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THE STUDY OF TRACE ELEMENTS IN SOME TYPES OF DRINKING TEA BY DIFFERENT ANALYTICAL METHODS

In Egypt, drinking tea is very common and popular. The measurements of toxic elements and heavy metals become essential for human biosystems. Trace elements are of great importance in physiological processes of all living organisms. Instrumental neutron activation analysis (INAA) as well as flame atomic absorption spectrometry (FAAS) have been applied to determine the concentrations of the trace elements of interest. Three types of tea leaves from different sources (Ceylon, Kenya and India) in addition to five different fabricated tea samples collected from Egyptian local market have been investigated. The concentrations of fifteen elements (Ce, Mn, Co, Fe, Cu, Zn, Ni, Rb, Ru, Pb, Cs, La, Ce, Eu and Hf), whose ranges were from 0.05 to 1283.10 ppm, were determined. The data obtained prove that there is a broad agreement between both techniques used. The elements' concentrations in all local samples investigated are in the same range as the foreign tea samples. The comparison of our results with those reported in other studies testifies to the same range of the concentrations measured as well.

1. INTRODUCTION

Accurate information on the concentrations of trace metals in different environmental samples is required for a variety of reasons, including their role in health, nutrition and environmental pollution. A variety of inorganic elements from food or beverages are assimilated by human body. In addition to many elements, which are essential to human health and are found in agricultural products, some elements toxic to human biosystem may also come from polluted soil, fertilizer and pesticides.

It is therefore important to investigate the daily intake of trace elements from various diets. Trace elements prove to be indispensable for physiological processes in all living organisms. Besides some essential elements, necessarily required for their ex-

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istence and appropriate growth, plants can also take up a number of toxic elements from the soil. The soil as well as the climate affect the characteristics of the leaves and therefore the distribution of the inorganic constituents which derive from the soil, the fertilizer and the specific agricultural technique used [1]. The determination of minor and trace elements in tea leaves is very important due to high tea consumption by Egyptian population. During the past years, extensive studies of trace elements in various tea leaves have been carried out [2]–[7]. MIERZWA et al. [2] determined the concentrations of Ba, Cu, Fe, Pb, and Zn in tea leaves by slurry sampling electrothermal atomic absorption and liquid sampling inductively coupled plasma atomic emission spectrometry. Also FARDY et al. [4] and SURTIPANTI et al. [6] determined respectively manganese in the Australian diet as well as toxic and essential element concentrations in foodstuffs from local market using the NAA.

In the present paper, a spectroscopic determination for popular kinds of tea leaves of different origins was carried out using instrumental neutron activation analysis (INAA) and flame atomic absorption techniques (FAAS).

2. ANALYTICAL METHODS

2.1. SAMPLING

It is well known that tea as a plant is not produced in Egypt, because the weather is not suitable for its growing. Due to this fact as well as a high consumption of tea as a popular drink, every year Egypt imports a huge quantity of tea from abroad. Of these types of tea being imported, three types coming from different sources (India, Ceylon and Kenya) are investigated. In addition to these types, there are five other kinds being collected from local market. During packing, local types of tea (which originally come from imported ones) are enriched with different additives to give them a special flavour. Five samples have been prepared. Sample 1, El-Arosa tea, imported from Kenya and packed in Egyptian company, sample 2, El-Jawhara, imported from Ceylon and packed in Egypt, sample 3, Blue tea pot, imported from India and packed in Egypt, sample 4, Lipton, is a special mixture of Indian, Kenyan and Ceylon fine tea types, and sample 5, Brooke Bond, is a collection of topic types of tea from Kenya, India, Ceylon and Indonesia packed in Egypt.

2.2. SAMPLE PREPARATION AND IRRADIATION FOR INAA

Five samples from each of previously described local types were selected for the experimental work. About 0.1 g samples of dried tea leaves were packed in a clean aluminium foil. The standard materials V-8, V-10 [8] (the Rye flower and Hay, respectively) were also packed in aluminium foil. For measuring the thermal flux in the

site of irradiation, 0.03 g gold sheet was wrapped in the same type of Al-foil. In addition, an empty Al-foil of the same weight was used to measure the background level.

