Zimbabwe Journal of Science & Technology pp 21 – 30 Vol.14 [2019]
e-ISSN 2409-0360
Zimbabwej.sci.technol

Quality assessment of some selected canned foods and energy drinks for human consumption by the determination of tin levels analysed by spectrophotometry technique using mixed surfactants

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ABSTRACT

The qualities of some selected canned foods and energy drinks for human consumption were investigated by the determination of tin levels in the samples. Forty five replicates of nine different types of canned foods and energy drinks; meat (beef), fish in tomato sauce, fish in vegetable oil, tomato paste, baked beans, infant food (cereal), infant milk and energy drinks (malt and red grape) were used in the study. The levels of tin in these samples were analysed by spectrophotometry technique using mixed surfactants of cetyltrimethylammonium bromide, nonylphenoxyPolyethoxyethanol with bromopyrogallol red as chromogenic reagent. The Sn(IV) levels were within the range of 65.9±0.47 to 460.5±6.12 mg/kg. Repeatability as coefficient of variation ranged from 0.36 – 1.62% depending on food evaluated. The recovery rates obtained by standard addition method were between 87.3 to 134.35% and averaged 110.8%. Statistical analysis using analysis of variance shows significant difference in means of tin levels at 95% confidence level. The results of the study show that the tin levels in most of the samples (67%) are within the safe limit for canned foods and energy drinks 250 and 150 mg/kg respectively as allowed by World Health Organisation, yet there is the need to monitor the levels of tin in canned foods and energy drinks from time to time by relevant agencies to ensure the quality and safety of these products for human consumption.

Keywords: Canned food; Tin; spectrophotometry; surfactants; consumption; W.H.O.

Received: 06.06.18 **Accepted:** 29.04.19

1. Introduction

Canned foods of meat, fish, tomato paste, beans, infant cereals, milk and all sorts of canned energy drinks are commonly sold in our markets and departmental stores. In this era of technological advancement with increasing departure from the natural ways of preparing meals, there seems to be much reliance on processed foods. This is due to the fact that canned foods require no further tedious preparations other than slight heating if necessary and thus provide the needed ease for people who are always on the move to meet the daily essentials of life. Most canned foods containers are corrugated iron with tin metal as an active metal to drastically reduce the deteriorating effects of corrosion and for the purpose of preservations. If a tin-plated iron can is used for package, the content of tin in food is indicative of the quality of the food in storage although inorganic tin is nontoxic for living systems (Huang et al., 1997). Cases of poisoning from inorganic tin metal, its oxides, and its salt are 'almost unknown'; on the other hand certain organo tin compounds are almost as toxic as cyanide (Graf, 2005). Nausea, vomiting and diarrhoea have been reported after ingesting canned food containing 200 mg/kg of tin (Blunden, 2003). This observation led, for example, the food standards agency in the United Kingdom to propose upper limits of 200 mg/kg. Food and especially canned food represent the main source of human exposure to tin. Several highly sensitive and sophisticated methods of analysis for tin content determination in canned foods and energy drinks such as spectrofluorimetry (Manzoori et al., 2006) atomic absorption spectrometry (Cameron and Brittain,2007), inductively coupled plasma atomic emission spectroscopy (Perring and Basic-Dvorzak, 2002), X-ray- microanalysis and electrochemical impedance spectroscopy (Pournaras et al., 2008) etc. have been cited in literature. These methods are also generally tedious and not free from

interferences of other elements. In contrast spectrophotometric methods are preferred due to their simplicity and speed in routine analysis. There is however very scanty literature on the application of UV/Visible spectrometry (Huang et al., 1997; Ramesh and Harish, 2014) for the determination of tin levels in canned food and energy drinks. The present work is poised to evaluate the levels of tin in some selected canned foods and energy drinks sold in the markets, supermarkets and small grocery retail outlets by UV/Visible spectrophotometry technique using mixed surfactants so as to ascertain the quality and safety of these products for human consumption and also add concise information to the existing body of knowledge.

2. Materials and methods

2.1 Materials

Canned foods of meat (beef), fish in tomato sauce, fish in vegetable oil, tomato paste, baked beans, infant food (cereal), infant milk and energy drinks (malt and red grape) were used in this study. Reagents used in this work included 0.1% cetyltrimethylammonium bromide (CTAB), 0.2 % nonylphenoxyPolyethoxyethanol (OP), 0.01 % bromopyrogallol red (BPR), 95% ethanol, tetraoxosulphate(VI) acid. All reagents were prepared using distilled water.

