



FTIR Estimation and Heavy Metals Accumulation in different Vegetables and Fruits

^{1*}Dr. Shobhana Ramteke, ¹Namrata Sahu, ²Dr. Bharat Lal Sahu

¹School of Studies in Environmental Science, Pt. Ravishankar Shukla University, Raipur-492010, CG, India

²Assistant Professor, Department of Chemistry, Guru Ghasidas Vishwavidyalaya Central University, Bilaspur, CG 495009, India.

Email – ¹shubrmk21@gmail.com, ²bharatred007@gmail.com

Abstract: In recent years, decreased cost, miniaturization and advances in computing power and data processing software have led to widespread introduction of Fourier-transform (FT) spectrometers across different disciplines. In this work, applications of FT infrared (FTIR) spectroscopy are summarized covering the analysis of fresh fruit and vegetables, and some of their processed products. Laboratory-based spectrometers, FTIR spectroscopy for high-resolution mapping, and portable, hand-held units for field work are described.

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. Trace levels of heavy metals such as As, Fe, Cr, Mn, Hg, Pb, Cd, Zn, and Cu. were determined in 18 different varieties of fruits and vegetable sample such as Kela, Papita, Anar, Ramphal, Jam, Ber, Sitafal, Nibu, Badam, Imli, Munga, Tiwara, Sem, Karela, Bhata, Kaddu and Sarsoo were collected from koudikasa Ambagarh Chowki block Rajnandgaon CG were discussed.

Key Words: Heavy metals ; FTIR estimation ; Identification ; Contamination.

1. INTRODUCTION:

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. [1] The present study focuses on the toxicity level of various contamination among the common man in urban areas and the level of contamination in fruits and vegetables in sites of Koudikasa, Ambagarh Chowki block, Rajnandgaon, CG India. 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. [2-4] The major contaminants found in fruit and vegetables are pesticide residues, crop contaminants such as aflatoxins, patulin, ochratoxin etc. and heavy metals.[5] Infrared (IR) is based on vibrational spectroscopy, and explores the relationship between the interaction of light with matter (solids, liquids, or gases) in that part for the electromagnetic spectrum beyond the visible (390–700nm) between 714 and 1×10^6 nm. The infrared region is sub-divided into three (near-, mid- and far-infrared). [6-9] The boundaries between the three are not consistent within the literature, and practically, are decided on by detector responses, i.e., the near infrared (NIR) ($14,000\text{--}4000\text{cm}^{-1}$ or 714–2500 nm), the mid-infrared (MIR) ($4000\text{--}400\text{cm}^{-1}$ or 2500–25000nm) and the far infrared region ($400\text{--}10\text{cm}^{-1}$ or $25,000\text{--}1 \times 10^6$ nm) [10-15]. NIR and MIR are the regions containing the greatest number of applications pertaining to fruit and vegetable crops and their processed products.[8] 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 [5-10].

2. MATERIALS AND METHODS :

SAMPLE COLLECTION OF FRUITS AND VEGETABLES

The sampling network for the fruits and vegetable collection is presented in **Figure 1**. Eighteen types of vegetables and fruits are collected from the arsenic and fluoride contaminated area, Koudikasa, Ambagarh Chowki block, Rajnandgaon, CG, India. (21°6'N & 81°2'E) as prescribed. The vegetables and fruits samples were kept in the polyethylene bottle and dried in an oven at 80°C for 12 hrs. The samples were milled and sieved out particles of ≤ 1 mm for the analysis [14].