The whole samples were irradiated for 4 h at the second Egyptian reactor with thermal neutron flux of $5.9 \times 10^{13} \text{ n/cm}^2 \cdot \text{s}$. The samples were left to cool for 5 days, and then analyzed using non-destructive neutron activation technique which becomes an appropriate method owing to the rapid developments of high-resolution hyperpure germanium detector. The crystal has a volume of 76.11 cm^3 and full width at half maximum of 1.9 keV at 1332.5 keV γ -ray line of ^{60}Co , the peak to Compton ratio was 55.6 and detection efficiency was 30%.

The absolute efficiency of the HPGe spectrometer and the energy calibration up to 3 MeV were determined using the multigamma ray standard sources [9]. The samples were positioned individually at about 10 cm in front of the detector, and the accumulating time was two hours for good statistics, this work was repeated weekly for one month.

The detector was in conjunction with a 4096 computerized multichannel analyzer using Mastro 32 version software analyzer. The trace elements in the aluminium envelopes of the specimens were considered as background γ -ray lines to be subtracted in the case of interference with those of the investigated samples [10]. Activation equations were applied in order to determine the element contents, and the neutron flux was determined by single comparative technique using gold foil [11]. The most intensive and well resolved γ -ray lines for each element shown in the γ -ray spectra of the samples under investigation were used for the calculation of element.

2.3. SAMPLE DISSOLUTION FOR FAAS

In the FAAS method, complete dissolution of the samples was carried out using an open acid digestion procedure and HNO_3 . For this purpose, 0.5 g of dried sample was treated with 20 cm^3 of HNO_3 and heated in a beaker on a hot plate until it evaporated almost completely. Further 10 cm^3 of HNO_3 were added to the residue and again evaporated almost completely to ensure the complete dissolution of a sample. Redistilled water was then added to the residue, which could be dissolved to a clear solution. The solution was then transferred into a 50 cm^3 flask and completed to volume.

2.4. INSTRUMENTAL USED

A Perkins-Elmer FAAS (model 2380) equipped with a burner-nebulizer for an air-acetylene flame was utilized with the flow rates of air and acetylene gas reaching $9.35 \text{ dm}^3/\text{min}$ and $0.7 \text{ dm}^3/\text{min}$, respectively. The light sources were hollow cathode lamps for all elements except for zinc, cadmium and lead (electrodeless discharge lamp). The wavelengths were selected after consideration of line sensitivity and freedom from spectral interference based on manufactures guide of FAAS. The instru-

mental parameters and wavelengths are listed in table 1. Absorbance was read on the peak height mode.

Table 1

Instrumental facilities and operating parameter

Elements	Wavelength (nm)	Slit bandwidth (nm)
Mn	279.5	0.2
Cu	324.7	0.7
Ni	232.1	0.2
Pb	283.3	0.2
Cd	228.8	0.7
Zn	213.9	0.7
Co	240.7	0.2

3. RESULTS AND DISCUSSION

3.1. NEUTRON ACTIVATION ANALYSIS

The accuracy of the system is defined as a full agreement between the result obtained and a true value measured [12]. So, to examine the accuracy of the results obtained by INAA, the certified reference (v-10) HAY, from International Atomic Energy Agency, Vienna, Austria (IAEA), was used. Table 2 gives the comparison between the present work and the certified values, also, calculation of the recoveries percentage, where

$$\text{recoveries} = \frac{\text{concentrations in the present work} \times 100\%}{\text{concentration in the certified value}}$$

Table 2

Comparison between the results of the present work and certified values of the standard material HAY, also the percentage recoveries

