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Study of Soil Contamination in Fenugreek Plant/Soil System with Matrix Terms of X-Ray Fluorescence Measurements

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Abstract

In X-ray fluorescence (XRF) elemental analysis, energies and intensities of characteristic X-rays of elements in a sample identify the elements and their amounts respectively. In targets of practical use, intensities of X-rays are not directly proportional to concentrations of the elements because of absorption and enhancement (matrix) effects. Empirical formulations for each relative absorption and enhancement terms in terms of analyte amounts and measured X-ray intensities from the sample to study its matrix effects have been developed in our lab. For a category of samples, the variation pattern of the terms with respective analyte amounts was found to be substrate dependent. In the present work, these studies have been applied to potassium/calcium fluorescent X-ray measurements on plant and soil samples procured from a pot experiment performed on fenugreeks in 20 pots; 10 pots filled with normal soil and rest with soil from sewage area. Moreover, to vary potassium/calcium contents in the collected samples, variable potassium and calcium fertilizers were applied to each set. In the samples, potassium/calcium contents were determined using well established XRF method for thick samples. Then absorption term for Ca/K and enhancement term for K were evaluated and plotted against the determined K/Ca concentrations. Different polynomial fits were tried on these plots to have a best fit for the data values.

Key words: Empirical Formulation, Fenugreek, Fluorescent X-rays, Matrix Effects, X-ray fluorescence.

1. INTRODUCTION

Absorption and enhancement (matrix) effects in X-ray fluorescence (XRF) analysis disturb the relationship between intensities of analyte X-rays and its concentration. To overcome these difficulties, different groups [1] have proposed different methods for compensation, correction or evaluation of inter-element effects in samples with dark (unknown) matrices. Bansal and Mittal in 2009 and Bansal et al. in 2012 [2-4] followed an approach to study matrix effects in terms of absorption and enhancement terms. They verified the relations experimentally for synthetic samples and applied to maize plant and soil samples treated with Ca/K fertilizers.

Human influences like industrial activity, agricultural activities, waste disposal etc. are introducing toxins including heavy metals to the soils [5] which get transmitted to plants thus they spread in food chains. In soil these chemicals compete with macronutrients and affect their take up by plants as per ability of plant species to take up and accumulate the chemicals from the soil. Therefore, soils from university campus which was less contaminated and from highly contaminated cite of city i.e. sewage were taken as base material to grow fenugreek plants in pots. Fenugreek has good nutritional and medicinal value. Ca and K being major mineral constituents have been checked for the impact of soil toxicity. The pots were treated with different amounts of potassium and calcium fertilizers to check the cumulative effect of macronutrient fertilizers.

2. MATERIALS AND METHODS

2.1 POT EXPERIMENT

Pot experiment in months of February and March was performed on two soils, normal (OS) and sewage soil (SS). A set of 10 pots with normal soil+sand+clay in 1:1:1 proportion as growing medium and another set of 10 pots with sewage soil+sand+clay in 1:1:1proportion were undertaken to study the interfering effect of heavy Z soil contaminants on the matrix terms of macronutrients K/Ca in plants and soils. In a spacious airy laboratory room of dimensions ~ 24 ft. X 21 ft. X 12 ft. with proper natural day light (day time luminance of 150-200 lx) and no artificial luminance at night, 80–100 uniform sized seeds of fenugreek were germinated in each pot. The pots were watered with 200 ml water when it was required. The pots were treated with different amounts of K (KCl) and Ca ($CaCO_3$) fertilizers on15th, 21st and 35th day after sowing of seeds to check the cumulative effect of macronutrient fertilizers. 5 pot of each kind were treated with 200 ml solution of varying concentrations of $CaCO_3$, i.e. 1, 10, 20, 30 and 50mM. Remaining 5 pots of each kind 5 pots were treated with 200 ml of KCl with similar concentration.

On full growth, plants were cut from above the soil surface, washed under running water, dried at room temperature for two days and in oven at 100–120^{o}C for 5–6 h for consecutive two days and then grinded. The thick pellets of 2.5cm diameter [6] were prepared. Pot soils were collected at depth 0–5cm from individual pots and dried at 70–80^{o}C for 5–6h for four days, sieved through 53μm sieve mesh. The sieved samples were also pressed in the die to prepare pellets of 2.5cm diameter.