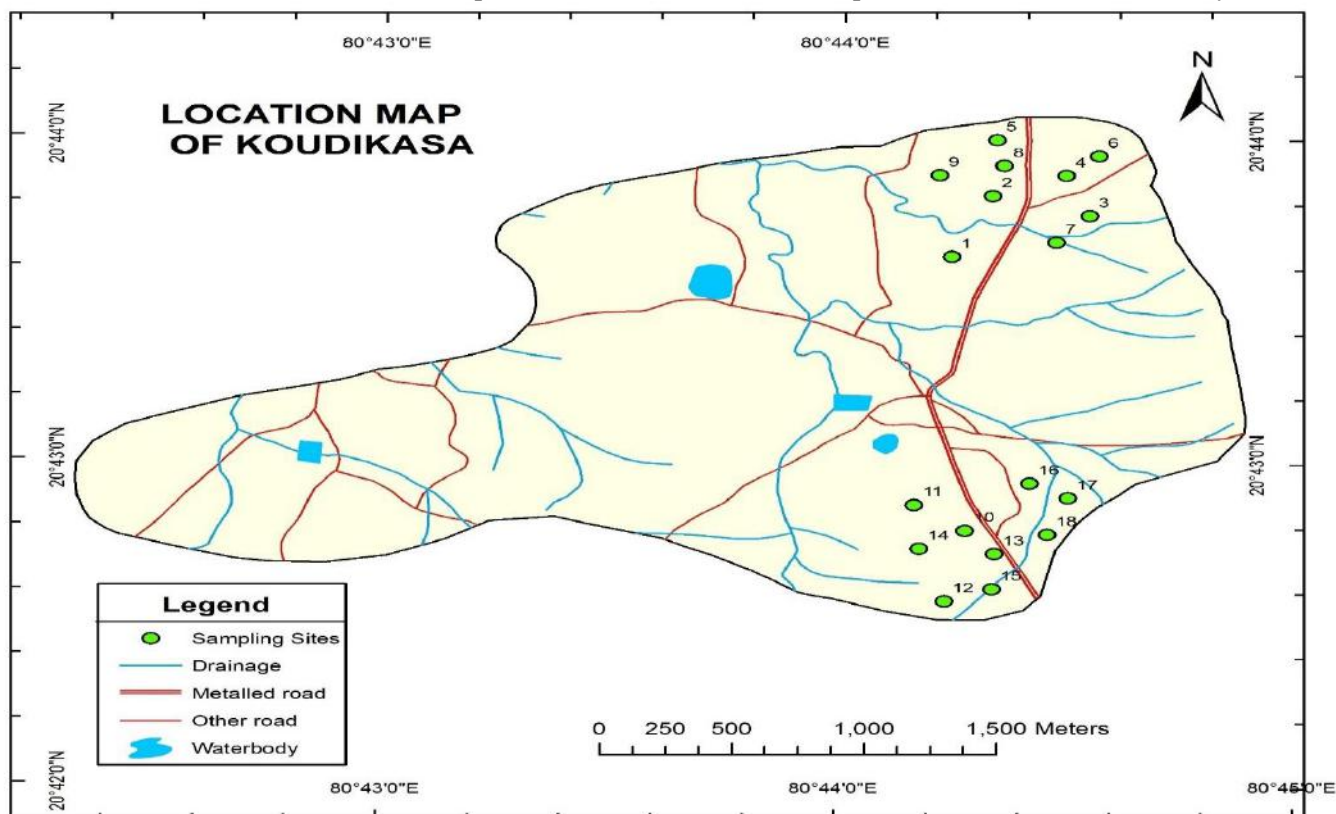
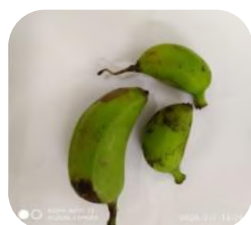


Figure 1: Representation of the study area.

2.1 MATERIALS :

Eighteen different types of fruits and vegetables has been selected and collected from the sampling location and been summarized in (**Figure 2**) The traditional and botanical name of the fruits and vegetables selected for the proposed studies is presented in **Table 1**.



Musa paradisiaca



Carica papaya



Pusika granatum



Anona reticulata



Solanum melongina



Annona squamosa



Psidium guajava



Ziziphus mauritiana



Citrus limon



Cucurbita



Iamarindus indica



Moringa olifera



Prumus dulcis



Solanum lycopersicum



Brassica



Lablab purpureus



L.Momordica charantia



Lathyrus sativus

Figure 2: Representation of the Fruits and vegetable collected from the sampling location.

