Determination of Toxic and Trace Elements in the Milk by Using X-Ray Fluorescence Technique

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الخلاصة:

تم تحديد العناصر السامة والنزرة في انواع مختلفة من الحليب ومن مناطق ومواقع مختلفة من العراق وذلك بأستخدام تقنية الأشعة السينية المتفلورة ، وقد تم ايجاد تركيز العناصر الآتية في نماذج الحليب وهي:-

Cl , K , Ca , Ti, Mn , Fe, Ni , Cu, Zn , Br, Rb ,Sr.

Abstract:

Radioisotope induced XRF technique have been used and applied to determine the elemental contents of some types of Iraqi milk.

The characteristic X-Rays were excited by Fe-55 and Cd-109 annular sources.

The concentration of Cl , K , Ca , Ti, Mn , Fe, Ni , Cu, Zn , Br, Rb and Sr are determined.

Introduction:

Milk is an important natural food for infants children as well as adults. On the basis of the data on the elements concentration in milk it is possible to determine the mean contents of the elements in diet of children. A certain number of elements are essential for life, while there are toxic elements and heavy metals which demonstrate their toxic influence on human health as well as for growth already at small concentration. Some disease are clearly correlated with the imbalance of trace elements in the human body. A review of the data of trace elements in milk was prepared and a summary of these data was presented in Tyengar ' report published in 1978 (1). Marhora and Vasconcelios (2) have analyzed milk and determined the concentration of eight elements by the Neutron Activation

Analysis(NAA) method, while Al-Jobori and his group have determined eleven elements by the NAA method(3). The aim of this study is to determine the mineral composition of different samples cattle milk, collected from different locations of Iraq using x-ray fluorescence (XRF) technique using radioactive excited sources.

The XRF technique has proved to be a simple ,quick, reliable one and capable for multi-trace element analysis in biology and medicine (4). Important properties of x-ray spectra are their simplicity for a given element and the fact they are reproduced homogenously from one element to another.

All of the elements can be identified by their x-ray spectra, which are modified in a regular way in passing from one element to it ' s neighbor in the periodic table.

X-ray emission spectrum of the elements present in a sample is excited by primary x-ray sources and the characteristic lines emitted are detected in a crystal spectrometer. The wavelengths of the lines can be readily be determined with sufficient accuracy to make identification lines for all elements in the sample by comparison with tables of known lines for all the elements.

The energy absorbed in the sample is so small that it is not heated and consequently the analysis is nondestructive(5).

Experimental:

Sample preparation:-

Natural cattle milk samples were collected from different regions (6 Governorates from north to south) of Iraq directly in polyethylene containers. The precaution, as recommended by IAEA, were followed to avoid contamination of samples(8).

The samples were dried by freeze-drying and grind to a fine homogenate powder using well cleaned agate mortar. A round (140 gm) milk powder was powder was obtained in average per one liter milk.

A given mass (a bout 0.5 gm) of each homogenous dry sample for analysis is taken and pressed to a pellet from (21 mm. in diameter and a thickness of about 1-1.5 mm.) about 0.145 gm/ cm mass per unit area.

Geometry arrangement:-

One of the major advantages of XRF method is the range of acceptance angles for the excitation source-sample and the sample-detector-to minimizing the scattered radiation from the sample to the detector (6). To accomplish this, a very specific geometry for the source-sample-crystal-detector is employed Fig.(1).
It was found that the most effective source to sample and sample to detector distance are (9 mm.) and(16 mm.) respectively.

Primary X-rays sources:-

The conventional sources for monochromatic primary x-ray are the electron capture radioisotopes which are almost ideal(6). Characteristic x- rays were excited by Cd-109 (18.5 x 10 Bq) and Fe-55 (30.7 x 10 Bq) annular radio isotopic sources (emitting Ag and Mn x-rays in the energy range of 22.2 KeV and 5.89 KeV respectively) have been used.

Counting:-

The x-rays emitted by the element of interest have energies in the range of up to a few tens of KeV, therefore the detector the employed was Si(Li) semiconductor detector (SL 30180 Canberra mode) of (30 mm.) active area and (3 mm.) drift depth with a (Be) window (0.254 mm.) thick, and resolving power of (179 eV) for (5.9 KeV) Fe-55(Mn- K_{α}), connected to a preamplifier. The pulses for the preamplifier were amplified by spectroscopic amplifier.

The analog signals were converted in a (4096)channels pulse height analyzer (Laben-Master 4000) . To minimize the statistical errors as possible as can, a (7200 sec) counting time was found sufficient to assure good statistics. With our geometry has to be found to gives the best peak to background ratio and consequently best efficiencies for elements of interest and their lowest minimum detection limits (MDL).

The criterion used for detection limit for each element was Currie' s equation(7):

$$D.L = (2.71 + 3.29)\, B.G \times \frac{Concentrat\,ion}{Net\ area}$$

Were B.G is the number of background counts.

