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## Peak energy shift with fertilization in mint plants: EDXRF measurements with synchrotron photon source

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### ABSTRACT

EDXRF measurements with synchrotron photons were performed for K X-rays of potassium, calcium and iron in mint plants and soils from a pot experiment with nutrient fertilization treatments keeping all other environment factors; soil, light, temperature and watering same. X-ray peak energies with precision  $10^{-4}$  of channel width were evaluated using SOLVER fitting, a powerful program included in Microsoft Excel for Windows. Results showed energy shifts with fertilizations that may be because of change in the structure and chemical environment of detecting elements in both plants and soils. Potassium and calcium fertilizations affect potassium peak energy more than calcium and iron peak energies in mint saplings and the soils.

**Keywords:** EDXRF, Synchrotron photons, Peak energies, Chemical environment

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### INTRODUCTION

Potassium and calcium are among the essential macronutrients and iron is a micronutrient of the plants. Thorough understanding of plant nutrition is difficult, partially because of the variation between different plants and even for species or individuals of a given clone, the variations do exist ([http://en.wikipedia.org/wiki/Plant\\_nutrition](http://en.wikipedia.org/wiki/Plant_nutrition)). Between the potassium and calcium, potassium is primary and calcium is secondary macronutrient. Potassium is unique among the essential nutrients in the diverse roles it plays in plant chemical processes. So, its uptake and utilization often interacts with the availability and uptake of other nutrients e.g. calcium ([www.ipni.net/bettercrops](http://www.ipni.net/bettercrops)). It is an attractive area to investigate if these interactions are causing changes in overall structure and bonding in plants and soils. Iron is most important for the respiration and photosynthesis processes of the plants. It is also implied in many enzymatic systems like chlorophyll synthesis.

In the context of use of EDXRF technique to study the status of macro/micro nutrients in plants and their soils, it is observed that the environment of an atom affects the emitted X-ray peaks in the form of shift in its peak energy, variation in line width and index of asymmetry. The measured change in energy produces information about the type of chemical bonding, structure of molecules/complexes and their activity in changing environment. Plenty of work has been done on chemical shifts depicting their dependence on valencies, oxidation states, number of ligand atoms, effective charge of absorbing atoms and coordination number etc [1-4]. Chemical shifts in X-ray emission lines were studied with the use of synchrotron radiation by Artemiev et al. [5]. Changes occur in line width and index of asymmetry with the change in percentage composition of an element in a compound [6, 7].

Energy dispersive systems have poor resolution, but these systems offer advantages of simultaneous multi-element detection with high efficiency. These systems detect normal Gaussian peaks with excellent energy and resolution stability. Kontos and his group [8, 9] have applied EDXRF technique to detect the chemical shift of K X-rays of Cr

and Mn in their compounds using a computer program in EXCEL called SOLVER. The present paper reports an interesting EDXRF measurement where the shift in energy of potassium, calcium and iron K X-ray peaks in mint plants from the soils treated with different amounts of KCl and CaSO<sub>4</sub> fertilizations has been searched using synchrotron photons. The details of the measurements and findings are discussed here.

## MATERIALS AND METHODS

### 2.1 Pot Experiment and preparation of samples

In authors' lab, a pot experiment was performed on mint plants with potassium and calcium fertilizations as was earlier done for maize plants [10]. Twelve pots containing a mixture of soil and sand in 1:1 ratio were used to germinate 35-40 seeds of mint in each pot. The pots were watered with 200 ml water on an alternate day. On 9<sup>th</sup> and 11<sup>th</sup> day after the germination of seeds, fertilizations with CaSO<sub>4</sub> and KCl were done. Five pots were treated with KCl solutions; 50, 100, 150, 200, 250 mg of KCl per 200 ml of water, other five pots were treated with CaSO<sub>4</sub> solutions; 50, 100, 150, 200, 250 mg of CaSO<sub>4</sub> per 200 ml of water, one pot was treated with both Ca and K fertilizers in equal amounts; 150 mg each and one pot was left untreated.