Element	Certified ⁽⁸⁾ (ppm)	Present work (ppm)	Recoveries (%)
Zn	24	23.6±1.18	98
Sc	14	13.8±0.69	98.5
Rb	7.6	6.9±0.35	90.7
Mo	0.9	0.8±0.04	88.8
Hg	13	11.8±0.59	90.7
Fe	185	190.0±9.5	102.7
Cr	6.5	5.8±0.29	89
Co	0.13	0.15±0.01	115.3

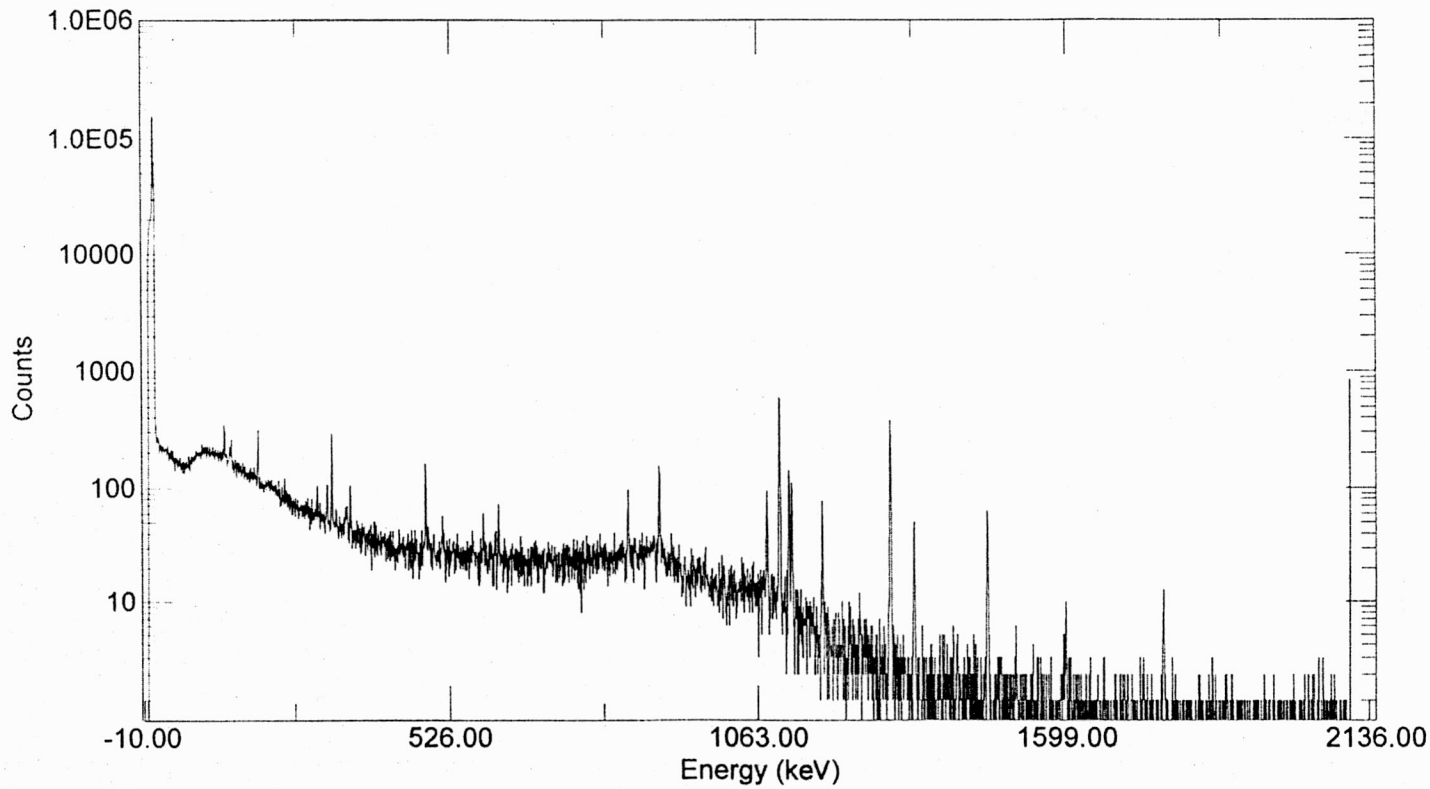


Fig. 1. The gamma-ray single spectrum for the ore tea sample of Kenya

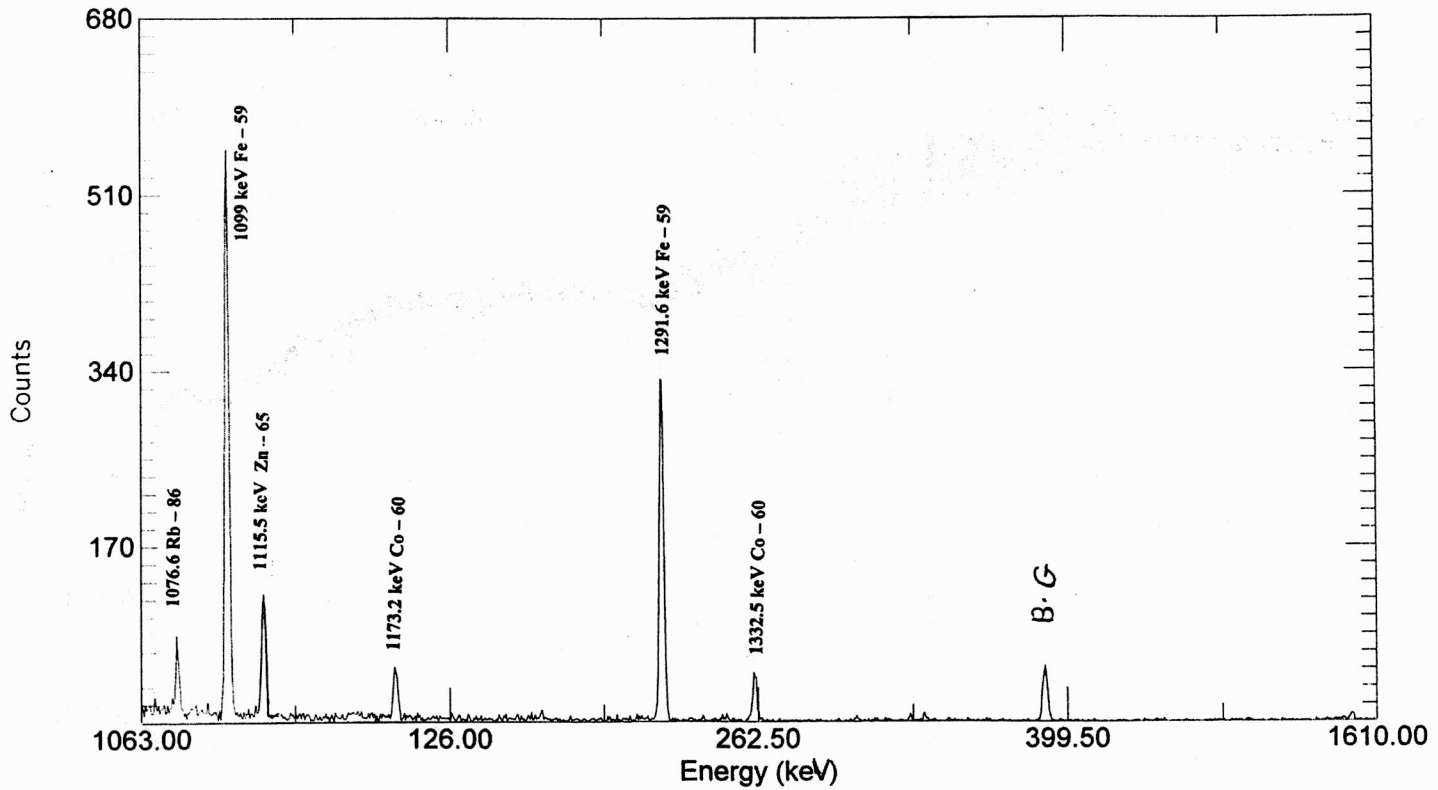


Fig. 2. The partial gamma-ray spectrum of the fabricated tea sample (1)