Table 1: Details of various fruits and vegetables samples of study area.			
S.NO	TYPE	TRADITIONAL NAME	BOTANICAL NAME
1.	Fruit	Kela	<i>Musa paradisiaca</i>
2.	Fruit	Papita	<i>Carica papaya</i>
3.	Fruit	Anar	<i>Pusika granatum</i>
4.	Fruit	Ramphal	<i>Anona reticulata</i>
5.	Fruit	Jam	<i>Psidium guajava</i>
6.	Fruit	Ber	<i>Ziziphus mauritiana</i>
7.	Fruit	Sitafal	<i>Annona squamosa</i>
8.	Fruit	Nibu	<i>Citrus limon</i>
9.	Fruit	Badam	<i>Prumus dulcis</i>
10.	Fruit	Imli	<i>Iamarindus indica</i>
11.	Vegetable	Munga	<i>Moringa olifera</i>
12.	Vegetable	Lakhdi, Tiwara	<i>Lathyrus sativus</i>
13.	Vegetable	Sem	<i>Lablab purpureus</i>
14.	Vegetabl	Karela	<i>L.Momordica charantia</i>
15.	Vegetable	Baigan, Bhata	<i>Solanum melongina</i>
16.	Vegetable	Kaddu	<i>Cucurbita</i>
17.	Vegetable	Sarsoo	<i>Brassica</i>
18.	Vegetable	Tamatar	<i>Solanum lycopersicum</i>

2.2 METHODOLOGY:

SAMPLE PREPARETION

The collected fruit and vegetable samples were thoroughly washed and rinsed with distilled water respectively. The samples were then sliced to small pieces and oven dried at 80° C for 48 hours. The dried samples were then grounded into a fine powder form and sieved all the samples and stored in a fresh plastic polythene bag ready for digestion and further analysis through Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Adsorption Spectroscopy (AAS) (Figure 3).

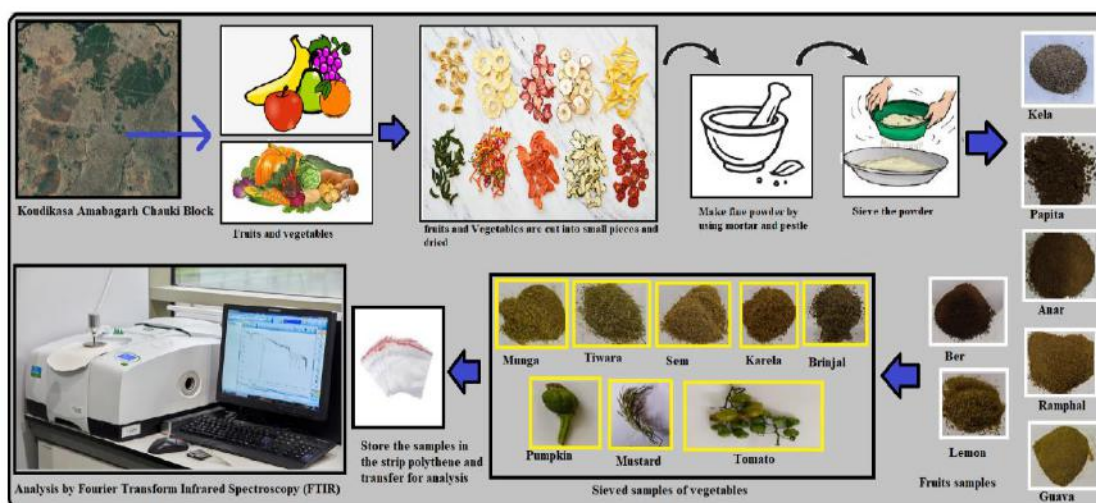


Figure 3: Representation of the sample preparation and the method for the fruits and vegetable samples.