2.2 Sampling method

Non-random sampling technique was employed with emphasis on popular brands. The canned foods and energy drinks samples were purchased from the market, supermarkets and small grocery retail outlets in Jalingo metropolis, Taraba State, Nigeria. A total of forty five replicates of nine different types of canned foods and energy drinks samples were used in the study. This provided replicates of five for each type of canned foods and energy drinks investigated and hence data for statistical analysis. All the canned foods and energy drinks samples were within their shelf lives at the time of our investigations.

2.3 Experimental

2.3.1 Digestion of solid samples

Prior to analysis of the different samples, the solids samples were first digested following procedures described by Huang et al., (1997). 2.0 g of each of the sample in replicates of five were approximately weighed and ash at 600 ^{o}C. Afterwards, the ash obtained for each replicate was dissolved in 10 mL of concentrated HCl and diluted to mark in a 50 mL volumetric flask with distilled H_2O and 1M NaOH so that the final pH was approximately 1.

2.3.2 Spectrophotometric determination of tin using mixed surfactants

Working standard/samples were analysed following procedure adopted byHuang et al., 1997. To a 10 mL colorimetric tube was added 3.0 mL of 0.01 % BPR, 0.8 mL of 0.2 % OP, 0.2 mL of 0.1 % CTAB, and 2.0 mL of ethanol were added in that order using pipette and syringe. After mixing, 1mL of the working standard solution (or sample digest) was added and diluted to the mark with 0.10 M H_2SO_4. Resulting solution was transferred to a cuvette and read off using UV/visible spectrophotometer at a wavelength of 304 nm. Calibration curve for the analysis of Sn(IV) was first constructed. Several concentrations of Sn(IV) of 0.5, 1.0, 1.5, 2.0 and 2.5 µg/mL were prepared and their corresponding absorbance read off using a T60, 2007 model UV/Visible spectrophotometer (PG Instruments, UK) at a wavelength of 304 nm. The level of Sn(IV) in mg/kg was calculated using the formula:

$$\text{mg/kg } Sn^{4+} = \frac{\frac{instrument\ reading\left(\frac{\mu g}{ml}\right)}{volume\ of\ sample} \times \frac{volume\ of\ digest(mL)}{aliquot} \times 10^{-3}}{weight\ of tin\ content\ (kg)} \times \text{dilution factor}$$

The order of addition of reagents has been reported to have great effect on the absorbance. The chromogenic reagent and surfactants must be added before the Sn(IV) or sample solution (Huang et al., 1997). The chromogenic reaction was completed immediately after all reagents were added in the aforementioned order,

and the chromogenic system has stability for at least 4 hours. It is also reported by same workers Huang et al., (1997) that in the proposed method of analysis, ethanol has a sensitizing effect on the determination of tin. The optimum amount of 95 % ethanol was 2-3 mL. An excess of ethanol over the optimum would cause the absorbance to decrease. Ethanol also had a stabilizing effect on the micelle system used for the tin determination (Zhao, 1991).

2.3.4 Recovery study

In order to check the accuracy of the method, a recovery study was carried out on the nine samples under investigation using the method of standard addition (Huang et al., 1997; Skoog, 2004). 1mL of the digested solution of each of the sample in replicates of three were spiked with 1 mL of 15 or 20 µg/mL of Sn(IV) solution final concentration. The responses before and after addition were measured by using UV/visible spectrophotometer at a wavelength of 304 nm following the procedure adopted by Huang et al., (1997) for the determination of Sn(IV). Recovery percent was calculated using the formula:

Recovery percent = 100 × (A – B) / T

Where: A= measured concentration of analyte after spiking (amount found); B = measured background concentration; T = the concentration of the spike (amount added)

2.3.5 Statistical Data Treatment

SPSS 16.0 Statistical and Microsoft Office Excel software were employed for the statistical data treatment. Analysis of variance (ANOVA) and least significant difference (LSD) at 95% confidence level were carried out on the result of the tin levels of the 45 replicates food samples obtained from the study. Standard deviations and coefficient of variations were also calculated to checkmate for indeterminate errors and ascertain precisions.

3. Results and Discussions

The calibration curve for the analysis of Sn(IV) used in the study is shown in Figure 1. The regression coefficient of the curve gives unity value and indicative of good linearity and in agreement with Beer's – Lambert law (Skoog, 2004).