It is clear that there is good agreement, and the recoveries of more than 90% have been achieved. Determination of metal levels in tea leaves can play a key role in detecting a trace element in plant leaves. The ore and fabricated tea brands' samples can be employed on a semiquantitative basis in comparative studies to trace the sources of hazard effect on the human body.

A total of 11 elements have been identified using INAA technique which depends mainly on the abundance of each element as well as on the neutron capture cross-section for the isotopes of interest. All these elements are long-lived isotopes which are measured by a delayed technique.

The collected gamma-ray spectra have been analyzed qualitatively to identify the constituents of each sample. The gamma-ray single spectrum for the Kenyan sample is shown in figure 1. Table 3 lists the concentrations of 11 elements measured in the raw tea samples of Ceylon, Kenya and India. From this table it is evident that in the Ceylon raw tea sample the concentrations of trace elements are lowest, while in the raw Kenyan tea sample – the highest. The raw Indian tea sample is characterized by the medium concentrations of trace elements.

Table 3

Elemental analysis (in ppm) for different types of raw tea samples

Element	Ceylon	Kenya	India
Cr-51	0.83±0.04	6.39±0.32	7.41±0.37
Fe-59	–	1283.10±64.16	1168.09±58.40
Co-60	–	0.42±0.02	0.13±7×10 ⁻³
Zn-65	5.20±0.26	12.84±0.64	2.61±1.31
Rb-86	63.69±3.18	93.76±4.69	93.72±4.69
Ru-103	–	1.25±0.06	–
Cs-134	–	0.39±0.02	–
La-140	2.75±0.14	5.14±0.26	2.79±0.14
Ce-141	–	0.18±9×10 ³	–
Eu-152	–	0.06±3×10 ⁻³	–
Hf-181	–	0.11±5×10 ⁻³	0.3±0.02

It is worth mentioning that the trace elements detected in these samples depend on their origin, rain, wind, fertilizer, natural or industrial contamination and different interfering human activities which may have profound effects on the resulting product. The partial gamma-ray spectrum of the fabricated tea sample 1 is shown in figure 2.

Table 4 gives mean concentrations of the trace elements tested in some samples of fabricated brands of tea collected from the local Egyptian market. The errors in the determinations obtained are mainly statistical errors of the net area under the peak. In fact, the errors due to the basic nuclear determinations used in this work have no significant influence in comparison with the errors in the net peak area calculations.

Table 4 proves that the concentrations of the elements being determined have fluctuated in various kinds of tea samples. Such elements as chromium and hafnium were found in sample 1, but they were absent in sample 5.

Table 4

Elemental analysis (in ppm) of fabricated tea samples from local market of Egypt

Element	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Cr-51	3.59±0.18	2.01±0.10	5.35±0.27	6.75±0.34	—
Co-60	0.29±0.01	0.13±7×10 ³	0.25±0.01	0.60±0.03	—
Fe-59	1194.06±59.70	1267.06±63.35	983.90±49.19	718.22±35.91	—
Zn-65	19.39±0.97	27.21±1.36	33.32±1.67	28.39±1.42	32.21±1.61
Rb-86	69.61±3.48	34.76±1.74	60.69±3.03	51.75±2.59	47.98±2.39
Ru-103	1.18±0.06	—	—	—	—
Cs-134	—	—	0.11±6×10 ³	—	0.58±0.03
La-140	2.24±0.11	3.31±0.17	8.95±0.45	7.03±0.35	7.14±0.36
Ce-141	0.56±0.03	—	—	—	—
Eu-152	0.05±3×10 ³	—	0.07±4×10 ³	0.08±4×10 ³	0.06±3×10 ³
Hf-181	012±6×10 ³	0.06±3×10 ³	0.15±8×10 ³	0.31±0.02	—

3.2. FLAME ATOMIC ABSORPTION

A) *Analytical calibration curves.* In order to construct the calibration curves for such elements as Mn, Cu, Ni, Pb, Cd, Zn and Co, a series of standard solutions were prepared from a stock solution containing varying concentration of the individual elements. The solutions were nebulized into the flame under optimum conditions (table 1).