3. ANALYSIS:

HEAVY METAL and FTIR ANALYSIS

Analysis for the heavy metals of interest was performed using atomic absorption spectrometry. Measurements were made using standard hollow cathode lamps for As, Fe, Cr, Mn, Hg, Pb, Cd, Zn, and Cu. The standard operating conditions for the analysis of heavy metals using atomic absorption spectrometry used. An in-depth development of how FTIR spectrometers work is beyond the scope of this review. Rather, we comment on the major types of systems available, the purpose and function of their key components, and sample preparation. Specific references are included within each section that cover these instruments in greater detail.

4. RESULT AND DISSCUSSION:

Heavy Metal Contamination in Fruits and Vegetables

The current reports detail the levels of As, Fe, Cr, Mn, Hg, Pb, Cd, Zn, and Cu found in a selection of fruits and vegetables that were gathered from market and production sites in the Rajanadgaon neighbourhood of Koudikasa. In order to determine the degree of food contamination, the observed concentrations of As, Fe, Cr, Mn, Hg, Pb, Cd, Zn, and Cu in the fruit and vegetables were compared with the suggested limit set by the FAO/WHO in 1999. **Table 2** summarises the mean concentrations and range of heavy metals (As, Fe, Cr, Mn, Hg, Pb, Cd, Zn, and Cu) found in fresh fruit and vegetables sampled. **Figures 4** illustrate this information. Based on the dry weight of the sample, the concentrations of heavy metals were calculated. The findings demonstrated the following levels of heavy metals in fruits and vegetables: The total concentrations of As, Fe, Cr, Mn, Hg, Pb, Cd, Zn, and Cu in Kela, Papita, Anar, Ramphal, Jam, Ber, Sitafal, Nibu, Badam, Imli, Munga, Tiwara, Sem, Karela, Bhata, Kaddu, and Sarsoo are 1985.2, 2241.4, 1422.4, 1466.8, 1761.3, 1313.2, 1791.4, 2325, 1671.4, 1356, 1450.5, 1509.6, 1193.9, 1172.8, 2272.8, 1900.5, 2124.4, and 2269.6 mg/kg, respectively. Certain fruits and vegetables have been found to contain higher levels of heavy metal contamination than others. These higher levels may be directly linked to pollutants found in pesticides, farm soil, irrigation water, or geogenic sources. Apart from its function as a biocatalyst, Cu is necessary for body pigmentation, for the maintenance of a healthy central nervous system, and for the prevention of anaemia, and it is interrelated with the function of Zn and Fe in the body [15]. Like Cu, Zn is an essential element for plants and animals, but only a small increase in its level may cause interference with physiological processes. The presence of Zn seems to be essential to neutralize the toxic effects of Cd (**Table 2**). The Minimum and Maximum value for As, Fe, Cr, Mn, Hg, Pb, Cd, Zn and



Cu (n = 5) in fruits and vegetables are ranged from 0.4-2.4, 777.3-1632.1, 5.7-15.3, 205.6-576.8, 0.1-0.4, 0.7-2.9, 0.7-2.2, 62.5-111.6 and 29.6-55.2 mg/kg, respectively, with the mean concentration value was ranged from 1.34 ± 0.25 , 1180 ± 128.55 , 10.37 ± 1.41 , 402.36 ± 47.71 , 0.21 ± 0.05 , 1.69 ± 0.31 , 1.35 ± 0.20 , 92.78 ± 7.51 and 44.25 ± 3.93 mg/kg, respectively (**Figure 4**). The highest concentration of Fe is found in all the fruits and vegetables samples of Kaudikasa region.

Table 2: Heavy metal concentration in fruits and vegetables.