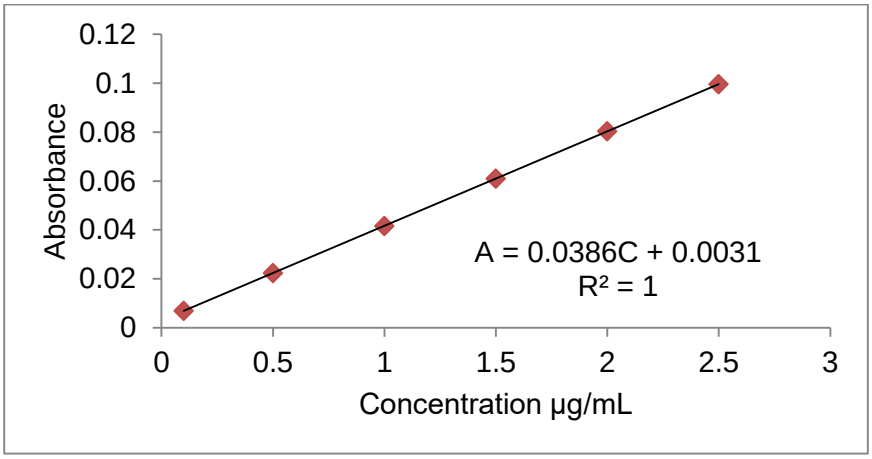

Figure 1. Calibration curve for the analysis of Sn(IV) used in the study

No outliers were observed in any of the set of five replicate measurements for tin content in canned food samples except for the energy drink (red grape) where two of the readings were rejected. The in-depth analysis of results is shown in 3.1 and summarised in Tables 1 and 2. The results of Sn(IV) in the samples analysed during the study are displayed in Table 1.

3.1 The conversion of µg/mL Sn^{4+} to mg/kg Sn^{4+} for the various food samples used in the study

1. **Tomato paste**
   Instrument reading of Sn(IV) level (µg/mL) = 64.48
   Volume of digest = 50 mL
   Aliquot of digest = 1 mL
   Volume of sample = 1 mL
   Weight of tin content for tomato paste (kg) = 0.07
   Dilution factor = 10

$$\text{mg/kg } Sn^{4+} = \frac{\frac{instrument\ reading\left(\frac{\mu g}{ml}\right)}{volume\ of\ sample} \times \frac{volume\ of\ digest(mL)}{aliquot} \times 10^{-3}}{weight\ of tin\ content\ (kg)} \times \textit{dilution factor}$$

   = (64.48 /1 × 50 /1 × 10^{-3} × 10)/0.07

   = 460.57 mg/kg

2. **Fish in tomato sauce**
   Instrument reading of Sn(IV) level (µg/mL) = 51.36
   Volume of digest = 50 mL
   Aliquot of digest = 1 mL
   Volume of sample = 1 mL
   Weight of tin content for fish in tomato sauce (kg) = 0.093
   Dilution factor = 10

$$\text{mg/kg } Sn^{4+} = \frac{\frac{instrument\ reading\left(\frac{\mu g}{ml}\right)}{volume\ of\ sample} \times \frac{volume\ of\ digest(mL)}{aliquot} \times 10^{-3}}{weight\ of tin\ content\ (kg)} \times \textit{dilution factor}$$

   = (51.36 /1 × 50 /1 × 10^{-3} × 10)/0.093

   = 276.1 mg/kg

3. **Meat (beef)**
   Instrument reading of Sn(IV) level (µg/mL) = 64.85
   Volume of digest = 50 mL
   Aliquot of digest = 1 mL
   Volume of sample = 1 mL
   Weight of tin content for meat (beef) in kg = 0.199
   Dilution factor = 10

$$\text{mg/kg } Sn^{4+} = \frac{\frac{instrument\ reading\left(\frac{\mu g}{ml}\right)}{volume\ of\ sample} \times \frac{volume\ of\ digest(mL)}{aliquot} \times 10^{-3}}{weight\ of tin\ content\ (kg)} \times \textit{dilution factor}$$

   = (64.85 /1 × 50 /1 × 10^{-3} × 10)/0.199

   = 162.9 mg/kg

4. **Baked beans**
   Instrument reading of Sn(IV) level (µg/mL) = 64.69
   Volume of digest = 50 mL
   Aliquot of digest = 1 mL
   Volume of sample = 1 mL