In order to analyze mint saplings, the saplings were cut from stems above the soil surface. Soils around the mint roots from the pots were also collected. Each mint sample was washed with tap water to remove unwanted particles attached to it, dried at room temperature and weighed. The weighed sample was then dried in oven at 100-120° C for 5-6 hours for two days and again weighed after cooling it to room temperature and weight loss due to drying was determined. The samples were grounded with an electric grinder and then in pulsator. The fine powder of material was accurately weighed and pressed in 25 tons semi automatic hydraulic pellet press to obtain infinite thick pellets of 2.5 cm diameter. For soil targets, each soil was dried, grounded and passed through standard test sieves with No. 180. Since, the soils, seeds and environmental conditions such as light, water and air were kept same as far as possible for all the pots except fertilization in the processing of pot plants, therefore, the observed variations of characters of macro/micro nutrients would be due to fertilization.

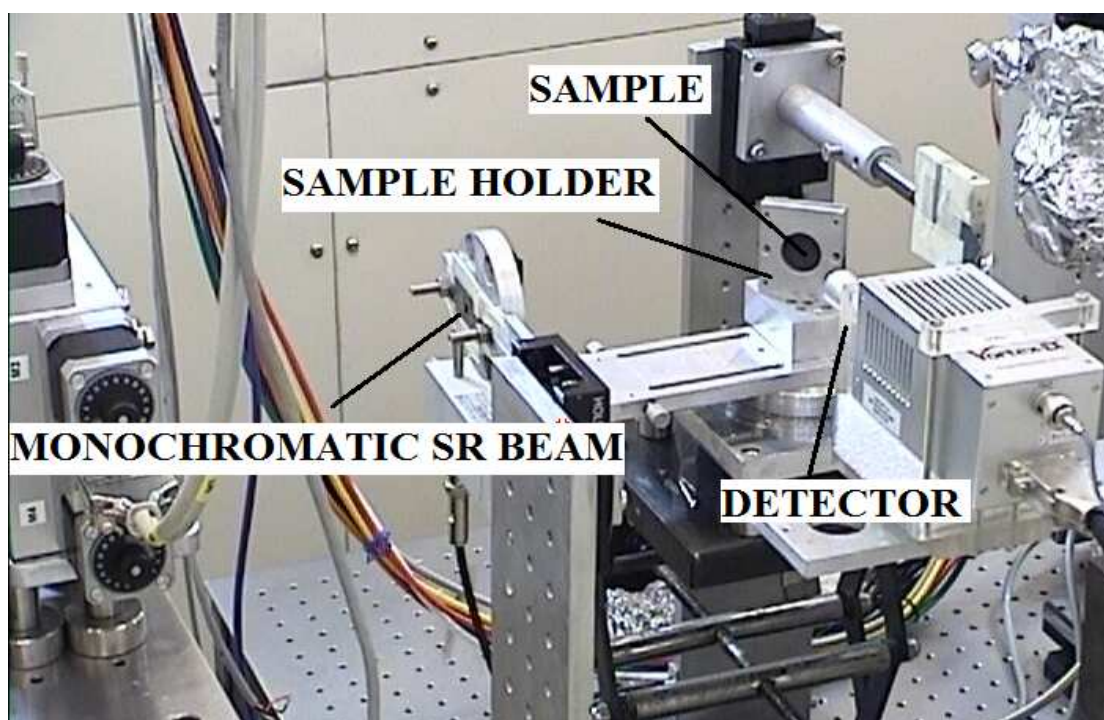


Fig. 1 Photograph of the experimental setup used for synchrotron induced EDXRF measurements of samples.

### 2.2 Experimental Set-up

The X-ray fluorescence measurements on briquette targets of powder material of collected plants and soils from different pots were performed on the microfocal X-ray fluorescence beamline (BL-16) of Indus-2 synchrotron radiation facility at RRCAT, Indore. The BL-16 beamline works in the 4-20 keV photon energy range. The optics of the beamline comprises of a Si(111) double crystal monochromator and a Kirkpatrick-Baez (KB) focusing optics with a combination of slits, beam viewer, fluorescence screens etc. The beamline operates under high vacuum ( $< 10^{-6}$  Torr). Fig.1 illustrates the geometry of the experimental setup used for the synchrotron induced X-ray fluorescence

measurements. The incident X-ray energy of 8.0 keV, monochromatized using the double crystal monochromator, was used as excitation energy for the mint and soil samples. The emitted fluorescent X-rays from the samples were collected using Vortex (SII, Nano, USA) energy dispersive spectroscopy detector having an energy resolution of ~138 eV at 5.898 keV (Mn-K $\alpha$  X-rays) energy. The XRF spectra for all samples were recorded for a spectrum acquisition live time of 200s. The measurements were under taken for Indus-2 operation of 2.0 GeV, 100 mA. A typical emitted X-ray spectrum of mint sample is shown in fig. 2.