S.No	Sample	As	Fe	Cr	Mn	Hg	Pb	Cd	Zn	Cu
1	Kela	1.1	1369.3	9.3	444.7	0.1	2.3	1.3	105.2	51.9
2	Papita	1.9	1572.8	11.8	505.8	0.3	2.8	1.1	99.3	45.6
3	Anar	0.8	998.3	5.7	302.9	0.1	1.6	0.7	62.5	49.8
4	Ramphal	1.2	1004.3	9.8	322.9	0.3	1.2	1.2	91.3	34.6
5	Jam	1.6	1144.9	12.3	456.9	0.3	1.9	1.7	100.4	41.3
6	Ber	0.8	877.5	6.2	298.6	0.1	0.7	0.9	96.6	31.8
7	Sitafal	1.7	1212.7	7.7	409.8	0.2	2.5	1.5	100.6	54.7
8	Nibu	2.4	1632.1	10.9	510.8	0.4	2.9	2.2	108.1	55.2
9	Badam	1.7	1120.2	11.2	401.7	0.1	1.2	1.8	98.8	34.7
10	Imli	1.1	876.8	8.9	355.8	0.1	1.1	1.2	70.5	40.5
11	Munga	1.3	989.1	9.7	303.7	0.2	1.3	1.9	95.4	47.9
12	Tiwara	1.4	1000.3	10.7	350.6	0.3	1.8	1.2	99.1	44.2
13	Sem	0.4	887.1	6.8	205.6	0.1	0.8	0.9	62.6	29.6
14	Karela	0.5	777.3	6.9	287.9	0.1	0.8	0.7	64.7	33.9
15	Bhata	1.7	1509.7	14.7	576.8	0.3	1.9	1.4	111.6	54.7
16	Kaddu	0.9	1233.1	13.8	502.8	0.2	1.6	1.1	101.8	45.2
17	Sarsoo	1.8	1466.7	14.9	498.8	0.3	1.9	1.6	91.7	46.8
18	Tamatar	1.9	1577.7	15.3	506.4	0.3	2.1	1.9	109.9	54.1