B) *Detection limits and precision.* The standard deviation of the 10 successive measurements for the blank sample and the slope of the standard (aqueous) calibration curve were used to calculate the measurement limits for the elements [13]. The pH value in the blank solution was adjusted as well as in the sample solution.

Table 5

Detection limits (DL) and precision of measurement (RSD)

Element	DL (ppm)	RSD (%)
Mn	0.01	0.596
Cu	0.0596	0.822
Ni	0.047	0.918
Zn	0.0014	0.634
Pb	0.16	1.05
Cd	0.0154	1.26

The precision of the absorbance determination calculated as the relative standard deviation (RSD) of ten determinations of the absorbance for the spectral lines is also given in table 5. Fluctuations originate namely from the nebulization process.

C) *Results of analysis.* The results of analysis obtained for the tea samples under investigation using FAAS are given in table 6. It can be seen that the concentrations of the determined elements fluctuate. The absence of nickel and lead in the raw samples may be due to the fact that these two elements are present in the additive material or due to the industrial technique. The values of manganese concentration in various tea samples are higher, which may reflect the content of that element in the soil or environment where the plants grow [14]. Finally, full agreement has been found between the sensitivity measured and the sensitivity reported in literature [15].

Table 6

Concentration of elements (in ppm) in different kinds of tea samples using FAAS

Element	Concentration in the samples in ppm								Sensitivity	
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Indian	Kenyan	Ceylon	Measured	Literature
Cd	nd	nd	nd	nd	nd	nd	nd	nd	0.048	0.025
Cu	33.75	267.5	21.25	17.5	15	15	6.25	17.5	0.148	0.1
Mn	1100	765	740	712.5	840	65.5	607.5	240	0.069	0.05
Ni	5	5	10	16.25	16.25	nd	nd	nd	0.146	0.12
Pb	12.5	12.5	12.5	12.5	25	nd	nd	nd	0.55	0.5
Zn	19	27	33.75	28.75	32.5	2.5	12.5	5	0.0183	0.02

nd – not detected.

Table 7

Comparison between element concentrations range (in ppm) in different types of tea samples from different countries determined by various analytical methods

Element	Analytical instrument	Egyptian fabricated tea in the present work	Taiwan tea [3]	Indonesian tea [16]
1	2	3	4	5
Na-24	INAA	–	24.40–78.10	–
Mg-27	FAAS	–	2670–3210	–
K-40	INAA	–	16900–20300	–
Sc-46	INAA	–	0.017–0.027	0.10–0.88
Ca-47	INAA	–	4460–6280	0.28–0.94
Cr-51	INAA	2.01–6.75	–	0.18–1.03
Mn-56	INAA	240.00–1100.00*	932–1064	–
Fe-59	INAA	718.22–1283.10	–	161.33–894.11
Co-60	INAA	0.13–0.60	0.17–0.37	0.06–0.18
Cu-64	FAAS	6.25–267.50*	9.60–20.90	–
Zn-65	INAA, FAAS	2.50–33.75*	18.90–22.10	11.17–33.50

1	2	3	4	5
Ni-65	FAAS	5.00-16.25*	3.00-6.10	-
Se-75	INAA	-	-	3-60 ppb
As-76	INAA	-	-	0.14-1.50
Br-82	INAA	-	-	2.82-4.95
Rb-86	INAA	34.76-61	-	50.42-144.61
Ru-103	INAA	0-1.18	-	-
Pb-109	FAAS	12.50-25.00*	0.90-1.69	-
Cd-115	INAA	-	0.035-0.041	-
Sb-24	INAA	-	-	0.09-0.88
Cs-134	INAA	0.11-0.58	-	0.07-0.38
La-140	INAA	2.24-8.95	-	0.13-3.84
Ce-141	INAA	0-0.56	-	-
Eu-152	INAA	0.05-0.08	-	0.01-0.06
Hf-181	INAA	0.06-0.30	-	-
Hg-197	INAA	-	-	10-80 ppb

* Flame atomic absorption (FAAS).

