

Elemental Assessment of Various Milk Packs Collected From KPK, Pakistan

¹Ruqia Nazir, ²Muslim Khan, ¹Hameed Ur Rehman, ³Zubia Masood, ¹Muhammad Masab,
¹Rumana Saeed, ⁴Naila Gul, ⁴Faryal Saad, ¹Irum Parveen,
¹Fathma Shehnaz, ¹Muhammad Zakir, ⁴Noor-Ul-Akbar and ⁵Nelofer Jamil.

¹Department of Chemistry, Kohat University of Science and Technology (KUST),
Kohat-26000 Khyber Pakhtunkhwa, Pakistan

²Department of Chemistry, Karl Franzens University Graz, University Austria

³Department of Zoology, University of Karachi, Karachi-75270, Pakistan

⁴Department of Zoology, Kohat University of Science and Technology,
Kohat-26000 Khyber Pakhtunkhwa, Pakistan

⁵Department of Chemistry, Sardar Bahadur Khan Women University, Quetta, Pakistan

Abstract: Nine random milk samples were collected from different outlets in KPK, Pakistan and analyzed using Atomic Adsorption Spectrophotometer (AAS) to investigate the concentration of various heavy metals in them. Maximum concentrations of Nickel, Iron, Copper and Chromium were (Mention these Max. Conc.) in Every Day Milk, Dairy Pure, Dairy Queen, Good Milk, Chaika, Tarang and Olper Milk respectively. Public health significance and hazardous effects of the above mentioned metals were discussed below.

Key words: Milk samples, Heavy metals, Atomic Adsorption Spectrophotometer

INTRODUCTION

Catholic varieties and series of concentrations of metals are scattered everywhere in the nature. Although in human, most of metals have come through meal. However, not all consumed metals are retained, several pass straight through and lost in faeces while the remaining, firstly undergo absorbed and then lost via urine, sweat, bile excretion. Toxic metals are obstinate as pollutants in the environment and come to the forefront of dangerous constituents causing health threats in human. Among toxic metals Lead, Cadmium and Aluminium are the most important ones. Agricultural procedures and industrialization have resulted in increasing heavy metals concentration in water, air, soil and consequently, these metals are taken by various animals and plants in the food chain [1-4]. Milk and dairy products have been acknowledged all over the globe for their constructive influence on human health because they are quantitatively essential in the diet and their regular intake is suggested especially for youngsters where they provide a great sense of eating satisfaction due to their flavour and attribute sleek flavour as well as they are good resources of proteins, calcium mineral,

riboflavin, phosphorus, blood potassium, supplement A and supplement D [5,6]. Milk and milk products may contain variable amounts of different toxic contaminants [7]. The level of these harmful materials is an essential part of safety and quality of milk and milk items. Metals are widely unconfined in the environment and have two major roots: human activities and geological background [8]. About 38 micro and trace elements (such as Ca, Co, Cu, Cr, Fe, Mg, Mn, Mo, Na and Zn) in raw milk were reported from different regions of the world showing that the location has significant impact on the contents of many micro- and trace elements in milk [9,10]. In Pakistan, some of the milk and its products are produced from various native sources, however others are imported. Ca, K, Na, Mg, Cu, Fe, Mn, Zn, Cd, Cr, Pb and Ni were investigated from some high brands of milk manufactured in Pakistan [11, 12]. The jeopardy associated with the exposure to these toxic metals in food products had aroused widespread concern in human health. Critical and prolonged symptoms including nausea, vomiting, dizziness, diarrhoea, sleeping disorders, loss of appetite and reduced conception rate are the symptoms of heavy metal toxicity. Also, it connected to Alzheimer's, Parkinson's, autism, lupus, amyotrophic lateral sclerosis,

Corresponding Author: Ruqia Nazir, Department of Chemistry, Kohat University of Science and Technology (KUST),
Kohat-26000 Khyber Pakhtunkhwa, Pakistan.

cardiovascular disease, depressed growth, impaired fertility, nervous and immune system disorders [13, 14]. The mineral composition of milk and milk products has also been investigated and the micro-biological quality, such as microorganism occurrence has also been surveyed [15, 16]. But, the influence of technological treatments such as storage needs more experimentally examination. So, the present work was performed to determine the level of contamination of dairy products with some toxic heavy metals (lead, cadmium, aluminium and tin).