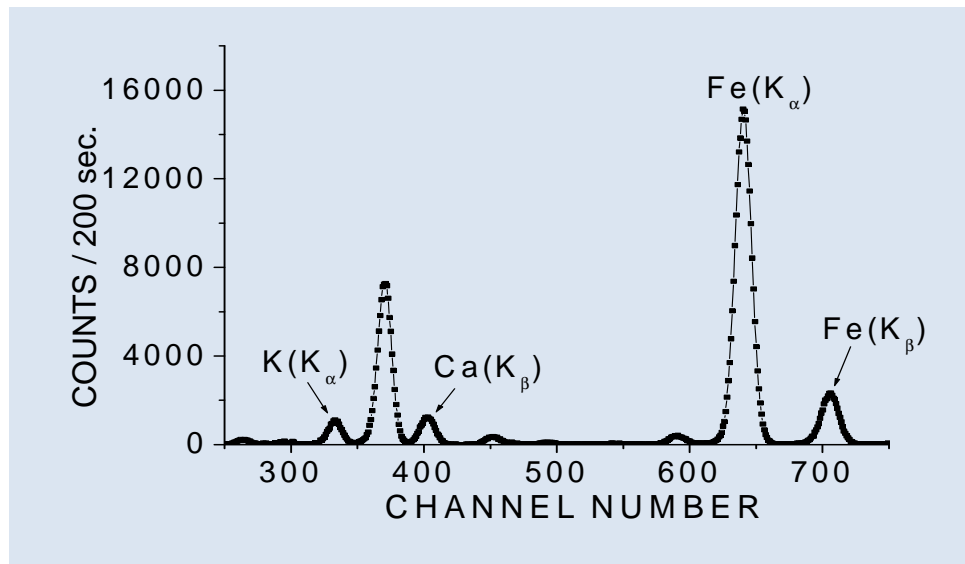


Fig. 2 A typical background subtracted X-ray fluorescence spectrum of a mint sample.

### 2.3 Methodology

Since the recorded fluorescence counts strongly depend upon the Indus-2 ring current which was decaying with time, therefore, the ionization chamber current  $I_0$  (mean of starting and end currents during a data acquisition) was used to account the variation of incident photon flux falling on the sample. The obtained net area counts of a fluorescence peak were generally normalized with the value of ionization chamber current ( $I_0$ ).

To determine the shift in K X-ray peak energies of potassium, calcium and iron, the powerful program SOLVER included in EXCEL has been used for peak fittings and to find the peak positions of distinct peak K $\alpha$  of potassium, K $\beta$  of calcium and K $\alpha$  and K $\beta$  of iron. The SOLVER program had already been successfully used in peak fitting for the modeling of data from chromatography, fluorescence decay and ion selective electrodes [11]. SOLVER is an ideal tool for mathematical modeling of experimental data because of easier user interface, dynamic display of iterative search process and universal availability of EXCEL. It does not follow a complicated, black-box approach, rather it is user oriented as the user has to feed the raw data and the required parameters to initiate the model building process.

The advantage of fitting of X-ray peaks in the collected data with an energy dispersive detector is their excellent representation by a normal distribution. To eliminate the problem of low energy tail, fitting of a fluorescence peak was performed in  $\pm 2\sigma$  region (two standard deviations from both sides of the peak centroid) which included 95% of the peak events, where the effect of tail was negligible.

Gaussian function for X-ray peak,

$$C = H * e^{-\frac{(x-m)^2}{2\sigma^2}} \text{----- (1),}$$

with C as calculated counts, H as maximum peak height, x as channel number, m as peak centroid and  $\sigma$  as standard deviation was fitted to the said distinct peaks by inserting H as maximum count at the peak channel, m as peak channel and  $\sigma = FWHM / 2\sqrt{2\ln 2}$  where FWHM is full width at half maximum known from the spectra recorded with ORTEC-MCA software. The equation (1) computes the counts (C) at the channels (x) covering the peak region up to  $\pm 2\sigma$  channels. The sum of squared residuals between computed and experimental counts were minimized by SOLVER program and fresh parameters H, m and  $\sigma$  were computed. The m value obtained was precise up to  $10^{-4}$  decimal position. The solver fitting applied on K $\alpha$  potassium peak of obtained spectra of one of the mint samples is shown in figure 3 as an example along with the experimental peak.

