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Determination of heavy metal content in fruits and fruits juices consume in urban areas of Lucknow, India

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Abstract
Heavy metals normally occur in nature and are essential to life but can become toxic through accumulation in organisms. Heavy metals also cause adverse effect in human metabolic system, skin diseases, heart problems, etc. Arsenic, cadmium, chromium, copper, nickel, lead and mercury are the most common heavy metals. Sources of heavy metals include mining, industrial production, smelters, petrochemical plants, pesticide production, chemical industry, untreated sewage sludge and diffuse sources such as metal piping, traffic and combustion by-products etc. Fruits and vegetables are highly nutritious form as key food commodity in the human consumption. These food commodities are reported to be contaminated with toxic and health hazardous chemicals. The present study focuses on the toxicity level of heavy metals among the common man in urban areas and the level of heavy metal contamination in fruits and fruit juices in five sites of Lucknow district Bangla Bazar, Alambagh, Charbagh, Telibagh, and Rajajipuram.
Trace levels of heavy metals such as Fe, Pb, Cu and Cd were determined in 5 different varieties of fruits sample such as apple, banana, pomegranate, grapes and orange purchased from local market of Lucknow. The study shows that, the urban consumers are at greater risk of purchasing fresh fruits with high levels of heavy metals beyond the legally permissible limits. Fe (450.21 µg/g) and Pb (224.4 µg/g) concentration was found higher than other metal.

Keywords: Heavy metals, Fruits, Contamination

1. Introduction

1.1 Heavy metals

Heavy metals are not biodegradable and have the potential for accumulation in the different body organs leading to unwanted side effects (Jarup, 2003 and Sathawara *et al*., 2004) [4, 16]. Emissions of heavy metals from the industries and vehicles may deposit on the vegetable surfaces during their production, transport and marketing. Mercury, lead and cadmium are toxic heavy metals because of their ability to travel long distances in the atmosphere (Zahir *et al*., 1999) [26]. Rapid and unorganized urban and industrial developments have contributed to the elevated level of heavy metals in the urban environment of developing countries such as Egypt (Radwan and Salama, 2006) [14], Iran (Maleki and Zarasvand, 2008) [7], China (Wong *et al.*, 2003) [24] etc.

1.2 Deleterious heavy metals in fruits

Heavy metals are widely dispersed in the environment. Heavy metal contamination of the food items is one of the most important aspects of food quality assurance (Marshall, 2004). Heavy metals are among the major contaminants of food supply and may considered the most important problem to our environment (Zaidi *et al.*, 2005) [25]. They enter the food chain and occur in different concentrations in human food (Roychowdhary *et al.*, 2003). Fruits and vegetables are highly nutritious and form as key food commodity in the human consumption. They are highly perishable due to their low shelf life. Recently, (Sharma *et al*., 2008a and Sharma *et al*., 2008b) [18, 19] have reported that atmospheric deposition can significantly elevate the levels of heavy metals contamination in vegetables commonly sold in the markets of Varanasi, India. These food commodities are reported to be contaminated with toxic and health hazardous chemicals. The uptake of heavy metals in vegetables are influenced by some factors such as climate, atmospheric depositions, concentrations of heavy metals in soil, nature of soil and the degree of maturity of the plants at the time of harvest (Lake *et al*., 1984 and Scott *et al*., 1996) [6, 17]. Chemicals like calcium carbide/ethephon and oxytocin are reportedly being used in fruit and vegetable mandis/farms for artificial ripening of fruits, increasing the size of fruits and vegetables respectively. The major contaminants found in fruit and vegetables are pesticide residues, crop contaminants such as aflatoxins, patulin, ochratoxin etc. and heavy metals. Moreover, direct aspiration of the fruit juices and milk can cause flame fluctuations and accumulation of solid deposits on the burner head (Bellido-Milla *et al*., 2000) [1].