Table 7 gives the comparison between the concentration ranges determined by means of various analytical methods in the present work and in the studies of different types of tea from different countries (Taiwan [3] and Indonesia [16]). From this table it is clear that Na-24, Mg-27 and K-40 are present in the tea fabricated in Taiwan, and absent in Egyptian and Indonesian tea. Also, Sc-46 and Ca-47 are present in the Taiwanese and Indonesian tea and absent in the tea fabricated in Egypt. Cr-51, Fe-59, Rb-86, Cs-134, La-140 and Eu-152 are found in Egyptian and Indonesian tea, but are not detected in the Taiwanese tea. Co-60 and Zn-65 are the only trace elements which are present in all sample types; approximately within the same range.

4. CONCLUSIONS

Analytical methodology for the determination of trace elements in part per million (ppm) or less is somewhat limited. Activation analysis is generally considered to be a useful method for trace inorganic species in such low concentrations. This technique still has a unique characteristic of being non-destructive. With FAAS it is possible to determine both qualitatively and quantitatively some metals in the range of few micrograms per gram or cubic centimeter ($\mu\text{g/g}$ & $\mu\text{g/cm}^3$) of the test sample. A particular advantage of this method is that interference with other elements is greatly reduced, even if present in relatively large amounts.

From the results obtained full agreement has been found between the data obtained by INAA and FAAS for zinc concentration which gives great confidence for the results of the two techniques.

It is also evident from tables 3, 4 and 6 that some of these elements cause an adverse effect on the body owing to accumulation of these elements due to a daily intake. For example, chromium causes carcinoma, also lead causes many diseases which are dangerous for the human body, e.g. carcinoma, nephritis, anaemia and headache. Nickel is responsible for carcinoma and myocarditis, copper causes cirrhosis, manganese – Parkinson's disease, and zinc – hepatosplenomagalay and aneamia [17].

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MIKROPIERWIASTKI W NIEKTÓRYCH TYPACH HERBATY OZNACZONE RÓŻNYMI METODAMI

W Egipcie herbata jest bardzo popularnym napojem. Wiadomo, że rośliny razem ze składnikami pokarmowymi pobierają również związki toksyczne i metale ciężkie. Niektóre metale ciężkie są niezbędne do prawidłowego metabolizmu wszystkich organizmów żywych. Dlatego oznaczenie ich stężenia jest takie ważne. Analiza aktywacyjna instrumentalna i płomieniowa spektroskopia emisyjna atomowa posłuży do oznaczenia stężeń interesujących nas mikropierwiastków. Badano trzy typy liści z krzewów herbacianych pochodzących z Cejlonu, Kenii i Indii oraz pięć różnych typów herbaty wyprodukowanej w Egipcie z importowanych liści. Oznaczono w nich 15 mikropierwiastków (Ce, Mn, Co, Fe, Cu, Zn, Ni, Rb, Rn, Pb, Cs, La, Ce, Eu i Hf), których stężenia mieściły się w zakresie 0,05–1283,10 ppm. Otrzymane wyniki świadczą, że obie techniki pozwalają otrzymać porównywalne stężenia. Stężenia mikropierwiastków w badanych próbkach herbaty z lokalnego egipskiego rynku i w próbach herbat importowanych mieściły się w tym samym zakresie. Dane te są zgodne z wynikami otrzymanymi przez innych autorów.