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ANALYTICAL ENERGY DISPERSIVE X-RAY FLUORESCENCE MEASUREMENTS WITH A SCANTY AMOUNTS OF PLANT AND SOIL MATERIALS^{**}

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Elemental evaluations in scanty powdered material have been made using energy dispersive X-ray fluorescence (EDXRF) measurements, for which formulations along with specific procedure for sample target preparation have been developed. Fractional amount evaluation involves an itinerary of steps; (i) collection of elemental characteristic X-ray counts in EDXRF spectra recorded with different weights of material, (ii) search for linearity between X-ray counts and material weights, (iii) calculation of elemental fractions from the linear fit, and (iv) again linear fitting of calculated fractions with sample weights and its extrapolation to zero weight. Thus, elemental fractions at zero weight are free from material self absorption effects for incident and emitted photons. The analytical procedure after its verification with known synthetic samples of macro-nutrients, potassium and calcium, was used for wheat plant/soil samples obtained from a pot experiment.

Keywords: fluorescent X-rays, elemental analysis, macro-nutrients, scant amounts.

ЭЛЕМЕНТНЫЙ АНАЛИЗ МАЛЫХ ОБЪЕМОВ РАСТИТЕЛЬНЫХ И ПОЧВЕННЫХ МАТЕРИАЛОВ МЕТОДОМ ЭНЕРГОДИСПЕРСИОННОЙ РЕНТГЕНОВСКОЙ ФЛУОРЕСЦЕНЦИИ

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Элементный анализ малых объемов порошковых материалов выполнен методом энергодисперсионной рентгеновской флуоресцеции. Использованы специально разработанные рецептура и методика приготовления образцов. Количественная оценка доли каждой фракции включала в себя сбор элементных характеристик рентгеновских отсчетов в спектрах энергодисперсионной рентгеновской флуоресцеции, записанных при различных содержаниях материала; аппроксимацию линейной функцией зависимости между рентгеновскими отсчетами и содержанием материала; расчет элементных фракций, исходя из линейной зависимости; аппроксимацию линейной функцией зависимости между вычисленными фракциями и полным весом образца и последующую экстраполяцию вычисленных фракций к нулевому полному весу образца. Экстраполированные к нулевому полному весу образца элементные фракции не зависят от эффектов самопоглощения для падающих и излучаемых фотонов. После проверки на известных синтетических образцах, содержащих макроэлементы, калий и кальций, разработанная аналитическая процедура использована для анализа образцов пшеницы/почвы, полученных из экспериментов в горшках.

Ключевые слова: рентгеновская флуоресценция, элементный анализ, макроэквиваленты, малые количества.

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Introduction. In the energy dispersive X-ray fluorescence (EDXRF) technique of elemental analysis, energies of emitted characteristic X-rays from a material provide qualitative information about constituent elements, and intensities (numbers) of X-rays give quantities of the elements. Thus, both energies and intensities provide elemental analysis of material. Generally, conversion of intensities into concentrations involves a relationship of measured characteristic X-rays intensities with excitation source intensity, concentration of the analyte element, interaction probability of exciting radiation with the analyte, and overall composition of material and its absorption properties. For targets of practical use, the conversion of intensities into concentrations of material constituents becomes cumbersome as the characteristic X-rays of the analyte are strongly absorbed in the sample itself if they are able to excite the X-rays of some other element in the sample. As a result, the other element's characteristic X-rays are strongly enhanced. The absorption and enhancement of X-rays are known as matrix effects and disturb the linearity between characteristic X-ray intensities and analyte concentrations. Therefore, analysis of unknown samples presents a real challenge where a meaningful conversion of the intensities to the concentrations requires careful consideration of the interfering effects. Grieken and Markowicz [1] have provided valuable information on the various quantification methods including their fundamentals, advantages, and limitations. In our laboratory, an approach for elemental analysis of thick samples [2] is being followed, in which enhancement is avoided by selective excitation of the analyte element in the sample and absorption is taken into account in terms of X-ray count ratios of the sample and its two standards; the first standard is the analyte itself or its compound, and the second standard is a known mixture of the first standard and the sample. The approach has been successfully followed to find potassium and calcium nutrient status of spinach [3], radish [4], potato [5], rice [6], maize [7, 8], and fenugreek [9]. In the recent past, a pot experiment was performed in the lab on wheat that was grown on soils collected from different locations to study the effect of soil environment on plant nutrients. Wheat plant yields from pots were scanty for elemental analysis using the existing thick sample method. To handle the problem of low yields, an alternative method for sample preparation was conceived, and the required mathematical formulation was developed for determination of fractional amounts. The analysis of measured characteristic X-ray data involves a procedure to evaluate the elemental concentration from a single atomic layer of material sample where the intensities bear a linear relationship with the amounts. The details of the measurements, developed formulations, and procedures followed are given here.