1.3 Heavy metal in fruits is harmful to our tissue

The contamination of food with heavy metals is a serious problem. Heavy metals are taken up from the digestive tract and exhibit harmful influence on tissues. The uptake of heavy metals in human digestive tract usually does not exceed 5 to 10 % of their concentration in food. On the other hand, some metals exhibit toxic properties in relatively low doses and moreover their concentration in tissues gradually increases due to accumulation process (Beckett *et al.*, 2007) [2]. The excessive content of these metals in food is associated with a number of diseases such as cardiovascular, kidney, nervous as well as bone diseases (WHO, 1992, WHO, 1995, Steenland and Boffetta, 2000) [22, 23]. Abnormal ingestion causes neurological anomalies, hepatic and renal disturbances (Underwood, 1977) [21]. Dietary intake of heavy metals causes carcinogenesis, mutagenesis and teratogenesis (IARC, 1993 and Pitot and Dragan, 1996) [3, 12].

1.4 Regulations

Regulations have been set up in many countries and for different industrial set up to control the emission of heavy metals, which is very important for the routine monitoring and risk assessment and regulation of environment. Regular survey and monitoring programmes of heavy metal contents in foodstuffs have been carried out for decades in most developed countries (Jorhem and Sundstroem, 1993, Pennington *et al*., 1995, Milacic and Kralj, 2003 and Saracoglu *et al*., 2009) [5, 15, 10, 11]. Care should be taken in order to reduce pollution at water source points, improve post harvest handling, enhance better coordination in fresh crops trading system to improve food safety standards, improve sanitary conditions for the city food markets and increase awareness in consumers and policy makers on the toxicity of heavy metal contamination in the food intake. (Mahdavian and Somashekar, 2008) [8]. The study focus on biomonitoring contamination of heavy metals Fe, Pb, Cu and Cd in different fruit samples such as apple, banana, pomegranate, grapes and orange collected from the selected urban areas of Lucknow such as Bangla Bazar, Alambagh, Charbagh, Telibagh and Rajajipuram. The study was done to detect the heavy metal content in fruit and fruit juices in order to assure a significant improvement in food safety.

2. Materials and Methods

2.1 Study Area and Sample Collection

Fresh fruit samples including oranges, banana, pomegranate, grapes and apple were collected from the five main sites of Lucknow city namely Bangla Bazar, Alambagh, Charbagh, Telibagh, and Rajajipuram. Sampling was done randomly from different retailers and vendors within these sites (Fig.10:11).

2.2 Sample Preparation

The collected fruit samples were thoroughly washed and rinsed with distilled water. The samples were then sliced to small pieces and oven dried at 150º C for 48 hours. The dried samples were then grounded into a fine powder form and stored in a fresh plastic polythene bag ready for digestion (Fig.12:13).

2.3 Sample Digestion

2.3.1 Nitric acid-Perchloric acid digestion

One gram of sample was placed in a 250 ml digestion tube and 10 ml of concentrated HNO_3 and $HClO_4$ was added Zheljazkov and Nielson (1996) [27]. The sample was heated for 45 min at 90ºC and then the temperature was increased up to 150ºC after that the sample was boiled for at least 8 hrs until a clear solution was obtained. Concentrated digestion mixture was added to the sample (5 ml was added at least three times) and digestion occurred until the volume reduced to about 1 ml. The interior walls of the tube were washed down with a little distilled water and the tube was swirled throughout the digestion to keep the wall clean and prevent the loss of the sample. After cooling, 5 ml of 1% HNO_3 was added to the sample. The solution was filtered with Whatman no. 42 filter paper and < 0.45 lm Millipore filter paper. It was then transferred quantitatively to a 25 ml volumetric flask by adding distilled water.