MATERIALS AND METHODS

Collection of Samples: Nine milk samples of different labels (such as nestle milk, olpers milk, good milk etc.) were collected from KPK Pakistan in their original packing, manufactured in various cities of Pakistan.

Preparation of Samples: 10ml of each milk sample was relocated to clean and acid washed china dish. The digestion of milk was carried out using nitric acid and hydrogen peroxide [12]. The digested samples were then filtered through Whitman filter paper=42 and diluted up to 25ml in graduated cylinder and then transfer into plastic bottle in order to avoid the entrance of tiny solid impurities (if any) in the suction pipe.

Analysis of the Prepared Samples: For the determination of Ni, Fe, Cd etc., the prepared samples were analysed using Atomic adsorption Spectrophotometer (AAS).

RESULTS AND DISCUSSION

Analysis of milk samples showed their contamination by some heavy metals scums, revealing a wide range of hazardous influences on human health. All metals turned to be toxic to human body, beyond certain limits. This could be applied to essential metals like Fe; Mn and Se, as well as to non-essential metals that all examined dairy product samples contained iron, nickel, cobalt and chromium and there were substantial changes in the levels of all these elements but the change befell may be significant or non-significant. From the below mentioned results, it is evident that all examined milk samples were contaminated with fickle amounts of heavy metals. Higher values of these metals in milk may have been arisen from contamination during handling, exposure and processing [17]. The heavy metal contents vary widely due to many factors such as, characteristics of the manufacturing practices, possible contamination coming from the equipment during the process and differences between species [18,19]. Oxidation of equipment and containers

were affected by some parameters such as quality of raw materials of containers and equipment, pH. Augmentation of oxidation will increase the metal contents of milk samples. Metal contents of original milk will consequently affect the metal intensities in milk powder and metalloids like Co and Cd compounds. The arithmetical analysis is specified.

Chromium: Chromium was discovered by Vaquelin in 1798 [20, 21]. It is the 21st utmost abundant mineral in earth crust and found in combine state either with iron, oxygen or both in the form of chromite ore [22]. Its hurtful effects on humans, animals and plants health are partially correlated to the valence state, among all states, chromium (VI) is the most toxic and carcinogenic than others ones [23]. Out of nine milk sample three samples i.e. dairy queen, dairy pure and every day milk were reported to have chromium in them; the recorded values were 2.103 ± 0.000 , 0.414 ± 0.000 and 0.391 ± 0.000 individually. It's vital to create awareness among people about the hazardous effect of chromium in milk packs. Nonetheless, Chromium plays a vital role in boosting up of insulin for typical glucose metabolism. Chromium deficiency can cause glucose intolerance, cardiovascular disease and impaired fertility [24, 25]. Irrespective of its necessity a slight high dose may cause lung cancer, acute renal tubular necrosis and renal failure [26, 27].

Nickel: Deposits of nickel ores are mainly located in Canada, Australia, Indonesia and Cuba. Very low concentration of nickel is found naturally [28]. It is highly toxic in volatile state. It has been found that the toxicity of nickel increases with increase in its solubility [29]. Nickel toxicity occurs in animals and plants due to intake of contaminated water. Excessive doses of nickel up to 0.5 g may be toxic for humans [30, 31]. All analysed milk samples i.e. good milk, nestle milk, dairy queen, olpers, chaika, every day milk, tarang, dairy pure and qudrat milk contained nickel up to 0.286 ± 0.008 some extent, the analysed data were 0.245 ± 0.012 , 0.254 ± 0.002 , 0.248 ± 0.008 , 0.280 ± 0.003 , 0.273 ± 0.004 , 0.286 ± 0.008 , 0.273 ± 0.008 , 0.269 ± 0.008 and 0.263 ± 0.014 respectively. It has been observed that nickel contents in milk shows considerable variations [32].