2.2 POTASSIUM/CALCIUM DETERMINATIONS IN SAMPLES

The existing X-ray fluorescence (XRF) method (Mittal et al., 1987) has been employed to determine K/Ca in plants and soils. The method involves selective production of analyte X-rays in thick targets of sample and its two references. The material of first reference for K/Ca was KNO_3/CaO and that of second reference was the mixture of sample and first reference material in known ratio. Sample pellets and two references were irradiated with photons from low power X-ray tube with Rh anode. For the selective production of potassium K X-rays and calcium K X-rays anode voltage/filament current were set at 4kV/0.3mA and 5kV/0.2mA respectively. The emitted X-rays spectra were recorded with Amptek X123 spectrometer having Si PIN detector

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with 0.5mil. Be window and of dimensions 6mm^2/500μm with resolution 145eV at 5.959 keV Mn X-rays, in single reflection geometry. The fractional amounts of K (β) and Ca (α) in the plant and soil samples were calculated (Table 1).

Table 1. Determined fractional amounts of K/Ca in plant/soil samples treated with different amounts of K/Ca fertilizers.

S. No.	Treatment with fertilizer per 200ml of water	Determined fractional amounts of Ca and K in plant and soil samples (with 7% error)							
		Normal soil pots (OS)				Sewage soil pots (SS)			
		Ca amount (α)		K amount (β)		Ca amount (α)		K amount (β)	
		Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil
1	1mM $CaCO_3$	0.0076	0.0129	0.0247	0.0250	0.0110	0.0154	0.0209	0.0120
2	10mM	0.0135	0.0167	0.0175	0.0233	--*	0.0223	--*	0.0235
3	20mM	0.0133	0.0191	0.0229	0.0195	0.007	0.0253	0.0308	0.0183
4	30mM	0.0144	0.0319	0.0139	0.0227	0.0098	0.0326	0.0169	0.0163
5	50mM	0.0258	0.0290	0.0292	0.0371	0.0094	0.035	0.0169	0.0157
6	1mM KCl	0.0118	0.0225	0.0240	0.0357	0.0144	0.0148	0.0130	0.0276
7	10mM KCl	0.0087	0.0196	0.0320	0.0264	0.0096	0.0168	0.0140	0.0220
8	20mM KCl	0.0124	0.0136	0.0148	0.0262	0.0105	0.0205	0.0098	0.0182
9	30mM KCl	0.0057	0.0168	0.0048	0.0373	0.0057	0.0134	0.0300	0.0098
10	50mM KCl	0.0062	0.0193	0.0247	0.0169	0.0084	0.0152	0.0216	0.0266

*Sample was too less to be analysed.

2.3 ABSORPTION / ENHANCEMENT TERMS

The absorption term $\frac{\mu_{K/Ca}^{S(K/Ca)}(Ab)}{\mu_{K/Ca}^{KNO_3/CaO}(Ab)}$ at 4kV/5kV for K/Ca and enhancement term $\left[\frac{\mu_K^{S(Ca)}(En)}{\mu_K^{KNO_3}(En)}\Big/G\right]$ at 5kV for K, where μ's are absorption coefficient of sample for K/Ca X-rays in cm^2/g, were evaluated [3-4] for fenugreek plants and soil samples and plotted against the determined K/Ca (β/α) concentrations in plants and in respective soils. From the variation pattern of the terms with respective contents, a search was made for empirical polynomial relation between the determined terms and analyte amounts (β/α) for K/Ca following the criterion of lowest powers of amount terms and close agreement between actual and generated values. The obtained polynomial fits for plant and soil samples along with their mean absolute percentage deviations D_p are found. Typical plots for $\frac{\mu_K^{S(K)}(Ab)}{\mu_K^{KNO_3}(Ab)}$ in OS and SS soils and respective plants and $\frac{\mu_K^{S(Ca)}(En)}{\mu_K^{KNO_3}(En)}$ in soils are illustrated in fig. 1&2.