2.3.2 Sample digestion of fruit juices

Atomic Absorption Spectroscopic Standard solutions for Zn, Fe, Cu, Mn, Co, Cr and Ni were purchased from Fisher Scientific Company, USA. Working standard solutions were prepared by diluting the stock solution. All solutions were prepared with double distilled deionised water obtained by filtering distilled water through a Milli - Q purifier system (Millipore, Direct- Q 5, France) immediately before use (Fig.14:15). Samples were mineralized with 65% HNO_3, Merck Suprapure, and Perchloric acid ($HClO_4$). Items were kept in a clean place to avoid contamination. Sample digestion and preparation of analytic solution for AAS prior to quantization of analytic by Atomic Absorption Spectrometry, it is usually necessary to destroy the organic matrix and bring the element into clear solution. For this reason the juice sample was first digested with chemicals where the organic matrix of juice was destroyed and left the element into a clear solution. 'Wet Digestion' method (12-15) used in the study. 90 ml fruit juices sample taking in a 250 ml conical flask and 10 ml digestion mixture (HNO_3 and $HClO_4$). Digestion was completed in 90 minutes at 120°C. When cool, the mixture was diluted to a 30 ml volume with 2 N HNO_3 dilution mixtures.

3. Results and Discussion

Fruits are the important sources of nutrients and offer advantages over dietary supplements, because of low cost and wide availability. In daily diet of fruits have been strongly associated with reduced risk for some forms of cancer, heart disease, stroke and other chronic ailments. The study is aimed to trace the level of heavy metal in different types of fruits and fruit juices which are selected from the urban market of Lucknow, India (Fig 10:11). The result shows that the fresh fruits found with high levels of heavy metals beyond the legally permissible limits as defined by the Indian Prevention of Food Adulteration Act, 1954. It must be noted here that these norms are less strict International Standards. Iron level permitted for food is 15 mg/kg according to (Turkish Food Codex Anonymous Regulation 2002). WHO has established a provisional tolerable weekly intake for lead of 0.025 mg/kg of body weight. Permissible limit of Cd is 0.01 mg/g, according to Food Additive Organization/World Health Organisation 1999. Fe and Cd concentration was found higher than other metal (Table.5:7). In all the sample of juices, the concentration of Fe is the highest while Cd is lowest. Concentration of heavy metals Fe, Cd, Cu, Pd found in sample of fruits apple, banana, pomegranate, grapes, orange are as follows in the (Fig 1:5). In all the sample of fruits, the concentration of Fe and Pb was the highest while Cd is lowest (Table.1:4).

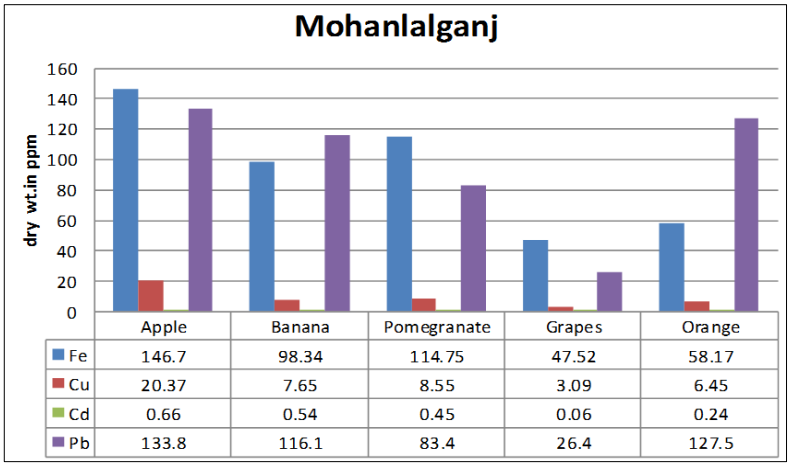

Fig 1: Concentration of heavy metals in fruits collected from Mohanlalganj Market, Lucknow (ppm)