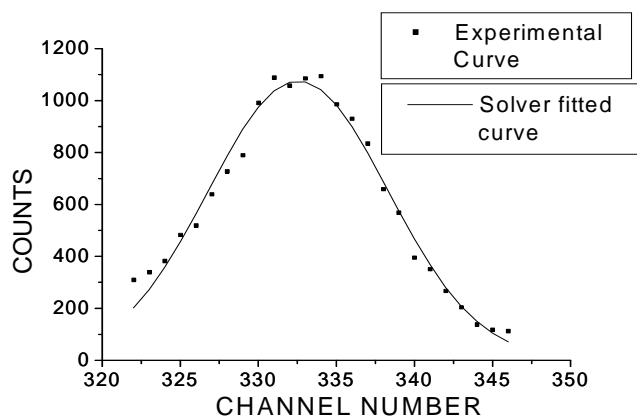


Fig. 3 Experimental and solver fitted peak in one of the spectra of mint samples.

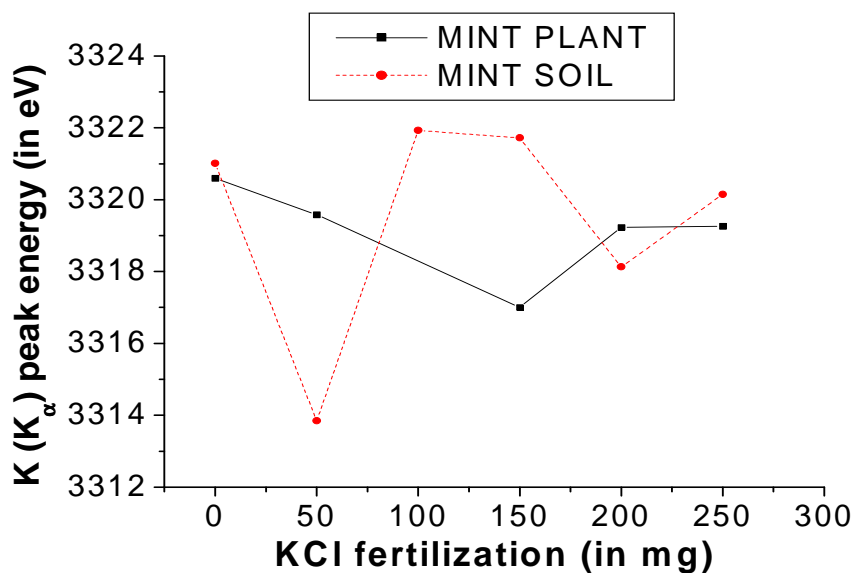
Table 1. Peak energy positions of K ( $K_{\alpha}$ ), Ca ( $K_{\beta}$ ), Fe ( $K_{\alpha}$ ) and Fe ( $K_{\beta}$ ) in mint plants and their soils from pots treated with different fertilizations