Results and Discussion:

The XRF technique has been used to calculate the concentrations of all elements "visible" from their fluorescence lines. The x-rays fluorescence spectroscopy give the relative concentration for different elements in a straight forward way. The x-ray spectrums of milk samples (Cow milk as an example) is shown in Fig.(2). The elemental content concentrations in the analyzed samples were calculated in ppm dry weight using relative comparison method.

Accuracy and prelusion of analysis were further established by simultaneous analysis of IAEA standard reference milk powder samples (A-11 and IAEA-153) and Orchard leaves (standard no.1571). Standard sample (A-11) was used as a standard model. By applying the relative comparison method for material content of the sample with other elements identified in samples, the values tabulated in Table(1) were obtained a clear good agreement was realized between the international values obtained for concentration with our experimental results.

The concentration of elements found in sheep , cow , goat , buffalo and camel milk are given in Tables(2-6) respectively . Table(7) shows the mean values of concentration and their ranges obtained in these investigations for each elements in milk samples. From that it can be seen that the concentration of (12) elements have been determined in the cattle milk.

These elements are Cl , K , Ca , Ti, Mn , Fe, Ni , Cu, Zn , Br, Rb and Sr while Mo not appear in all samples and it ' s concentrations were below the detection limit. From Tables(2-6) one can see that the values of the concentration of the milk taken from the same kind of cattle are differ from one region to another . From the results we conclude the following:

a) Sheep milk is rich with Ca , Mn, and Sr elements.
b) Cow milk is rich with Ca , Ti and Ni elements.
c) Goat milk is rich with Ti , Cu and Rb elements.
d) Buffalo milk is rich with Mn and Zn elements.
e) Camel milk is rich with Cl , K and Br elements.

From the Tables of the concentrations of the elements determined for the samples under the study we can say that poisonous elements such as Pb , Cd , Hg , Ni and As did not appear in the milk samples.

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Table(1): Analysis using (XRF) technique were performed by comparing experimental results with the international values of (A-11) standard sample.

Elements	Milk powder(IAEA/153)		Orchard Leaves(No.1571)	
	Present Work Mean ± S.D	Certified Value	Present Work Mean ± S.D	Certified Value
Cl %	1.25 ± 0.11	0.99	0.09 ± 0.03	0.07

K %	1.72 ± 0.13	1.76	1.49 ± 0.12	1.47
Ca %	1.18 ± 0.15	1.28	2.01 ± 0.23	2.09
Zn (ppm)	40.31 ± 1.42	39.6	25.01 ± 1.33	25.0
Br (ppm)	13.13 ± 1.75	12.7	11.73 ± 1.14	10.0
Rb (ppm)	13.10 ± 1.66	13.2	12.04 ± 1.37	12.0

Table(2): The elemental concentration in and detection limits for sheep milk from different location of Iraq.

City	Cl %	K %	Ca %	Ti	Mn	Fe	Ni	Cu*	Zn	Br	Rb	Sr
Nainwa	0.29	0.68	1.67	-----	0.29	4.58	0.028	98.15	29.80	47.15	5.27	38.79
Salah-aldin	0.46	0.87	1.31	60.86	0.51	5.57	0.023	157.51	33.33	50.02	5.65	32.93
Diyala	0.58	0.79	1.31	91.41	0.40	3.63	0.047	131.01	20.89	38.23	3.39	40.67
Najaf	0.87	0.24	1.16	17.15	0.22	3.72	0.018	349.43	4.70	56.74	6.18	60.66
D.L	0.17	0.13	0.11	13.29	0.16	1.34	0.018	77.60	2.71	4.88	1.05	5.87

* Concentration in µgm/gm.

Table(3): The elemental concentration and detection limits for cow milk from different location .

City	Cl %	K %	Ca %	Ti	Mn	Fe	Ni	Cu	Zn	Br	Rb	Sr
Nainwa	0.78	1.43	1.35	70.67	0.22	2.72	---------	0.275	44.509	15.47	4.292	3.79
Salah-aldin	0.31	1.34	1.26	91.41	------	3.54	0.016	0.411	32.39	6.298	1.52	6.34
Diyala	0.52	1.44	1.18	91.66	0.28	2.209	0.0795	0.154	35.595	22.35	2.012	5.19
Wasit	0.52	1.36	1.19	65.52	0.32	2.28	0.0985	0.518	40.755	21.53	5.28	5.95
Karbala	0.59	1.06	1.11	71.51	0.27	2.07	0.0575	0.098	36.74	19.07	3.31	6.47
D.L	0.29	0.16	0.041	37.88	0.16	0.88	0.016	0.085	6.9	1.87	0.78	1.85

Table(4): The elemental concentration and detection limits for goat milk from different location .