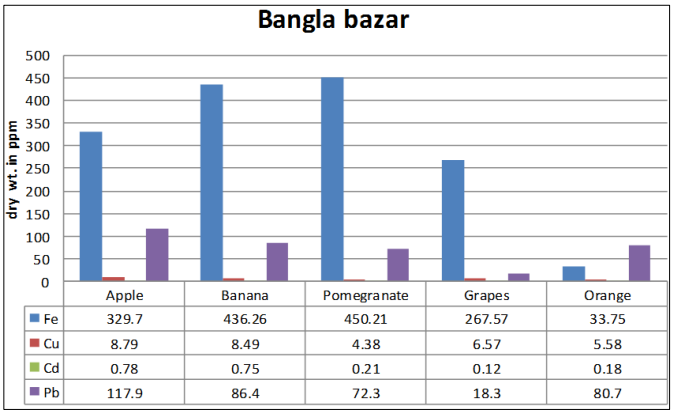

Fig 2: Concentration of heavy metals in fruits collected from Bangla Bazar Market, Lucknow (ppm)

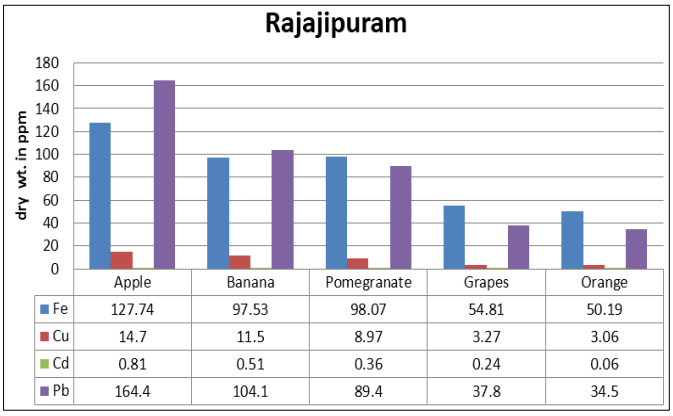

Fig 3: Concentration of heavy metals in fruits collected from Rajajipuram Market, Lucknow (ppm)

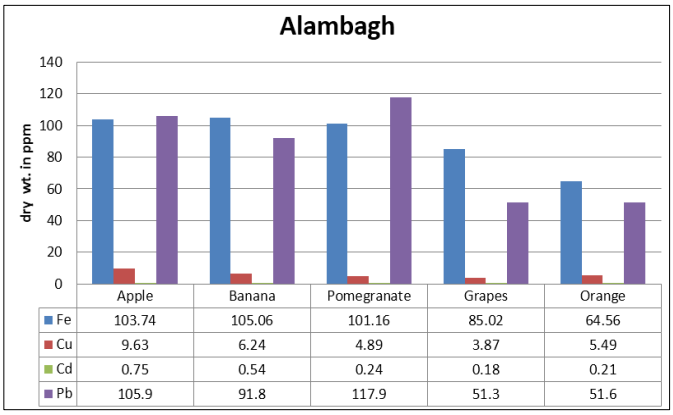

Fig 4: Concentration of heavy metals in fruits collected from Alambagh Market, Lucknow (ppm)

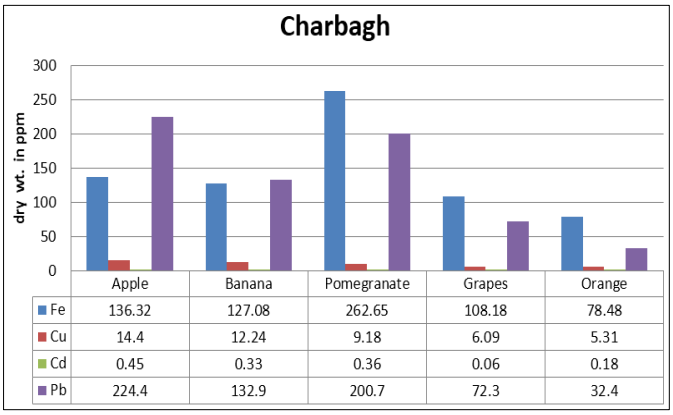

Fig 5: Concentration of heavy metals in fruits collected from Charbagh Market, Lucknow (ppm)

