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Matrix effects for calcium and potassium K-X-rays, in fenugreek plants grown in iron rich soils

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HIGHLIGHTS

- Matrix effects for Ca and K in Fenugreek plant and its soil with elevated iron level.
- Fenugreek plants grown in iron rich soil and treated with K/Ca fertilizers.
- The matrix terms correlated to analyte and enhancer element amounts.
- Interpolation of matrix terms with elemental amounts points to Fe toxicity of soil.

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ABSTRACT

The present work comprises the matrix effects study of the plant system (plant and soil) for macronutrients Ca and K with elevated levels of iron in the soil. The earlier derived matrix effect terms from fundamental relations of intensities of analyte and substrate elements with basic atomic and experimental setup parameters had led to iterative determination of enhanced elements rather than avoiding their enhancement. The relations also facilitated the evaluations of absorption for close Z interfering constituents (like Ca and K) in samples of a lot of particular category with interpolation of matrix terms with elemental amounts. The process has already been employed successfully for potato, radish, rice and maize plants. On similar lines, the observed prominent change in interpolation parameters for the plants in the present experiment serves as a tool to check the toxicity/contamination of the growing medium.

1. Introduction

X-ray fluorescence (XRF) technique for elemental analysis of a sample involves the characterization and quantification of its elements from the energy and intensity of characteristic X-rays emitted from the sample upon its irradiation with photons. However, the linear correlation of X-ray intensities with elemental concentrations has an inherent defect that X-ray intensities are not proportional to the concentrations of the elements for the targets of practical use due to matrix effects. Sometimes, the characteristic radiation emitted by an element to be detected (called analyte) is capable of exciting the X-rays of other element in the substrate. Thus, the other element causes absorption of the X-rays of analyte, whereas analyte enhances the X-rays of the other element. The absorption and enhancement of the characteristic X-rays are matrix effects. For unknown samples, it is difficult to account for these effects. Different methods exist in literature (Van Grieken and Markowicz, 2002; Vandana and Mittal 2001; Mittal et al., 1987; 1993) in which matrix effects have been evaluated, compensated or nullified. Bansal and Mittal (2009a, b) and Bansal et al. (2012) followed an approach to study matrix effects in terms of absorption and enhancement terms. In the approach, formulations for the terms were derived from the buildup experimental relations of both, selectively as well as enhanced produced analyte X-rays in terms of fundamental parameters and the parameters related to experimental set up. The relations were verified experimentally for synthetic samples and applied to maize plant samples treated with varying amounts of Ca/K fertilizers. A similar work has been carried out for fenugreek plants grown in soils with considerably high amounts of one of the substrate element, Fe that is a micronutrient.

From the random checks of different plants and soils with photon irradiations, it was found that fenugreek (*Trigonella foenum graecum* L.) plant contains Ca and K in the detectable limits of our

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experimental setup (Gupta et al., 2010) and soil from sewage is with higher contents of Fe as compared to other soils from; kitchen garden, farm area and river bed etc. The sewage soil, as pointed out by Cataldo and Wildung (1978) and Pichtel and Anderson (1997), is rich in organic matter as well as in heavy metals especially iron. Therefore, fenugreek plants from a pot experiment with sewage soil as growing medium were selected as samples. The pots were treated with different amounts of potassium and calcium fertilizers to check the cumulative effect of macronutrient fertilizers. The experiment was performed in the months of February and March by growing fenugreek seeds in different pots. Environmental conditions such as light, water and air were kept same for all the pots as far as possible. Thus, the applications of different quantities of calcium and potassium fertilizers to the pot soils during growth of saplings leads to variations in calcium and potassium amounts in the plants (Bansal and Mittal, 2009a) as seeds and soils are same except fertilization amounts. The details of pot experiment, formulations, elemental analysis of pot yields and outcomes of the experiment are given in the following sections.

2. Pot experiment

Our earlier studies on matrix effects in different plants involved the growth medium as homogeneous mixture of clay soil and sand (1:1) (Mittal et al., 1993; Vandana and Mittal 2001; Bansal and Mittal, 2009b; Bansal et al., 2012). Patterns of matrix terms for the different plants grown on similar substrate medium were found same. Generally, it is known that plants reflect the geochemical environment in which they grow and the nutrient balance in plants depends on the soil composition. Any invasion of a toxic element can lead to a series of very complex responses in plants (Krupa et al., 2002). To check such possibility, four different types of soils i.e. from kitchen garden, farm area, river bed and sewage dump area were selected. The soils were collected from respective sites with wooden tools to avoid any metallic contamination. The soils, in turn, were irradiated with photons from low power X-ray tube operated at anode voltage 8 kV (Fig. 1). The reflected spectra of soils recorded in Si-PIN detector and are shown in Fig. 1. The spectrum of sewage soil shows the iron level higher than in other soils and is utterly higher than the normal range generally found in soils. Keeping in view this particular character of sewage soil, the sewage soil + sand + clay soil was taken as growing medium to study the interfering effect of excess soil iron on the matrix terms of macronutrients (K/Ca) in plants and soils.