Fertilization (mg) of KCl/200 ml of water	Peak	Peak energy (eV)	
		Plants	soils
Unfertilized	Potassium ( $K_{\alpha}$ )	3320.596	3321.011
	Calcium ( $K_{\beta}$ )	4019.652	4020.061
	Iron ( $K_{\alpha}$ )	6393.168	6394.229
	Iron ( $K_{\beta}$ )	7044.490	7045.296
50	Potassium ( $K_{\alpha}$ )	3319.581	3313.844
	Calcium ( $K_{\beta}$ )	4018.840	4019.994
	Iron ( $K_{\alpha}$ )	6492.410	6394.165
	Iron ( $K_{\beta}$ )	7043.478	7045.229
100	Potassium ( $K_{\alpha}$ )	-	3321.930
	Calcium ( $K_{\beta}$ )	-	4020.161
	Iron ( $K_{\alpha}$ )	-	6394.303
	Iron ( $K_{\beta}$ )	-	7045.162
150	Potassium ( $K_{\alpha}$ )	3317.006	3321.716
	Calcium ( $K_{\beta}$ )	4018.624	4021.179
	Iron ( $K_{\alpha}$ )	6392.864	6394.177
	Iron ( $K_{\beta}$ )	7043.473	7045.213
200	Potassium ( $K_{\alpha}$ )	3319.231	3318.128
	Calcium ( $K_{\beta}$ )	4018.967	4021.078
	Iron ( $K_{\alpha}$ )	6492.790	6393.965
	Iron ( $K_{\beta}$ )	7044.132	7044.965
250	Potassium ( $K_{\alpha}$ )	3319.259	3320.147
	Calcium ( $K_{\beta}$ )	4019.136	4020.514
	Iron ( $K_{\alpha}$ )	6392.790	6394.362
	Iron ( $K_{\beta}$ )	7044.023	7045.661
Fertilization (mg) of CaSO <sub>4</sub> /200 ml of water			
50	Potassium ( $K_{\alpha}$ )	3320.986	3320.111
	Calcium ( $K_{\beta}$ )	4018.992	4021.065
	Iron ( $K_{\alpha}$ )	6393.081	6394.212
	Iron ( $K_{\beta}$ )	7044.226	7045.106
100	Potassium ( $K_{\alpha}$ )	3318.912	3320.715
	Calcium ( $K_{\beta}$ )	4018.714	4020.642
	Iron ( $K_{\alpha}$ )	6392.959	6394.232
	Iron ( $K_{\beta}$ )	7043.943	7045.185
150	Potassium ( $K_{\alpha}$ )	3320.151	-
	Calcium ( $K_{\beta}$ )	4018.203	-
	Iron ( $K_{\alpha}$ )	6392.430	-
	Iron ( $K_{\beta}$ )	7043.307	-
200	Potassium ( $K_{\alpha}$ )	3320.960	3321.375
	Calcium ( $K_{\beta}$ )	4020.254	4021.175
	Iron ( $K_{\alpha}$ )	6393.189	6394.211
	Iron ( $K_{\beta}$ )	7043.823	7045.145
250	Potassium ( $K_{\alpha}$ )	3319.786	3319.290
	Calcium ( $K_{\beta}$ )	4019.873	4021.244
	Iron ( $K_{\alpha}$ )	6393.241	6394.270
	Iron ( $K_{\beta}$ )	7043.913	7044.941
Equal amount (150 mg) of each KCl and CaSO <sub>4</sub>	Potassium ( $K_{\alpha}$ )	3318.970	3320.269
	Calcium ( $K_{\beta}$ )	4018.876	4021.321
	Iron ( $K_{\alpha}$ )	6393.233	6394.100
	Iron ( $K_{\beta}$ )	7043.894	7045.076

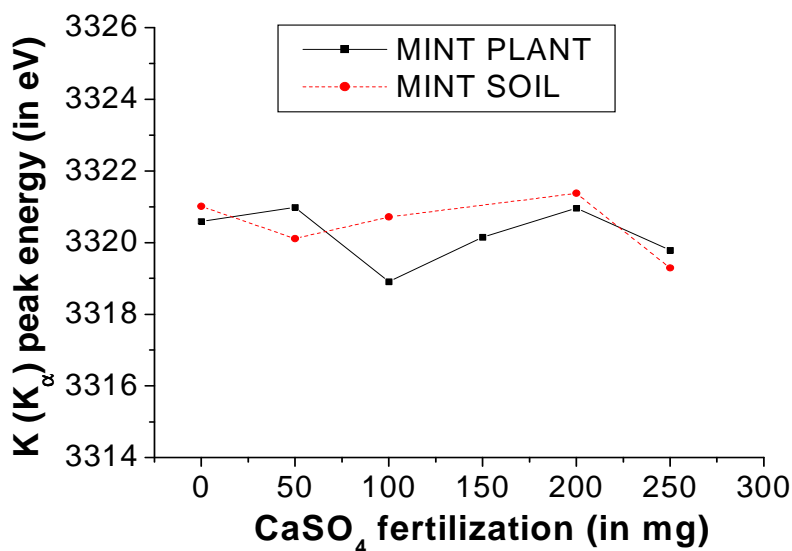
## RESULTS AND DISCUSSION

In the stated methodology, the obtained centroid positions were in the form of channel numbers and were converted into energies using energy calibration of the detector. Peak energy positions of distinct peaks; K ( $K_{\alpha}$ ), Ca ( $K_{\beta}$ ) and Fe ( $K_{\alpha}$ ) and Fe ( $K_{\beta}$ ) in mint plants and their soils for different fertilizations are considered here for interpretation of observations and are being listed in table 1 and plotted in fig. 4, 5, 6 and 7. The Ca ( $K_{\alpha}$ ) was not taken into consideration as it is totally merged with K ( $K_{\beta}$ ).