The highest and lowest concentration of heavy metals Fe, Cd, Cu, Pd in fruit samples in different urban areas of lucknow city are shown in the following Tables:-

Table 1: Fe concentration in fruits

Fe	Highest concentration of metal in (µg/g)	Lowest concentration of metal in (µg/g)
Apple	Bangla bazar-329.7	Alambagh-103.74
Banana	Bangla bazar-436.26	Rajajipuram-97.5
Pomegranate	Bangla bazar-450.21	Rajajipuram-98.07
Grapes	Bangla bazar-267.57	Mohanlalganj-47.52
Orange	Charbagh-78.48	Bangla bazar-33.75
Permissible limit	15 µg/kg	

Table 2: Cd concentration in fruits

Cd	Highest concentration of metal in (µg/g)	Lowest concentration of metal in (µg/g)
Apple	Mohanlalganj-20.37	Bangla bazar-8.79
Banana	Charbagh-12.24	Alambagh-6.24
Pomegranate	Charbagh-9.18	Bangla bazar-4.38
Grapes	Charbagh-6.09	Rajajipuram-3.24
Orange	Mohanlalganj-6.45	Rajajipuram-3.06
Permissible limit	0.1µg/g	

Table 3: Cu concentration in fruit

Cu	Highest concentration of metal in (µg/g)	Lowest concentration of metal in (µg/g)
Apple	Rajajipuram-0.81	Charbagh-0.45
Banana	Bangla Bazar-0.75	Charbagh-0.33
Pomegranate	Mohanlalganj-0.45	Bangla Bazar-0.21
Grapes	Rajajipuram-0.24	Mohanlalganj-0.06
Orange	Mohanlalganj-0.24	Rajajipuram-0.06
Permissible limit	4 mg/kg	

Table 4: Pb concentration in fruits

Pb	Highest concentration of metal in (µg/g)	Lowest concentration of metal in (µg/g)
Apple	Charbagh-224.4	Alambagh-105.9
Banana	Charbagh-132.9	Bangla Bazar-86.4
Pomegranate	Charbagh-200.7	Bangla Bazar-72.3
Grapes	Charbagh-72.3	Banal Bazar-18.3
Orange	Mohanlalganj-127.5	Charbagh-32.4
Permissible limit	0.025 µg/kg	

Concentration of heavy metals Fe, Cd, Cu, found in sample of fruit juices in different sites of Lucknow are as follows in the Tables:-

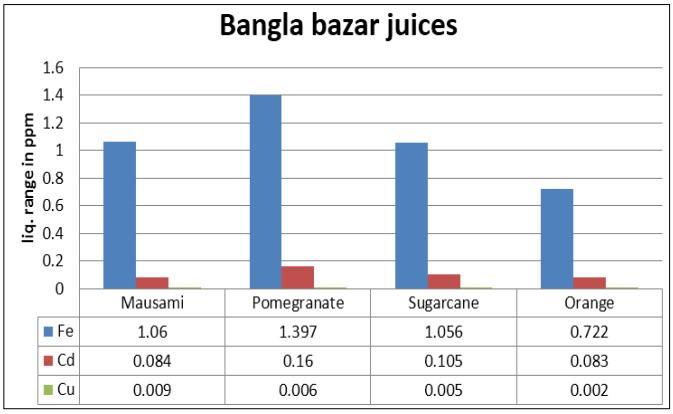

Fig 6: Concentration of heavy metals in fruits juices collected from Bangla Bazar Market, Lucknow in ppm