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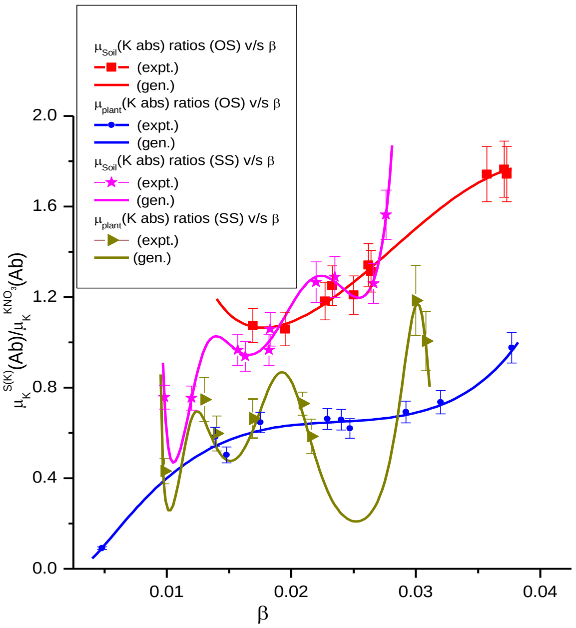

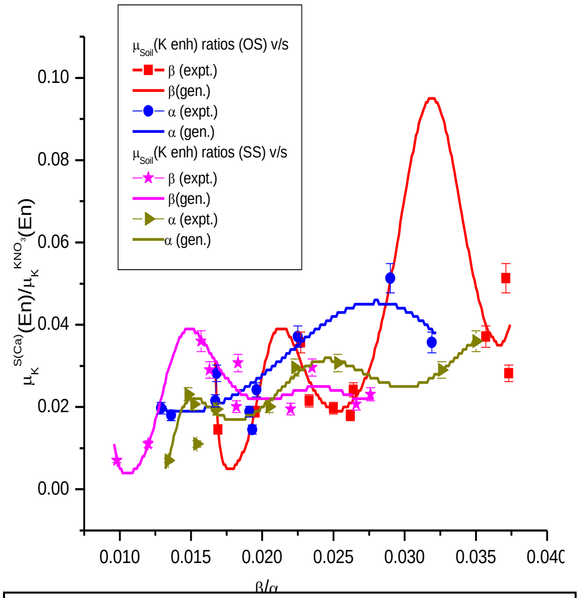

Figure 1. Plot of determined and generated values of $\dfrac{\mu_K^{S(K)}(Ab)}{\mu_K^{KNO_3}(Ab)}$ for soil/plant. v/s β.

Figure 2. Plot of determined and generated values of $\dfrac{\mu_K^{S(Ca)}(En)}{\mu_K^{KNO_3}(En)}$ in soils v/s β/α.

3. RESULTS AND DISCUSSION

The reproducibility of the present experimental set-up had already been established with synthetic samples [7]. The observations made from the calculated absorption and enhancement ratios are as follows:

1. Absorption terms for K/Ca are higher in soils than in plants for both OS and SS pots (fig 1). Because low Z organic (H, C, O etc.) substrate of plants results in lesser absorption of K/Ca X-rays as compared to higher Z silicon, the main inorganic constituent of soil.
2. Absorption terms for K/Ca for OS plants/soils are satisfying fits of lower order than for SS samples. As total metal concentrations in soils hold main controls on their contents in plants [8], it predicts excessive accumulation of heavy metals in SS plants. Heavy metals ions absorbed by the roots and trans located to shoot lead to impaired metabolism, reduced growth, decrease in soil microbial activity and soil fertility, yield losses and affect nutrient uptake [9]. It also disturbs the uptake of essential nutrients K and Ca in SS plants and their residue in soils system that in turn upsets the absorption and enhancement terms.
3. The range of values for K absorption ratios is similar in both the soils and in plants. Whereas, for Ca, it is towards the lower side for SS samples than for OS samples. This is because of the fact that K amounts are low in SS plant/soil samples (Table 1).
4. K enhancement ratios for soils are much higher than for plants. Because soils are containing good amounts of calcium than plants (Table 1) and calcium X-rays are main source of K enhancement so good amounts of Ca raised the K enhancement ratios.
5. K enhancement ratios v/s β for SS samples are showing significantly different order of fits than for OS but for α it satisfies fit (1, 2) which is (3, 4) for SS soil. Reason behind this is same as explained earlier,

contamination of soil directly affect the soil-plant transmission of nutrients and directs matrix terms towards the higher order fit w.r.t. analyte amounts as compare to low contaminated soil.

4. CONCLUSIONS

In sewage soil/plants, the presence of higher Z and low Z organic contamination disturbs the chemistry of nutrients [10] and effect the empirical matrix formulation as compared to that for normal plant/soil system. With term ratios for sewage samples more fluctuating with analyte contents than those for normal one, the empirical formulation can be used as a tool to check the existence of heavy metal/low Z organic contamination of the soil and its nutrient transmission capacity to the plant.

5. ACKNOWLEDGEMENT

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