- Due to degradation of pressed pellet samples, data could not be procured.

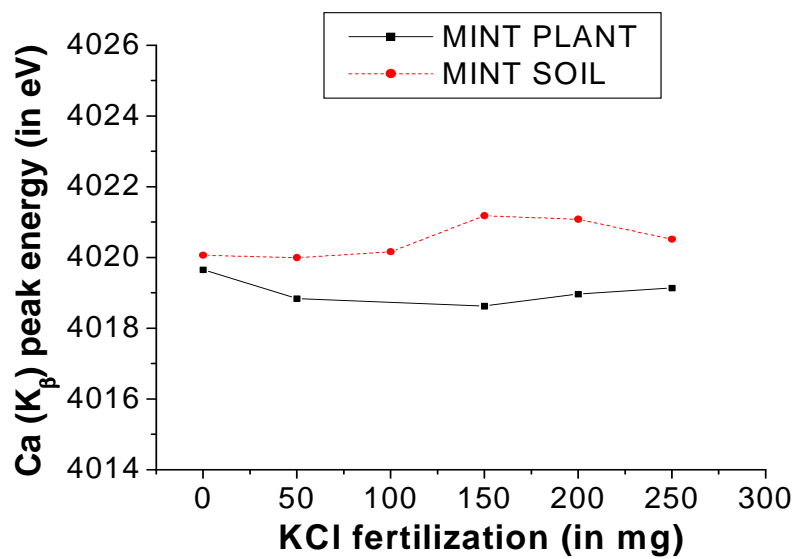


(a)

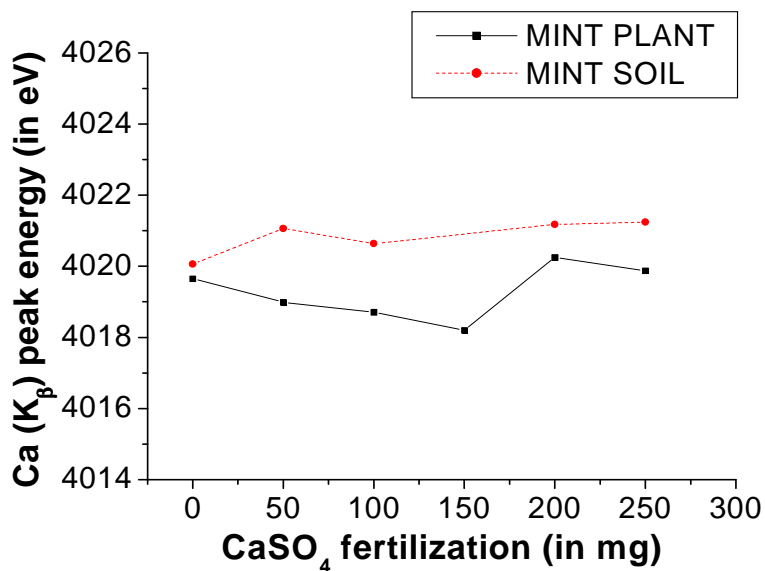


(b)

Fig. 4 Plot of potassium  $K_{\alpha}$  peak energies of mint plant and its soil  
(a) vs. KCl fertilization;  
(b) vs.  $\text{CaSO}_4$  fertilization.