Analytical evaluations from EDXRF measurements. EDXRF measurements in single reflection geometry (Fig. 1a) involve incident photons *i* on the sample *S* at an angle θ_1 with the normal to sample surface at the point of strike and *e* emitted fluorescent X-rays of element (*el*) of sample detected in a detector at an angle θ_2 with the normal.



Fig. 1. Ray diagram for 90° single reflection geometry (a) and plot of counts N_S^{el} vs. target thickness t_S (b).

The intensity of fluorescent X-rays N_S^{el} , the number of net counts under the photo peak of *el* of target *S*; detected by the detector is given as

$$N_{S}^{el} = I_{0} \frac{A_{v}}{M_{el}} t_{S}^{el} \beta_{S} \sigma_{K}^{el} (E_{i}) \omega_{K}^{el} a_{air} (e) \varepsilon_{K}^{el}, \qquad (1)$$

where I_0 is the photon flux striking on the surface of the sample seen by the detector; A_v is the Avogadro's number; M_{el} is the atomic weight of el; t_S^{el} is the amount of el (g/cm²) in S; β_S is the target self-absorption correction factor for incident *i* and emitted *e* radiation:

$$\beta_{S} = \left[\frac{1 - \exp\left[-\left(\mu_{S}(i)/\cos\theta_{1} + \mu_{S}(e)/\cos\theta_{2}\right)t_{S}\right]}{\left(\mu_{S}(i)/\cos\theta_{1} + \mu_{S}(e)/\cos\theta_{2}\right)t_{S}}\right]$$

where μ_s (cm²/g) are the absorption coefficients of the sample material at *i* and *e* energies, t_s is the weight of sample S (g/cm²); $\sigma_{K}^{el}(E_{i})$ is the photo-ionization cross-section in b/atom for el at the incident energy E_{i} ; ω_K^{el} is the fluorescence yield of *el* for the *K*-shell; $a_{air}(e)$ is the correction for absorption of *e* photons in the air column between sample and detector; ε_{K}^{el} is the efficiency of detector at emitted K X-ray energy of *el*.

The fractional amount, $x = t_S^{el}/t_S$, of *el* in *S* gives

$$N_{S}^{el} = I_{0} \frac{A_{v}}{M_{el}} x t_{S} \beta_{S} \sigma_{K}^{el} (E_{i}) \omega_{K}^{el} a_{air} (e) \varepsilon_{K}^{el} .$$
⁽²⁾

The term $[I_0a_{air}(e)\varepsilon_K^{el}]$ comprises source, geometry and detector factors that can be evaluated/compensated with an additional measurement in the same set-up with a standard (St), pure element el, or its compound in place of S. The counts N_{St}^{el} under el X-ray peak from St are

$$N_{St}^{el} = I_0 \frac{A_v}{M_{el}} t_{St}^{el} \beta_{St} \sigma_K^{el} (E_i) \omega_K^{el} a_{air} (e) \varepsilon_K^{el} .$$
(3)

The terms with subscript St corresponds to the material of the standard, and $t_{st}^{el} = (M_{el}/M_{St})nt_{St}$, where M_{St} is the molecular weight of St and n is number of atoms of el in one mole of St. The ratio of relations (2) and (3) gives

$$x = \frac{N_{St}^{el}}{N_{St}^{el}} \frac{M_{el}}{M_{St}} n \frac{t_{St} \beta_{St}}{t_S \beta_S} .$$

$$\tag{4}$$

Thus, evaluation of x requires ratios of measured counts, N_S^{el}/N_{St}^{el} , known atomic/molecular weights M_{el}/M_{St} , and calculated/evaluated absorption correction factors $t_{St}\beta_{St}/t_{S}\beta_{S}$ along with number *n*.