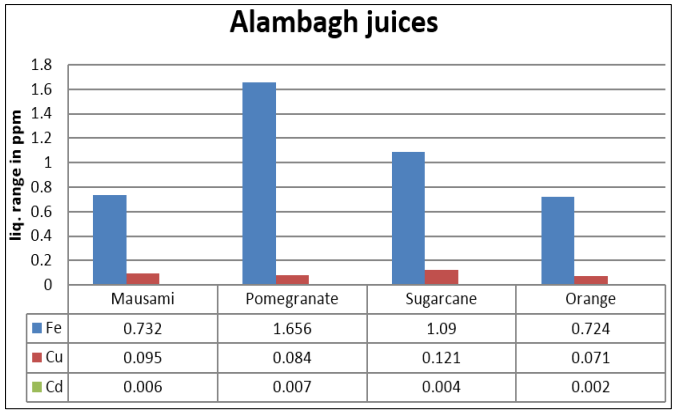

Fig 7: Concentration of heavy metals in fruits juices collected from Alambagh Market, Lucknow in ppm

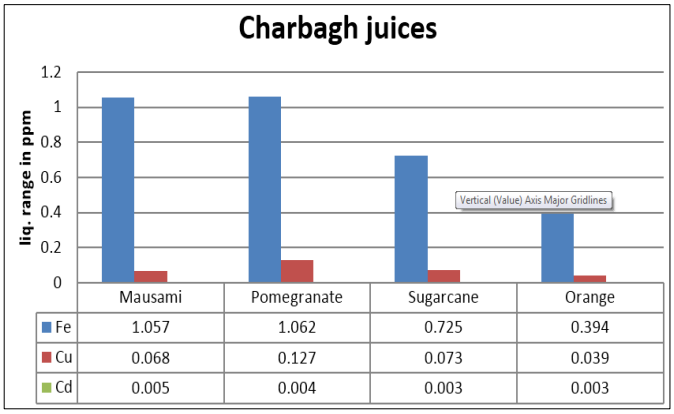

Fig 8: Concentration of heavy metals in fruits juices collected from Charbagh Market, Lucknow in ppm

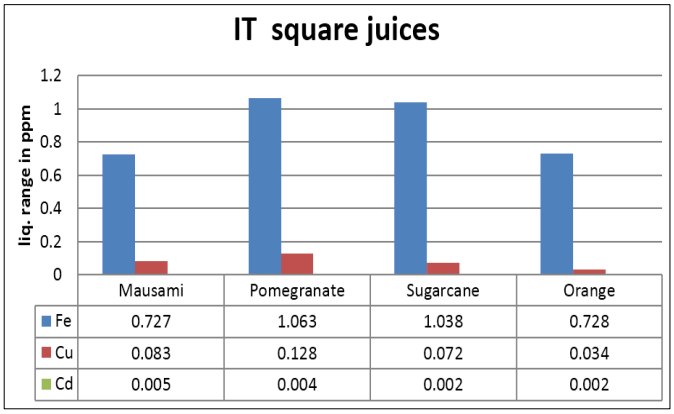

Fig 9: Concentration of heavy metals in fruits juices collected from IT Square Market, Lucknow in ppm

The highest and lowest concentration of metal in juices sample in different urban area of market in Lucknow city are as follows in the Tables:-

Table 5: Fe concentration in fruit juice

Fe	Highest concentration of metal in (µg/l)	Lowest concentration of metal in (µg/l)
Musami	Bangla bazar- 1.060	IT square- 0.727
Pomegranate	Alambagh- 1.656	Bangla bazar- 1.397
Sugarcane	Alambagh- 1.090	Charbagh- 0.725
Orange	IT square- 0.728	Charbagh- 0.394
Permissible limit	15 µg/l	

Table 6: Cu concentration in fruit juices

Cu	Highest concentration of metal in (µg/l)	Lowest concentration of metal in (µg/l)
Musami	Alambagh- 0.095	Charbagh- 0.068
Pomegranate	Bangla bazar- 0.160	Alambagh- 0.084
Sugarcane	Alambagh- 0.121	IT square- 0.072
Orange	Bangla bazar- 0.083	IT square- 0.034
Permissible limit	4 mg/kg	