Weight of tin content for baked beans (kg) = 0.200

Dilution factor = 10

$$\text{mg/kg } Sn^{4+} = \frac{\frac{instrument\ reading\left(\frac{\mu g}{ml}\right)}{volume\ of\ sample} \times \frac{volume\ of\ digest(mL)}{aliquot} \times 10^{-3}}{weight\ of\ tin\ content\ (kg)} \times \textit{dilution factor}$$

= (64.69 /1 × 50 /1 × 10^{-3} × 10)/0.200

= 161.9mg/kg

5. Energy drink (Malt)

Instrument reading of Sn(IV) level (µg/mL) = 51.9

Volume of digest = 50 mL

Aliquot of digest = 1 mL

Volume of sample = 1 mL

Weight of tin content for energy drink (malt) in kg = 0.35

Dilution factor = 10

$$\text{mg/kg } Sn^{4+} = \frac{\frac{instrument\ reading\left(\frac{\mu g}{ml}\right)}{volume\ of\ sample} \times \frac{volume\ of\ digest(mL)}{aliquot} \times 10^{-3}}{weight\ of\ tin\ content\ (kg)} \times \textit{dilution factor}$$

= (51.9 /1 × 50 /1 × 10^{-3} × 10)/0.35

= 74.0mg/kg

6. Fish in vegetable oil sauce

Instrument reading of Sn(IV) level (µg/mL) = 64.69

Volume of digest = 50 mL

Aliquot of digest = 1 mL

Volume of sample = 1 mL

Weight of tin content for fish in vegetable oil sauce (kg) = 0.125

Dilution factor = 10

$$\text{mg/kg } Sn^{4+} = \frac{\frac{instrument\ reading\left(\frac{\mu g}{ml}\right)}{volume\ of\ sample} \times \frac{volume\ of\ digest(mL)}{aliquot} \times 10^{-3}}{weight\ of\ tin\ content\ (kg)} \times \textit{dilution factor}$$

= (64.69 /1 × 50 /1 × 10^{-3} × 10)/0.125

= 258.7mg/kg

7. Energy drink (red grape)

Instrument reading of Sn(IV) level (µg/mL) = 50.13

Volume of digest = 50 mL

Aliquot of digest = 1 mL

Volume of sample = 1 mL

Weight of tin content for energy drink (red grape) in kg = 0.355

Dilution factor = 10

$$\text{mg/kg } Sn^{4+} = \frac{\frac{instrument\ reading\left(\frac{\mu g}{ml}\right)}{volume\ of\ sample} \times \frac{volume\ of\ digest(mL)}{aliquot} \times 10^{-3}}{weight\ of\ tin\ content\ (kg)} \times \textit{dilution factor}$$

= (50.13 /1 × 50 /1 × 10^{-3} × 10)/0.355 = 70.47mg/kg

8. Infant food (cereal)

Instrument reading of Sn(IV) level (µg/mL) = 52.74
Volume of digest = 50 mL

Aliquot of digest = 1 mL

Volume of sample = 1 mL

Weight of tin content for Infant food (cereal) in kg) = 0.400

Dilution factor = 10

$$\text{mg/kg } Sn^{4+} = \frac{\frac{instrument\ reading\left(\frac{\mu g}{ml}\right)}{volume\ of\ sample} \times \frac{volume\ of\ digest(mL)}{aliquot} \times 10^{-3}}{weight\ of tin\ content\ (kg)} \times \textit{dilution factor}$$

$= (52.74 /1 \times 50 /1 \times 10^{-3} \times 10)/0.400$

$= 65.9 mg/kg$

9. Infant milk

Instrument reading of Sn(IV) level (µg/mL) = 64.44
Volume of digest = 50 mL

Aliquot of digest = 1 mL

Volume of sample = 1 mL

Weight of tin content for Infant milk (kg) = 0.400

Dilution factor = 10

$$\text{mg/kg } Sn^{4+} = \frac{\frac{instrument\ reading\left(\frac{\mu g}{ml}\right)}{volume\ of\ sample} \times \frac{volume\ of\ digest(mL)}{aliquot} \times 10^{-3}}{weight\ of tin\ content\ (kg)} \times \textit{dilution factor}$$