In a spacious laboratory room, ten pots were used and 80–100 uniform sized seeds of fenugreek were germinated in each pot. The soils for plant growing media were prepared by mixing sewage soil, clay soil and sand in fixed proportions (1:1:1) homogeneously. All the three soils were mixed homogeneously. The experiment was carried for 40 days. Regular watering was done during the course. On 15th, 21st and 35th day after sowing of seeds, fertilizations with $CaCO_3$ (calcium fertilizer) (Helyar and Anderson, 1974) and KCl (potassium fertilizer) (White, 1987) were done. POT-1 was left untreated. The four pots (POT-2, POT-3, POT-4, POT-5) were treated with $CaCO_3$ solutions in moles as; 5 mM, 15 mM, 25 mM, 40 mM. The POT-6 was treated with 20 mM solutions of both $CaCO_3$ and KCl fertilizers, whereas the remaining four pots (POT-7, POT-8, POT-9, POT-10) were treated with KCl solutions; 5 mM, 15 mM, 25 mM and 40 mM, respectively.

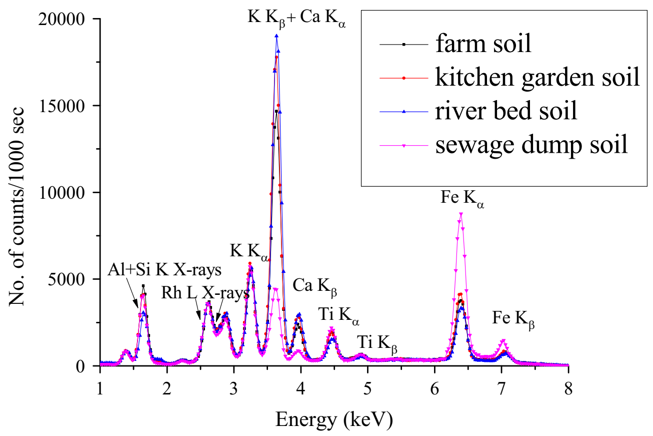

Fig. 1. Spectra for four different soils at 8 kV/0.05 mA.

On full growth the plants were cut from above the soil surface and washed under running water to remove the soil and foreign material (if any) on the plants. The plants were dried at room temperature for two days and in oven at 100–120 °C for 5–6 h for consecutive two days. The dried fenugreek plants were then grinded in an electric grinder and electric agate pestle mortar. The thick pellets of samples (Mittal et al., 1993) were prepared by pressing fine powder of the material in a die with 25 t semi auto Hydraulic pressing machine to obtain pellets of 2.5 cm diameter. For soil analysis, the respective soils were collected at depth 0–5 cm from individual pots and dried at 70–80 °C for 5–6 h for four days. The dried soil samples were sieved through sieve mesh no. 300 having aperture width of 53 μm. The sieved samples were also pressed in the die to prepare pellets of 2.5 cm diameter.

3. Formulations for element determination, absorption and enhancement terms

In a thick sample *S*, amount δ of one of its constituents, *x*, can be determined with the existing analytic method based upon XRF technique for thick sample pellets (Vandana and Mittal 2001; Bansal and Mittal, 2009a, 2009b; Bansal et al., 2012). The method involves, in turn, selective excitation of analyte element *x* in *S* and its two reference materials. First reference material is analyte *x* itself or its compound *X* with *n* atoms of *x*. Second reference *Sp* is a mixture of *S* and its first reference material in known ratio.

With δ' amount of first reference *X* is added to the unit amount of *S* for *Sp* preparation, the amount δ is determined simply from analyte X-ray counts in *S*, *X* and *Sp*; $N_x^S(i_x)$, $N_x^X(i_x)$ and $N_x^{Sp}(i_x)$, using relation (Mittal et al., 1987):

$$\delta = \frac{nM_x}{M_X}\delta' \frac{\left[\frac{N_x^X(i_x)}{N_x^{Sp}(i_x)} - 1\right]}{\left\{\left[\frac{N_x^X(i_x)}{N_x^S(i_x)}\right] - \left[\frac{N_x^X(i_x)}{N_x^{Sp}(i_x)}\right]\right\}} \tag{1}$$

where M_x is atomic weight of analyte *x*; M_X is molecular weight of analyte compound *X*, i_x is incident energy for selective excitation of *x*.

3.1. Absorption and enhancement terms

In sample *S*, if X-rays of analyte *a* with fractional amount α excites the X-rays of other element *c* of fractional amount β, then, it causes absorption of *a* X-rays and enhancement of *c* X-rays that is called matrix effects that disturb the linearity between the X-ray intensity and analyte amount in *S* and *Sp*. For *S*/*Sp* irradiation with i_a photons for selective excitation of *a* for its X-rays being counted in a detector (Fig. 2) as '$N_a^{S/Sp}(i_a)$' are after their absorption in the substrate and X-ray counts under the *c* photo peak of *S*/*Sp* in the same excitation as '$N_c^{S/Sp}(i_a)$' are enhanced (Bansal et al., 2012).

Once the amount α/β of elements *a*/*c* in the *S* (of unknown constituents) is determined from selective excitation of analyte *a*/*c*