The variation of mineral contents in milk samples is greatly influenced by lactation periods, seasons, climate and type of feeding [33-35]. It is an essential element for animals as well as for humans and plays physiological role in the body. It is a nonspecific activator of enzymes. However; excessive intake of nickel is associated with many complications such as dermatitis and itching of fingers, hands and forearms etc. [36].

Iron: Iron is an abundant element on earth in contrast to zinc [37, 38] and is a biologically essential component for all living organism [39, 40]. In the human body, it exists in two complex forms, heme and non-heme compounds. All living organisms require iron for the synthesis of its oxygen carrying proteins [41, 42]. Almost two-thirds of the body's iron is found in the haemoglobin present in circulating erythrocytes [43]. Recorded data showed that the iron concentrations were 1.588 ± 0.009 , 0.287 ± 0.008 , 0.385 ± 0.003 , 0.214 ± 0.005 , 0.361 ± 0.003 , 1.170 ± 0.019 , 1.004 ± 0.000 , 11.99 ± 20.47 and 0.020 ± 0.003 in good milk, nestle milk, dairy queen, Olphers, Chaika, every day milk, Tarang, dairy pure and qudrat milk respectively. Undouble iron is one of the most essential mineral or heavy metal yet; its high intake leads to serious disorders. Iron typically damage cells in the heart, liver and elsewhere, which can cause substantial adverse effects, including coma, shock, liver failure, adult respiratory distress syndrome, long-term organ damages and even death [44].

Copper: Copper is relatively the 8th most abundant element in the earth crust. It is assessed that copper atoms comprise 22 parts per million [ppm] of the Earth's crust.

Copper is the essential metal to all living organisms as a trace dietetic mineral because it is a crucial constituent of the respiratory enzyme complex i.e. cytochrome-c oxidase. The main regions where copper is found in humans are liver, muscle and bone [45]. All nine milk sample varied in copper concentration which may be due to lactation factor, type of feeding, manufacturing process etc. About 0.389 ± 0.001 , 0.380 ± 0.000 , 0.389 ± 0.000 , 0.384 ± 0.000 , 0.386 ± 0.001 , 0.383 ± 0.000 , 0.387 ± 0.000 , 0.385 ± 0.000 and 0.376 ± 0.000 copper concentration was recorded from good milk, nestle milk, dairy queen, olphers, chaika, every day milk, tarang, dairy pure and qudrat milk correspondingly. In spite of the fact that copper is essential for living organism it can also cause toxicity. Free copper may generates reactive oxygen species such as hydrogen peroxide, superoxide and the hydroxyl radical. These may damage proteins, lipids and DNA. Copper iedus (copper toxicity), deposition of copper in the cornea is an indication that the body is not metabolizing copper properly, may result in blindness [46].

It's evident from the above investigation that even the intake of essential metal in excess amount is precarious for health (Table and figure 1 show the concentration of metals detected in milk samples).

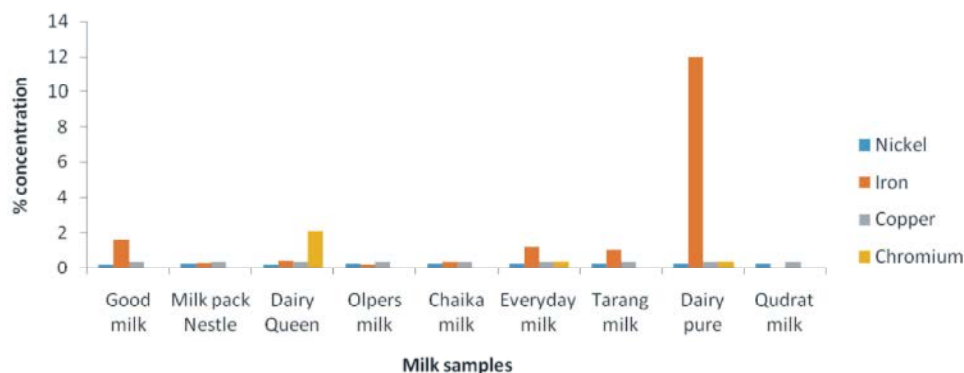


Fig. 1: Graph showing %concentration of various heavy metals in Milk Packs.