$= (64.44 /1 \times 50 /1 \times 10^{-3} \times 10)/0.400$

$= 80.6 mg/kg$

Table 1. Sn(IV) level in the canned foods used in the study

Sample (canned food)	[a]Sn(IV) level (µg/mL)	[a]Sn(IV) level (mg/kg)	CV (%)
Tomato paste	64.48	460.5±6.12	1.33
Fish in tomato sauce	51.36	276.1±1.52	0.55
Meat (beef)	64.85	162.9±2.39	1.47
Baked beans	64.69	161.9±1.87	1.16
Energy drink (Malt)	51.49	74.0±1.2	1.62
Fish in vegetable oil sauce	64.68	258.7±1.85	0.72
Energy drink (red grape)	[b]50.13	[b]70.47±0.25	0.36
Infant food (cereal)	52.74	65.9±0.47	0.71
Infant milk	64.44	80.6±0.83	1.03

[a]Mean of five replicate determinations ±Standard deviation ;**[b]**Mean of three replicate determinations.

The results showed that Sn(IV) levels in the canned foods and energy drinks samples investigated in the study were in the range of 65.9±0.415 – 460.5±2.69 mg/kg (Table 1) and the tin levels of 67% of the samples (Table 2) are within the permissible limits for canned foods and energy drinks (beverages) of 250 mg/kg and 150 mg/kg

respectively as allowed by W.H.O , (1989); Greger and Baier, (1981) as also cited by Steve and Tony, (2003). Within the European Union large discrepancies exist between national regulations and maximum permitted levels ranging from 50 mg/ kg to 250 mg/ kg. Table 2 shows a quality assessment checklist for the canned food and energy drinks samples used in the study.

Table 2. Quality assessment checklist for the canned food and energy drink samples used in the study

Canned food sample	Level of Sn(IV)found (mg/kg)	[c]Level of Sn(IV) (mg/kg) of standards employed in the study	Comment
Tomato paste	460.5±6.12	250	Above the safe limit
Fish in tomato sauce	276.1±1.52	250	Above the safe limit
Meat (beef)	162.9±2.39	250	Within the safe limit
Baked beans	161.9±1.87		
Energy drink (Malt)	74.0±1.2	150	Within the safe limit
Fish in vegetable oil sauce	258.7±1.85	250	Above the safe limit
Energy drink (red grape)	70.47±0.25	150	Within the safe limit
Infant food (cereal)	65.9±0.47	150	Within the safe limit
Infant milk	80.6±0.83	150	Within the safe limit

[c]Standard levels of tin in canned foods and beverages by Greger and Baier(1981) ; W.H.O. (1989).

Statistical analysis using Analysis of Variance (ANOVA) shows significant difference in the means of tin levels in the food samples investigated at 95% confidence level. However, the result of the least significant difference analysis indicates that there is no significant difference in the means of tin levels in the baked beans and meat (beef) canned foods; and that of energy drinks (red grape and malt) at 95% confidence level. The value obtained for tomato paste was very high (460.5 ± 6.12 mg/kg) in comparison with the other values (Table 1). A plausible reason for this could be that tomato paste is acidic and the leaching process of Sn(IV) into the sample is grossly enhanced http://www.googlenet.com.ng. Our results for tin levels in fish in tomato sauce (276.1± 1.5 mg/kg) and vegetable sauce (258.7±1.85 mg/kg) followed similar trends as documented by Tarley et al., (2001) in literature. They reported a similar variation of tin levels for canned sardine fish and fish in tomato sauce; with the highest value for fish in tomato sauce as we also reported. Tin levels in energy drinks and infant foods have the lowest values. Under normal circumstance the shelf life is set so that the tin content of food remains well below the legal limit throughout the product's shelf life. However, under certain conditions tin dissolution can accelerate, causing unacceptably high tin concentrations in the food within its shelf life. Consequently, the determination of tin in various canned foods is important for assessing food quality (Tradfir et al., 2004).

Repeatability as coefficient of variation (CV) ranged from 0.36 – 1.62 depending on the food type evaluated. The coefficients of variations were less than 2 % in all cases (Table 1). Earlier workers Huang et al., (1997) in a similar analysis for tin in canned meat using the same method that is applied in this work reported a CV of 2.7%. Other investigators, Ramesh and Harish, (2014) using a rapid extractive spectrophotometric method for the determination of tin in canned foods with 6-chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran reported a relative standard deviation of 0.98%. Jamshid *et al.,* 2006 who employed the spectrofluorimetric method for determination of tin in canned foods reported a coefficient variation of 0.74%. A coefficient of variation of 5 % or less has been reported in literature to connote good method performance (Westgate *et al.,* 1998). We therefore concluded that the method of analysis employed is reliable, sensitive and highly reproducible with high degree of precision. The result of the recovery assay of Sn(IV) in the selected canned foods and energy drinks used in the study is depicted in Table 3.