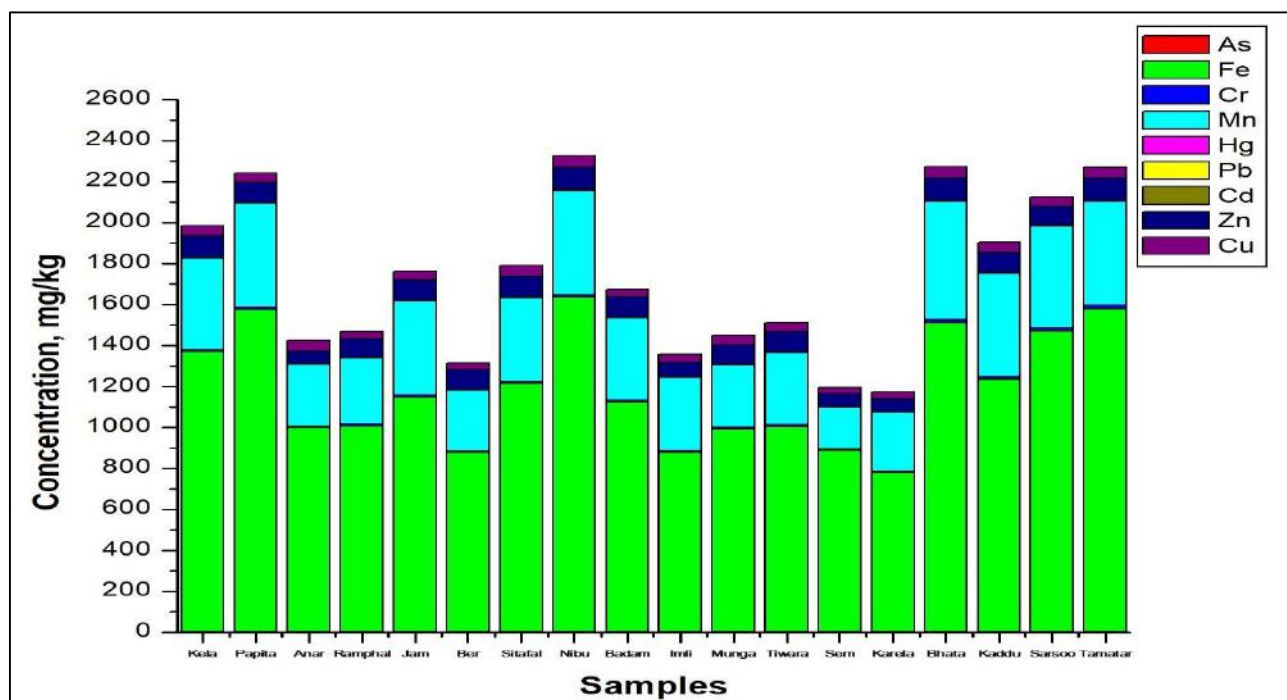


Figure 4: Heavy metal concentration in fruits and vegetables.



CORRELATION MATRIX

Among them, the highest concentration of Fe was observed in all fruits and vegetable samples. Among them, a good correlation ($r = 0.73$) of the As with the Fe was observed, and Pb is good correlated with Cu as shown in **Table 3**. The Fe showed good correlation with the heavy metals i.e. Cr, Mn, Cu and Pb in the all samples, indicating origin from similar sources. The As concentration in the fruits and vegetable samples of studied area was found to be higher than reported in other regions of the country and World.

Table 3: Correlation matrix of heavy metals

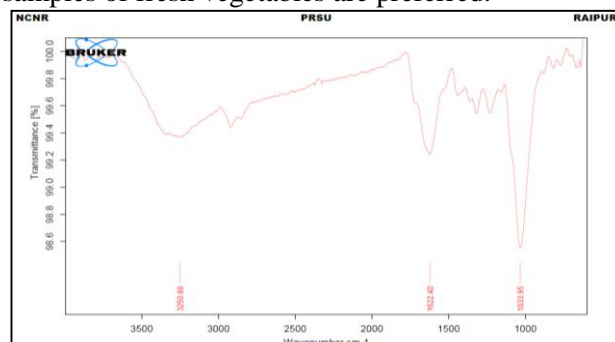
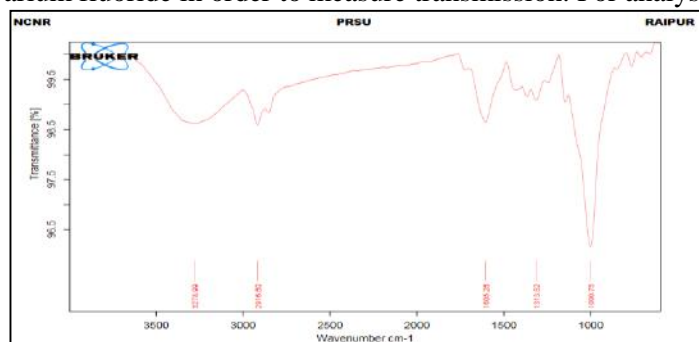
	As	Fe	Cr	Mn	Hg	Pb	Cd	Zn	Cu
As	1								
Fe	0.807	1							
Cr	0.642	0.725	1						
Mn	0.756	0.895	0.834	1					
Hg	0.771	0.677	0.672	0.634	1				
Pb	0.780	0.850	0.441	0.740	0.647	1			
Cd	0.813	0.575	0.565	0.521	0.571	0.492	1		
Zn	0.725	0.709	0.665	0.755	0.612	0.609	0.660	1	
Cu	0.622	0.732	0.430	0.680	0.480	0.809	0.487	0.539	1

FTIR SPECTRA OF FRUITS & VEGETABLES

The anhydrous fruit raw material's infrared spectra were acquired through a sequence of successive experiments [15]. The transitions between vibrational levels of the primary electronic state of the molecules, or oscillatory motion of the molecules, produce the spectra. The spectra's analysis reveals that each kind of raw material has a pattern that is strictly unique to it (**Figure 5**). All raw material types do, however, have regions of absorption bands that differ in intensity but are similar in location.