Table 1: Statistical analytical of results of heavy metals estimation in the examined milk samples

Samples of Milk	Mean concentration of nickel \pm S.D	Mean concentration of Iron \pm S.D	Mean concentration of Copper \pm S.D	Mean concentration of Chromium \pm S.D
Good milk	0.245 ± 0.012	1.588 ± 0.009	0.389 ± 0.001	N.D
Milk pack Nestle	0.254 ± 0.002	0.287 ± 0.008	0.380 ± 0.000	N.D
Dairy Queen	0.248 ± 0.008	0.385 ± 0.003	0.389 ± 0.000	2.103 ± 0.000
Olpers milk	0.280 ± 0.003	0.214 ± 0.005	0.384 ± 0.000	N.D
Chaika milk	0.273 ± 0.004	0.361 ± 0.003	0.386 ± 0.001	N.D
Every day milk	0.286 ± 0.008	1.170 ± 0.019	0.383 ± 0.000	0.414 ± 0.000
Tarang milk	0.273 ± 0.008	1.004 ± 0.000	0.387 ± 0.000	N.D
Dairy pure	0.269 ± 0.008	11.99 ± 20.47	0.385 ± 0.000	0.391 ± 0.000
Qudrat milk	0.263 ± 0.014	0.020 ± 0.003	0.376 ± 0.000	N.D

CONCLUSIONS

Investigations revealed that extremely toxic heavy metals (Cr, Ni and Cu) were detected. It is necessary to warn about the hazardous effects of these toxic metals on both child and adult. The feasting of such milk is considered as an additional source of exposure to these metals beside their direct sources from air, water and plants. Therefore, a strict and regular monitoring of heavy metals contamination of milk and other milk products is recommended.