Table 7: Cd concentration in fruit juices

Cd	Highest concentration of metal in (µg/l)	Lowest concentration of metal in (µg/l)
Musami	Bangla bazar- 0.009	IT square- 0.005
Pomegranate	Alambagh- 0.007	IT square- 0.004
Sugarcane	Bangla bazar- 0.005	IT square- 0.002
Orange	Charbagh- 0.003	Bangla bazar- 0.002
Permissible limit	0.1 µg/l	

Fig 10

Fig 11

Fig: 12

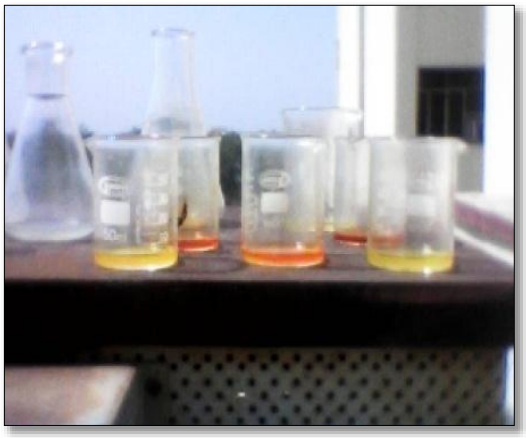

Fig 13

Fig 14

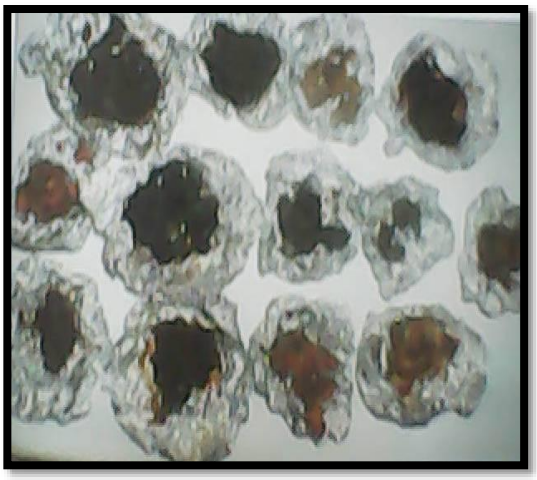

Fig: 15

4. Conclusion

Heavy metals are essential for biochemical and physiological functions and necessary for maintaining health throughout life. The problem arises when the irrigation water comes from sewage and industrial fed lakes, rivers or contaminated ground water. Some deleterious heavy metals elements are such as Lead (Pb), Cadmium (Cd), Mercury (Hg), Chromium (Cr) and Arsenic (As) are transmitted into fruits and other farm produces. Some of them are transited into high toxic compound. Keeping in view of the potential toxicity, persistent nature and cumulative behavior as well as the consumption of vegetables and fruits, there is necessary to test and analyze the food items to ensure that the levels of these heavy metal contaminants meet the agreed international requirements. The above study reveals the high exposure of fresh fruit products to the heavy metals Fe, Pb, Cu and Cd, which cause a problem to urban environment and ultimately to human food chain safety. In case of the fruit samples apple, banana, pomegranate, grapes, orange collected from the selected Lucknow markets Bangla Bazar, Alambagh, Charbagh, Telibagh, and Rajajipuram. Concentration of heavy metals Fe in fruit samples (in Pomegranate of Bangla bazar-450.21 µg/g) and Pb (in banana of Charbagh-132.9 µg/g) was found higher than other metals in all the five selected sites. Use of polluted water, bad practice in post harvesting handling of the fruit products with disregard to the food safety guidelines may have rise contamination levels of these fruit samples. The data will help to provide the status of heavy metal in fruits and fruit juices and also to assure food safety and to protect the user of fruits and fruit juices that might affect our health. It is concluded that, fruits and fruit juices consumed by urban consumers contains heavy metals more than their permissible levels.

5. Acknowledgements

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