City	Cl %	K %	Ca %	Ti	Mn	Fe	Ni	Cu	Zn	Br	Rb	Sr
Salah-aldin	0.6	1.07	1.12	82.1	0.29	2.9	0.029	0.225	11.24	78.064	6.026	32.04
Diyala	0.96	1.11	1.002	129.86	0.145	2.3	0.022	0.307	14.38	47.085	6.134	28.15
Wasit	0.95	1.52	0.93	55.59	0.295	3.61	0.019	0.356	30.13	37.74	8.601	31.8
Najaf	1.19	1.75	1.36	40.28	------	2.35	0.024	0.408	22.28	61.75	6.03	34.63
D.L	0.26	0.17	0.096	30.1	0.145	1.43	0.018	0.211	4.14	5.66	1.06	6.37

Table(5): The elemental concentration and detection limits for Buffalo milk from different location

City	Cl %	K %	Ca %	Ti	Mn	Fe	Ni	Cu	Zn	Br	Rb	Sr
Diyala	0.22	0.88	1.38	74.93	0.22	2.13	0.068	0.287	49.36	12.22	1.2	28.29
Wasit	0.32	0.37	0.64	38.67	0.51	4.21	0.019	0.11	93.35	11.50	1.58	2.33
D.L	0.14	0.15	0.09	29.42	0.15	0.84	0.019	0.11	10.33	3.94	0.64	1.39

Table(6): The elemental concentration and detection limits for Camel milk from different location .

City	Cl %	K %	Ca %	Ti	Mn	Fe	Ni	Cu	Zn	Br	Rb	Sr
Nainwa	1.38	1.52	0.91	----------	0.11	2.94	----------	0.53	40.79	89.26	2.35	19.13
Najaf	1.68	1.62	0.885	56.8	0.315	1.9	0.03	0.128	30.34	125.58	5.2	28.40
D.L	0.56	0.17	0.11	37.2	0.11	0.95	0.02	0.18	10.34	4.62	0.54	5.74

Table(7): Elemental concentration range and mean value in milk samples

Element	Cow milk		Sheep milk		Goat milk	
	Range	Mean± S.D	Range	Mean ±S.D	Range	Mean ±S.D
Cl %	0.31- 0.78	0.545 ± 0.16	0.29 – 0.875	0.55 ± 0.24	0.60 – 1.19	0.925 ± 0.24
K %	1.067 – 1.44	1.328 ± 0.15	0.24 – 0.875	0.64 ± 0.28	1.07 – 1.75	1.36 ± 0.23
Ca %	1.117 – 1.35	1.219 ± 0.088	1.16 – 1.67	1.36 ± 0.21	0.93 – 1.36	1.103± 0.18
Ti	65.52-91.66	78.15 ± 12.42	17.15-91.41	56.47± 37.32	40.28-129.8	76.96 ± 39.27
Mn	0.22 – 0.32	0.272 ± 0.041	0.22 – 0.51	0.353 ± 0.12	0.145-0.295	0.245 ±0.086

Fe	2.209 – 3.54	2.564 ± 0.59	3.27 – 5.57	4.375 ± 0.904	2.3 – 3.61	2.79 ± 0.61
Ni	0.016-0.098	0.062 ± 0.035	0.018-0.047	0.029 ± 0.012	0.019-0.029	0.023± 0.011
Cu *	98.14-518.4	291.61 ±174.98	98.15-349.4	184.02 ±112.9	225.29-408	324.47 ±77.99
Zn	36.74-44.50	37.99 ± 4.71	4.70 – 33.33	22.18 ± 12.77	11.24-30.13	19.50 ± 8.46
Br	6.29 – 22.35	16.94 ± 6.52	38.23-56.74	48.03 ± 7.67	37.74-78.06	56.16 ±17.63
Rb	1.52 – 5.28	3.28 ± 1.58	3.39 – 6.18	5.122 ± 1.21	6.026-8.601	6.697 ± 1.27
Sr	3.79 – 6.47	5.548 ± 1.102	32.93-60.66	43.26 ± 12.05	28.15-34.63	31.65 ± 2.66

* Concentration in µgm/gm.

Continue

Element	Buffalo milk		Camel milk	
	Range	Mean ±S.D	Range	Mean ±S.D
Cl %	0.22 – 0.323	0.27 ± 0.072	1.38 – 1.68	1.53 ± 0.21
K %	0.37 – 0.88	0.625 ± 0.36	1.52 – 1.62	1.57 ± 0.07
Ca %	0.64 – 1.38	1.01 ± 0.52	0.885 – 0.91	0.89 ± 0.017
Ti	38.67 – 74.93	56.80 ± 25.64	----------	----------
Mn	0.22 – 0.514	0.367 ± 0.207	0.11 – 0.315	0.21 ± 0.14
Fe	2.13 – 4.21	3.17 ± 1.47	1.9 – 2.94	2.42 ± 0.73
Ni	0.019 – 0.068	0.044± 0.034	----------	----------
Cu *	110.29-287.01	198.65±124.98	128.67-530.89	329.78±284.41
Zn	49.36-93.35	71.35 ± 31.10	30.34-40.79	35.56±7.39
Br	11.50-12.22	11.86± 0.50	89.26-125.5	107.42±25.68

Rb	1.2 – 1.58	1.39 ± 0.26	2.35 - 20	3.77 ± 2.015
Sr	----------	----------	19.13-28.40	23.77 ± 6.56

* Concentration in µgm/gm.

Fig.(1): Scheme diagram of XRF spectrometer.