Valence fluctuation frequencies of OH-groups involved in intra- and intermolecular hydrogen bonds, as well as CH₂ and CH₃ groups, are typically found in the frequency range of 3800-2600 cm⁻¹. The main characteristic frequencies of the valence vibrations of C=O and -C=C-, as well as the deformation vibrations of methyl and methylene groups and OH-groups, are displayed in the frequency range of 1800–1200 cm⁻¹.

For all varieties of fruit raw materials, maximum absorption peaks are found in the frequency range of 1100-1000 cm⁻¹. These peaks are explained by variations related to the C-O-H group in certain phenolic compounds (like primary and secondary alcohols), which are abundant in fruits and berries. Among the many classes of secondary compounds that determine biological value are phenolic compounds. It should be noted that analysis of the absorption maximum intensity and integral intensity (area under the spectral absorption curve) is necessary to describe the intensity of the IR spectra bands. Nearly every type of fruit raw material under investigation has absorption bands in the designated frequency ranges, varying in intensity, according to the spectrum analysis. Since glass absorbs infrared radiation, thin-section tissue samples need to be placed on infrared-transparent windows made of zinc selenide, calcium fluoride, or barium fluoride in order to measure transmission. For analysis, samples of fresh vegetables are preferred.



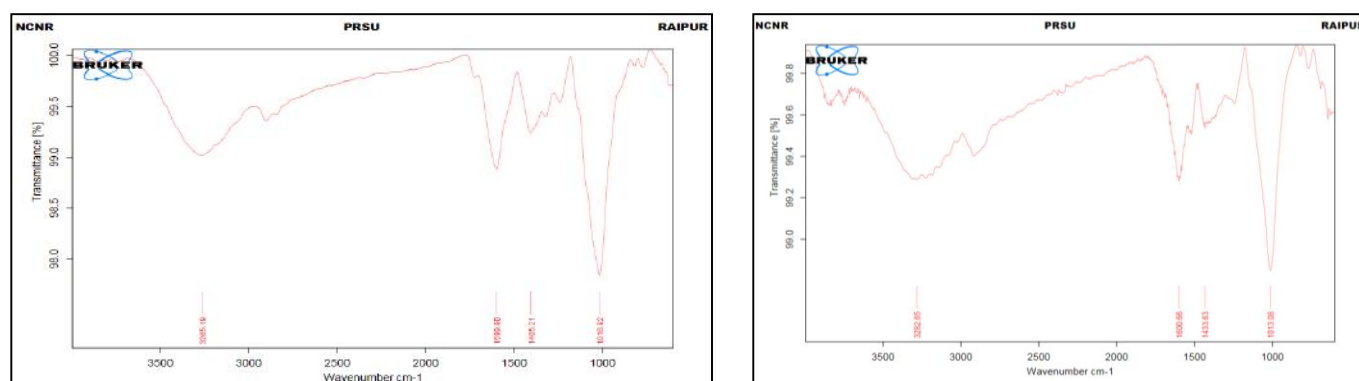


Figure 5: IR spectra for Banana fruit (A): Banana Outer Cover Peak (B) Banana Pulp Peak

5. 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. According to the aforementioned study, fresh fruit products are highly exposed to the heavy metals Fe, Pb, Cu, and Cd. This poses a threat to the safety of the human food chain and the urban environment. Fruit samples may have become more contaminated due to the use of contaminated water and improper post-harvest handling practices that disregard food safety regulations. The information will be useful in determining the presence of heavy metals in fruits and vegetables, ensuring food safety, and safeguarding consumers of fruits and fruit juices that may be harmful to their health. As a result, fruit raw material identification is possible using FTIR spectroscopy. The structure and chemical composition of each type of raw material determines the individual IR spectra that are obtained as well as the spectral characteristics (the area under the spectral absorption curve and the intensity of absorption bands), which are strictly unique for each type of raw material.