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REFERENCES

1. Salah, F.A.A.E., I.A. Esmat and A.B. Mohamed, 2013. Heavy metals residues and trace elements in milk powder marketed in Dakahlia Governorate. *Inter. Food Res. J.*, 20(4): Pages Make references like this style.
2. Ahmad, W.M.S., 2002. Studies on heavy metal pollution in poultry farms in relation to production performance. PhD thesis, Faculty of ??, Faisalabad University pakistan.(Revise this reference??).
3. Ukhun, M.E., J. Nwazota and F.O. Nkwocha, 1990. Level of toxic mineral elements in selected foods marketed in Nigeria, *Bulletin of Environmental Contamination and Toxicology*, 44: 325-330.
4. El-Batanouni, M.M. and G. Abo El-Ata, 1996. Metals in food. In the Proceedings of Food Born Contamination and Egyptian's Health Conference, Mansoura, Egypt. pp: 11-25. Make references like this style.
5. SalahFathy Ahmed Abd- El Aal, 2012. Assessment of Toxic Heavy Metals in Some Dairy Products and the Effect of Storage on its Distribution, *Journal of Ameri Sci.*, 8(8).
6. Yuzbas_I, N., E. Sezgin, Z. Yildirim and M. Yildirim, 2009. Changes In Pb, Cd, Fe, Cu and Zn Levels during The Production of Kasar Cheese, *J. Food Qual.*, 32: 73-83.
7. Ataro, A., R.I. McCrindle, B.M. Botha, C.M.E. McCrindle and P.P. Ndibewu, 2008. Quantification of Trace Elements in Raw Cow's Milk by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), *Food Chem.*, 111: 243-248.
8. Loska, K., D. Wiechula and I. Korus, 2004. Metal Contamination of Farming Soils Affected by Industry, *EnviInterl*, 30: 159-165.
9. Dobrzański, Z., R. Kolacz, H. Górecka, K. Chojnacka and A. Bartkowiak, 2005. The content of microelements and trace elements in raw milk from cows in the Silesian region, *Polish J. Environ. Stud.*, 14(5): 685-689.
10. Nwankwoala, A., S. Oduyungbo, K. Nyavor and N. Egiebor, 2002. Levels of 26 elements in infant formula from USA, UK and Nigeria by microwave digestion and ICP-OES, *Food Chem.*, 77(4): 439-447.
11. Perveen, F., M. Mumtaz and T.H. Usmani, 2005. Estimation of metal contents in different varieties of milk available in Karachi city, *J. Chem Soc. Pak.*, 27(6): 611-614.
12. Jaffar, M., M.H. Shah, N. Shaheen, A. Khaliq, S.R. Tariq, S. Manzoor and M. Saqib, 2004. Pre-and post-expiry metal levels in canned dry milk, *Nut Food Sci.*, 34(2): 65-71.
13. Yuzbas_I, N., E. Sezgin, M. Yildirim and N. Yildirim, 2003. Survey of Lead, Cadmium, Iron, Copper and Zinc in Kasar Cheese, *Food Chem.*, 20(5): 464-469.
14. Jake, D., 2005. A Report on Alzheimer'S Disease and Current Research, *Alzheimer Society of Canada*, 13: 645-655.
15. Lante, A., G. Lomolino, M. Cagnin and P. Spettoli, 2006. Content and Characterization of Minerals in Milk and in Crescenza and Squacquerone Italian Fresh Cheeses by ICP-OES, *Food Control*, 17: 229-233.
16. Han, B.Z., Y. Meng, M. Li, Y.X. Yang, F.Z. Ren, Q.K. Zeng and M.J.R. Nout, 2007. A Survey on the Microbiological and Chemical Composition of Buffalo Milk in China, *Food Control*, 18: 742-746.
17. Onianwa, P.C., G.C. Ikadeh and S.E. Nweze, 1996. Aluminium contents of some raw and processed Nigerian foods, *Food chemistry*, 8(4): 351-353.
18. Caggiano, R., S. Sabia, M. D'Emilio, M. Macchiato, A. Anastasio and M. Ragosta, 2005. Metal levels in fodder, milk, dairy products and tissues sampled in ovine farms of southern Italy, *Environmental Research*, 99: 48-57.
19. Yuzbasi, N., E. Sezgin, M. Yildirim and N. Yildirim, 2003. Survey of lead, cadmium, iron, copper and zinc in Kasar cheese, *Food Chemistry*, 20(5): 464-469. (Ref. 13 and 19 were repeated, revise with text and references S. Nos. in the text and list??).
20. Baruthio, F., 1992. Toxic effects of chromium and its compounds. *Biological Trace Elem. Res.*, 32: 145-153.

