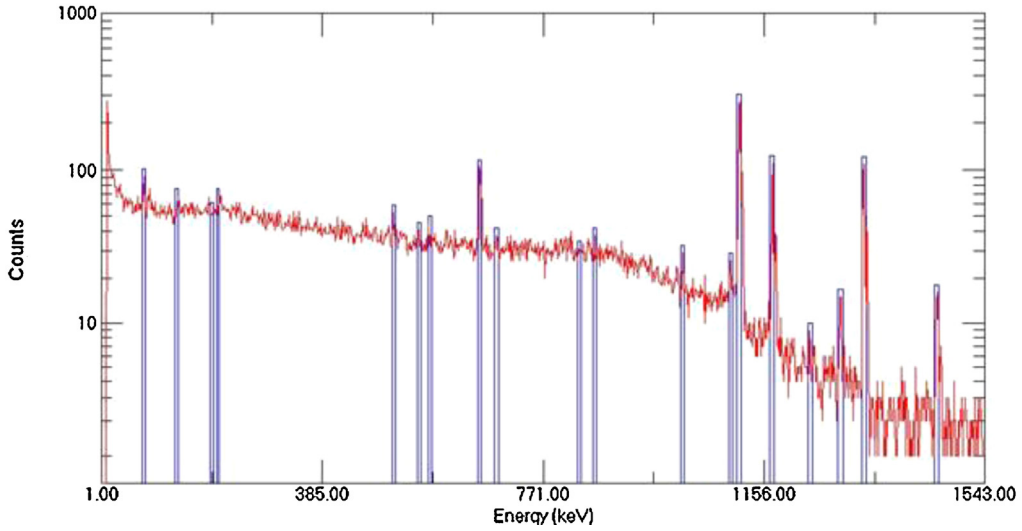

Fig. 3. Portion of Gamma ray spectrum 7227 s counting illustrates the analysis of Sn–6.5Zn–1.5Cu.

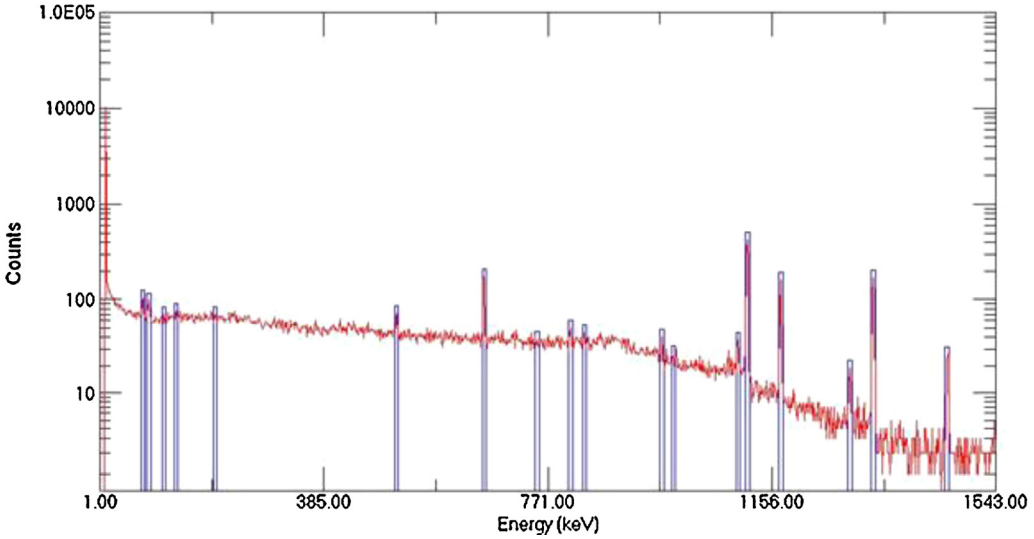

Fig. 4. Portion of Gamma ray spectrum 9676 s counting illustrates the analysis of Sn–6.5Zn–3Bi sample.

Table 5
The minimum, maximum and average values of the activities due to radium equivalent activity (Bq/kg), and gamma-radiation hazard (H_{ex}).

H_{ex}	Radium equivalent activity (Bq/kg)	Range
0.10	15.94	Minimum
0.24	65.36	Maximum
0.17	40.65	Mean

Another radiation hazard index, the representative level index, H_{ex}, used to estimate the levels of γ-radiation hazard associated with the natural radionuclides in specific alloy samples, is defined as [12].

$$H_{ex} = \left(\frac{A_{Ra}}{150}\right) + \left(\frac{A_{Th}}{100}\right) + \left(\frac{A_K}{1500}\right) \quad (2)$$

where A_{Ra}, A_{Th} and A_K are the activity concentrations in Bq/kg of ^{226}Ra, ^{232}Th and ^{40}K, respectively. The values of H_{ex} for the studied samples are given in Table 3. The studied solder samples clearly do not exceed the upper limit for the representative level, which is unity.

3.2. Radiation hazard index

This factor is used to estimate the level of the gamma radiation hazard associated with natural radionuclides

in specific alloy samples. The external hazard index is obtained from the Ra_{eq} expression through the assumption that its maximum value allowed (equal to unity) corresponds to the upper limit of Ra_{eq} (370 Bq/kg) according to UNSCEAR, 1993. This index value must be less than unity to keep the radiation hazard insignificant. Next, the external hazard index (H_{ex}) can be defined as [13],

$$\mathrm{Ir}\gamma = \left(\frac{A_{Ra}}{370}\right) + \left(\frac{A_{Th}}{259}\right) + \left(\frac{A_K}{4810}\right) \quad (3)$$

where A_{Ra}, A_{Th} and A_K are the specific activities of ^{226}Ra, ^{232}Th and ^{40}K (in Bq/kg), respectively, and were calculated for the investigated samples to indicate the different levels of the external γ-radiation due to different combinations of specific natural activities in specific solder samples.

4. Conclusions

The natural activities of radionuclides, heavy metals, and other poisonous elements in lead-free Sn–6.5Zn solders with different alloying elements were investigated in the present work. The radium equivalent activities calculated from the measured values of ^{226}Ra, ^{232}Th and ^{40}K activities in the three solder alloy samples were found to be lower than the upper recommended limit of 370 Bq/kg. These data serve as a basis for the assessment of radiological hazards to the workers involved in electronic devices and industrial applications in Egypt. The calculated external hazard indicates are less than unity. Therefore, the studied solder alloys are acceptable for use. The results of this assessment obtained by the gamma-ray spectroscopic analysis indicated the high levels of natural radioactivity, heavy metal and other poisonous elements. Therefore, specific measures can be implemented to protect workers. These safety rules and precautions should be applied for those working in this field.

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