REFERENCES:

1. Aleixandre-Tudo, J.L., Nieuwoudt, H., Aleixandre, J.L., du Toit, W., 2018. Chemometric compositional analysis of phenolic compounds in fermenting samples and wines using different infrared spectroscopy techniques. *Talanta* 176, 526–536.
2. Andrade, R.M.S., Ferreira, M.S.L., Goncalves, E., 2016. Development and characterization of edible films based on fruit and vegetable residues. *J. Food Sci.* 81, E412–E418.
3. Andrianjaka-Camps, Z.N., Baumgartner, D., Camps, C., Guyer, E., Arrigoni, E., Carlen, C., 2015. Prediction of raspberries purees quality traits by Fourier-transform infrared spectroscopy. *LWT Food Sci. Technol.* 63, 1056–1062
4. Armenta, S., Garrigues, S., de la Guardia, M., Rondeau, P., 2005. Attenuated total reflection Fourier-transform infrared analysis of the fermentation process of pineapple. *Anal. Chim. Acta* 545, 99–106.
5. Averett, L.A., Griffiths, P.R., Nishikida, K., 2008. Effective path length in attenuated total reflection spectroscopy. *Anal. Chem.* 80, 3045–3049.
6. Ayora-Canada, M.J., Lendl, B., 2000. Sheath-flow Fourier-transform infrared spectrometry for the simultaneous determination of citric, malic and tartaric acids in soft drinks. *Anal. Chim. Acta* 417, 41–50.
7. Ayvaz, H., Santos, A.M., Moyseenko, J., Kleinhenz, M., Rodriguez-Saona, L.E., 2015. Application of a portable infrared instrument for simultaneous analysis of sugars, asparagine and glutamine levels in raw potato tubers. *Plant Foods Hum. Nutr.* 70, 215–220.
8. Ayvaz, H., Sierra-Cadavid, A., Aykas, D.P., Mulqueeny, B., Sullivan, S., Rodriguez-Saona, L.E., 2016a. Monitoring multicomponent quality traits in tomato juice using portable mid-infrared (MIR) spectroscopy and multivariate analysis. *Food Control* 66, 79–86.



9. Ayvaz, H., Bozdogan, A., Giusti, M.M., Mortas, M., Gomez, R., Rodriguez-Saona, L.E., 2016b. Improving the screening of potato breeding lines for specific nutritional traits using portable mid-infrared spectroscopy and multivariate analysis. *Food Chem.* 211, 374–382.
10. Baeten, V., Pierna, J.A.F., Dardenne, P., Meurens, M., Garcia-Gonzalez, D.L., AparicioRuiz, R., 2005. Detection of the presence of hazelnut oil in olive oil by FT-Raman and FT-MIR spectroscopy. *J. Agric. Food Chem.* 53, 6201–6206.
11. Baranska, M., Schutz, W., Schulz, H., 2006. Determination of lycopene and β -carotene content in tomato fruits and related products: comparison of FT-Raman, ATR-IR and NIR spectroscopy. *Anal. Chem.* 78, 8456–8461.
12. Barros, A.S., Mafra, I., Ferreira, D., Cardoso, S., Reis, A., da Silva, J.A.L., Delgadillo, I., Rutledge, D.N., Coimbra, M.A., 2002. Determination of the degree of methyl esterification of pectic polysaccharides by FT-IR using an outer product PLS1 regression. *Carbohydr. Polym.* 50, 85–94.
13. Belton, P.S., Kemsley, E.K., McCann, M.C., Ttofis, S., Wilson, R.H., Delgadillo, I., 1995. The identification of vegetable matter using Fouriertransform infrared spectroscopy. *Food Chem.* 54, 437–441.
14. Beullens, K., Kirsanov, D., Irudayaraj, J., Rudnitskaya, A., Legin, A., Nicolai, B.M., Lammertyn, J., 2006. The electronic tongue and ATR-FTIR for rapid detection of sugars and acids in tomatoes. *Sens. Actuators B* 116, 107–115.
15. Bichara, L.C., Lanus, H.E., Ferrer, E.G., Gramajo, M.B., Brandan, S.A., 2011. Vibrational study and force field of the citric acid dimer based on the SQM methodology. *Adv. Phys. Chem.* 10. <https://doi.org/10.1155/2011/347072>.