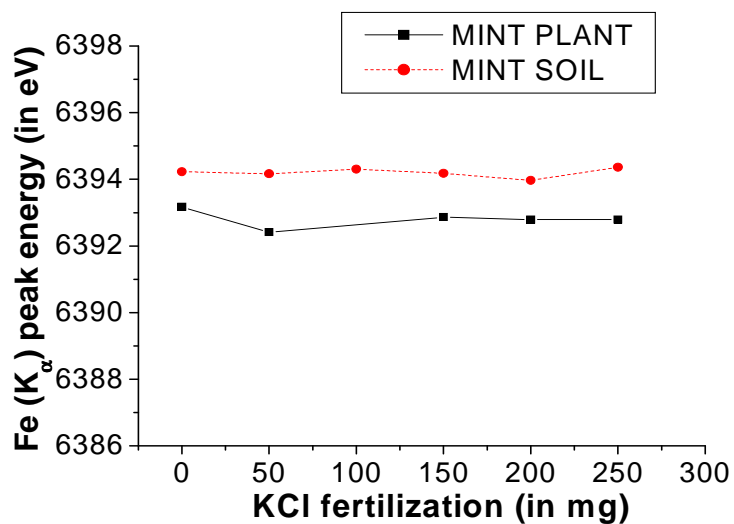


(a)

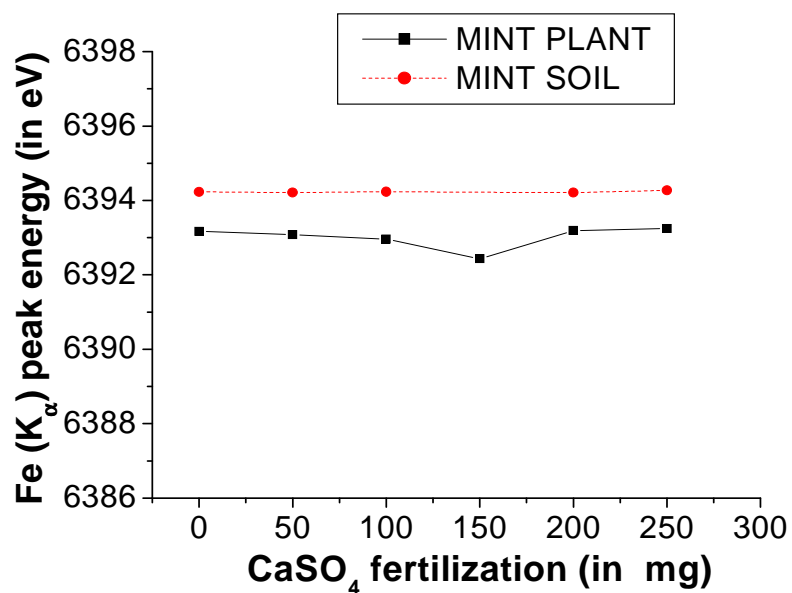


(b)

Fig. 5 Plot of calcium  $K_{\beta}$  peak energies of mint plant and its soil  
(a) vs. KCl fertilization;  
(b) vs.  $CaSO_4$  fertilization.

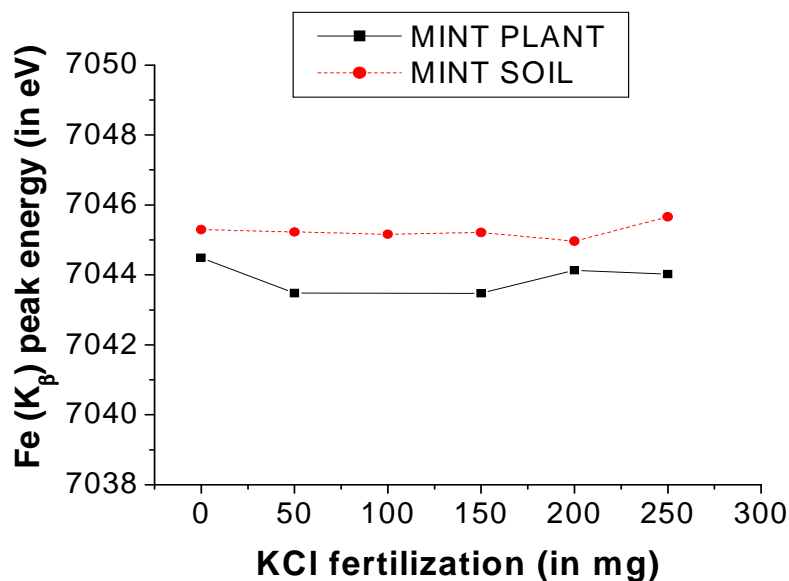


(a)