21. Barceloux, D.G., 1999. Chromium, *Clin. Toxicol.*, 37: 173-194.
22. Barnhart, J., 1997. Occurrences, Uses and Properties of Chromium, *Regul. Toxicol. Pharma*, 26(1): 3-7.
23. Jadhav, S.D. and Z.R. Turel, 1994. Determination of chromium in aquatic environment by substoichiometric thermal neutron activation analysis, *J. Radioana. Nucl. Chem.*, 177(1): 185-191.
24. Chang, X. and D.N. Mowat, 1992. Supplemental chromium for stressed and growing feeder calves, *J. Anim. Sci.*, 70(2): 559-565.
25. Page, T.G., L.L. Southern, T.L. Ward and D.L. Thompson, Jr., 1993. Effect of chromium picolinate on growth and serum and carcass traits of growing-finishing pigs, *J. Ani. Sci.*, 71: 656-662.
26. Ellis, E.N., B.H. Brouhard, R.E. Lynch, E.B. Dawson, R. Tisdell, M.M. Nichols and F. Ramirez, 1982. Effects of hemodialysis and dimercaprol in acute dichromate poisoning, *Journal of Toxicology-Clin. Toxicol.*, 19(3): 249-58.
27. Saryan, L.A. and M. Reedy, 1988. Chromium determinations in a case of chromic acid ingestion, *J. Anal. Toxicol.*, 12(3): 162-164.
28. Bastarache, E., 2003. Nickel Compounds Toxicity. <http://ceramicmaterials.com/ceramat/education/263.html>
29. Goyer, R., 1991. Toxic Effects of Metals, In: Casarett and Doull's Toxicology, 4th ed. Pergamon Press, New York. pp: 623-680. Make references like this style.
30. Daldrup, T., K. Haarhoff and S.C. Szathmary, 1983. Toedliche nickel sulphate intoxication. *Beri. Gerich. Med.*, 41: 141-144.
31. Sunderman, F.W.Jr., B. Dingle, S.M. Hopfer and T. Swift, 1988. Acute nickel toxicity in electroplating workers who accidentally ingested a solution of nickel sulfate and nickel chloride, *Am. J. Indust. Med.*, 14: 257-266.
32. Koops, J., H. Klomp and D. Westerbeek, 1982. Spectrometric determination of nickel with furiloxime, with special reference to milk and milk products and to the release of nickel from stainless steel by acidic dairy products and by acidic cleaning, *Nether. Milk Dairy J.*, 36: 333-353.
33. Tiscornia, E., 1977. Attualiconoscencesullacomposizionechimica del latte alimentare, Parte Terza. *Riv. Soc. Ital. Sci. Aliment*, 6: 423-449.
34. Varo, P., M. Nuortamo, E. Saari and P. Koivistoinen, 1980. Mineral element composition of finish foods, VII. Dairy products, eggs and margarine, *Acta Veterina. Scandina*, 22: 115-126.
35. Ford, L.E., M.L.A. Schroeder, M.A. Bland, K.S. Bleas and K.J. Scott, 1986. Keeping quality of milk in relation to the copper content and temperature of pasteurization, *Dairy Res.*, 53: 391-406.
36. Nielsen, G.D., 1992. Oral challenge of nickel-allergic patients with hand eczema. In: *Advances in Environmental Sciences and Technology*. Eds., Nieboer, Complete author name?? and J.O. Nriagu. 25: Nickel and Human Health: Current Perspectives, pp: 201-210, Wiley, New York. Make references like this style.
37. Wood, R.J., 2005. A. Ronnenberg Iron. In: M.E. Shils, M. Shike, A.C. Ross, B. Caballero and R.J. Cousins editors. *Modern Nutrition in Health and Disease*. 10th ed. Baltimore: Lippincott Williams and Wilkins, pp: 248-70.
38. Quintero-Gutiérrez, A.G., G. González-Rosendo, J. Sánchez-Muñoz, J. Polo-Pozo and J.J. Rodríguez-Jerez, 2008. Bioavailability of heme iron in biscuit filling using piglets as an animal model for humans, *Int. J. Biol. Sci.*, 4: 58-62.
39. Aisen, P., C. Enns and M. Wessling-Resnick, 2001. Chemistry and biology of eukaryotic iron metabolism, *Int J. Biochem Cell Biol.*, 33: 940-59.
40. Lieu, P.T., M. Heiskala, P.A. Peterson and Y. Yang, 2001. The roles of iron in health and disease, *Mol Aspects Med.*, 2: 1-87.
41. McDowell, L.R., 2003. 2nd ed. Amsterdam: Elsevier Science; Minerals in Animal and Human Nutrition, pp: 660.
42. Hurrell, R.F., 1997. Bioavailability of iron, *Eur J. Clin. Nutr.*, 51: S4-8.
43. Washington, D.C., 2001. National Academy Press; IOM. Institute of Medicine. Iron. In: *Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium and Zinc.*, pp: 290-393.
44. Cheney, K., C. Gumbiner, B. Benson and M. Tenenbein, 1995. Survival after a severe iron poisoning treated with intermittent infusions of deferoxamine, *J. Toxicol. Clin. Toxicol.*, 33(1): 61-6.
45. Johnson, M.D. and E. Larryed, 2008. "Copper". *Merck Manual Home Health Handbook*. Merck Sharp and Dohme Corp., a subsidiary of Merck and Co., Inc. Retrieved 7 April 2013.
46. Brewer, G.J., 2010. Copper toxicity in the general population, *Clin. Neurophysiol.*, 121(4): 459-60.