Table 3. Recovery assay of Sn (IV) in canned foods and energy drinks used in the study

Sample (canned food)	Added (µg)	[d]Found (µg)	Recovery %
Tomato paste	0	14.63	-
	15	29.22	97.27
Fish in tomato sauce	0	11.69	-
	15	27.41	104.8
Meat (beef)	0	14.71	-
	15	28.25	90.27
Baked beans	0	11.02	-
	15	27.02	106.65
Energy drink (malt)	0	8.798	-
	15	33.96	87.3
Fish in vegetable oil	0	11.69	-
	15	29.30	117.4
Energy drink (red grape)	0	11.41	-
	20	38.08	133.35
Infant food (Cereal)	0	12.01	-
	20	38.88	134.35
Infant milk	0	14.68	-
	20	44.48	[e]149.00

[d]Mean of three replicate determinations; [e]outlier

The recovery rate for the infant milk (149%) was fairly high thus considered as an outlier. The reason for this overestimation is not clearly known to us. It is probably due to determinate error(s) and hence excluded during analysis. The recovery rates were between 87.3 to 134.35% and averaged

110.8% after optimization of the operating conditions for the other samples. These values show that the method gives good recoveries and accuracy. Similar results are obtained in the works of Dabeka et al., (1985); Puchyr and Shapiro, (1986); and Huang et al., (1997) who determined the levels of Sn(IV) in canned foods by atomic absorption spectrophotometric using nitric acid-hydrochloric acid digestion and nitrous oxide-acetylene flame, HCl-HNO_3 leaching flame; atomic absorption spectroscopy and UV/Visible spectrophotometric technique

using mixed surfactants in that order. Tin content of 283.5 mg/kg in canned meat is reported by earlier investigators, Huang et al., (1997). Knapek et al., (2009) who used atomic absorption spectrometry for the determination of tin in canned foods reported 222 samples of 26 various kinds of canned fruit (e.g. pineapple, peach, mandarin), vegetables (e.g. bean, mushroom, tomato) and meat (sea products) in his work. The analytical results indicate that tin total concentrations from under 4 mg/kg to 353 mg/kg. In a similar study conducted by Dabeka *et al.,* (1985) who determined the levels of tin in five (5) different canned foods; (tomato paste, meat, pineapple juice, evaporated milk and green beans) using nitric acid hydrochloride acid digestion and nitrous oxide-acetylene flamed, reported a concentration range 10 - 450 mg/kg of tin in the samples. These results obtained by earlier investigators corroborate the outcome of our findings of tin level of 65.9 – 460.5 mg/kg in the present work. Estimation of tin in various canned foods and energy drinks is important in assessing food and drink quality.

The low levels of tin in some of the canned foods and energy drinks investigated in our work compared with the maximum limits of 150 – 250 mg/kg allowed by Greger and Baier, (1981) suggests that there is no rapid migration of tin from the can to the foods, an earlier assertion made by Tarley et al., (2001). The UV-Visible spectrophotometry via the use of mixed surfactant also served as a reliable and efficient method for the determination of tin in canned foods whose results are comparable with those obtained using other standard methods such as the atomic absorption spectrophotometry, spectrofluorimetry etc. One major advantage of this novel method applied in this work is that it is simple and very rapid. Samples for analysis are prepared within very short time. Long delays and tedious preparation of samples for other standard methods such as atomic absorption spectrophotometry is duly avoided. Such delays have been reported to lead to hydrolysis of analyte with the forming of insoluble Sn(IV) compounds and significant loss of Sn absorption signal as reported by Sanda et al., (2012).

4. Conclusion

The analytical method is found to be very simple, rapid, sensitive, selective and highly reproducible and therefore reliable for routine analysis for tin levels in canned foods and energy drinks where fast and less cumbersome method of analysis is of paramount important. The results of the study show that the tin levels in 67% of the samples are within the permissible limit for canned foods (250 mg/kg) and energy drinks (150 mg/kg) allowed by World Health Organisation, yet there is the need to monitor the levels of tin from time to time by relevant agencies to ensure the quality and safety of these products for human consumption.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing Interest

Authors have declared that no competing interests exist among them.

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