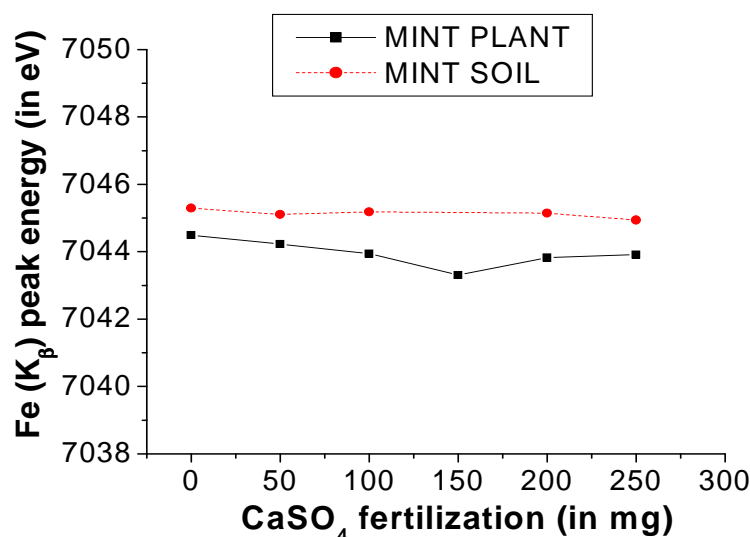


(b)

Fig. 6 Plot of iron  $K_{\alpha}$  peak energies of mint plant and its soil  
(a) vs. KCl fertilization;  
(b) vs.  $CaSO_4$  fertilization.



(a)



(b)

Fig. 7 Plot of iron  $K_{\beta}$  peak energies of mint plant and its soil  
(a) vs. KCl fertilization;  
(b) vs.  $CaSO_4$  fertilization.

The graphs give some exploring points to be discussed here as follows:

(1) Fig. 4, 5, 6 and 7 represent that the peak points of potassium  $K_{\alpha}$  for mint plant does not show clear cut distinction from those of the soil for different fertilizer treatments whereas peak points of calcium and iron show higher energies for mint soils than the respective plants. So, the element format of potassium seems similar in plant and soil while that of calcium and iron looks different in plant and its soil.

(2) On observing the difference in peak energies of treated plants and soil from the untreated ones, it is noticed that K ( $K_{\alpha}$ ) peak shows maximum observable shift (from 0.36 eV to 3.59 eV in mint plants and from 0.36 eV to 7.16 eV in corresponding soil samples). Ca ( $K_{\beta}$ ) peak shows much less peak shift, from 0.22 eV to 1.45 eV in mint plants and from 0.07 eV to 1.26 eV in corresponding soil samples. The energy shift values reduce further for Fe ( $K_{\alpha}$ ) peak, from 0.02 eV to 0.76 eV in mint plants and from 0.003 eV to 0.26 eV in corresponding soil samples and for Fe ( $K_{\beta}$ ) peak, from 0.26 eV to 1.18 eV in mint plants and from 0.07 eV to 0.37 eV in corresponding soil samples. The higher



shift in case of K ( $K_{\alpha}$ ) may be assigned to single unpaired valence electron of potassium which is prone to interact with electrons of other atoms and exerts more pull/push effect. In case of calcium and iron, the paired valence electrons in the *s* state are less prone to such interaction.

(3) Between the potassium and calcium fertilizations, the relative difference in K ( $K_{\alpha}$ ) peak points in mint saplings is more (~1.0-3.6 eV) for potassium treatment than (~0.36-1.68 eV) for calcium treatment. The observation may be interpreted that there is competition between the calcium and potassium because of their similar sizes and addition of any one of them reduces the uptake rate of the other. There are interactions between ions with similar chemical properties to compete for sites of adsorption, absorption, transport and function. In competitive binding, the amount of any ion bound will be related to the concentration of that ion relative to its competitors and the affinity constants for the ion-ligand pairs [12].

So, interactions between nutrients in higher plants occur when the supply of one nutrient affects the absorption, distribution or function of another nutrient. There are several ways in which nutrients can interact either within the soil or plant to affect nutrient absorption or utilization.

### CONCLUSION

It is concluded that potassium and calcium fertilizations affect potassium more than calcium and iron peak energies in mint saplings and the soils. Fertilizations with variation in its amount may be causing a change in the structure and chemical environment of plants and soils. There seems a controlled selectivity process involved in uptake of nutrients by plants. Moreover, there are mutual interactions and exchange of minerals and elements in plants and soils.

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