For known composition of St, β_{st} can be calculated from expression of β for St. But in sample S, unknown composition acts as a dark matrix for *el*, and β_s calculations are not possible. Therefore, to determine β_{s} , an approach [10] is followed as for a single reflection setup (Fig. 1a), and relation (2) can be written as

$$N_S^{\ el} = K t_S \beta_S,\tag{5}$$

where K embraces all other terms in Eq. (2) except t_S and β_S . Let $\beta_S = [1 - \exp(-Zt_S)]/Zt_S$, where $Z = \mu_{S}(i)/\cos\theta + \mu_{S}(e)/\cos\theta$, and relation (5) becomes

$$W_S^{el} = Kt_S\{[1 - \exp(-Zt_S)]/Zt_S\}.$$

A plot of N_S^{el} vs. t_S (Fig. 1b) shows that the thickness counts at t_S' become constant and independent of *t_S*. Thus, *t_S'* is the saturation thickness at which $t_S \to \infty$ and $\exp(-Zt_S) \to 0$. For thicknesses $< t_S'$, the plot is linear. At linear thicknesses t_S and $2t_S$, the counts ratio $\frac{N_S^{el}(t_s)}{N_S^{el}(2t_s)} = \frac{1 - \exp(-Zt_S)}{1 - \exp(-Zt_S)}$ yields

$$Zt_{S} = \ln\left(\frac{N_{S}^{el}(t_{S})}{N_{S}^{el}(2t_{S}) - N_{S}^{el}(t_{S})}\right) \text{ and } \beta_{S} = \left\lfloor\frac{2 - N_{S}^{el}(2t_{S})/N_{S}^{el}(t_{S})}{\ln\left(N_{S}^{el}(t_{S})/[N_{S}^{el}(2t_{S}) - N_{S}^{el}(t_{S})]\right)}\right\rfloor.$$
(6)

So, the linearity of X-ray intensity with t_S is the essential constraint on sample thickness t_S , and the expression for x becomes

$$x = \frac{N_{S}^{el}}{N_{St}^{el}} \frac{M_{el}}{M_{St}} n \frac{t_{St}^{el} \beta_{St}}{t_{S} \left[2 - \frac{N_{S}^{el} (2t_{S})}{N_{S}^{el} (t_{S})} \right/ \ln \left(\frac{N_{S}^{el} (t_{S})}{N_{S}^{el} (2t_{S}) - N_{S}^{el} (t_{S})} \right) \right]}.$$
(7)

Thus, with β_S determinations from X-ray counts $N_S^{el}(t_S)$ and $N_S^{el}(2t_S)$ at thicknesses t_S and $2t_S$, measured N_S^{el} and N_{St}^{el} counts for sample and standard, calculated value of $t_{St}^{el}\beta_{St}$; and known values of M_{el} and M_{St} , x for sample S is calculated.

The experimental measurements require preparation of material samples of thicknesses $< t_S'$, measurements of energy and intensity of emitted fluorescent X-rays, and evaluations of elemental fractions in the material.

Sample preparation. For sample target preparation from powdered material, weighed amount $<t_{S'}$ of sample on a Scientech, USA, digital weighing machine with precision 0.1 mg was pasted on adhesive tape in a fixed area of dimensions 2 cm² limited with a metallic cylindrical die. Another layer of adhesive tape was pasted to hold the material in between two plastic layers and pressed with fingers for the uniformity of sample and to exhaust the trapped air in the target. The target was ready to use. The accuracy of pressed sample weight was checked with a weighed sample pasted on weighed adhesive tape pieces, and the pressed sample was again weighed and the tape weight was subtracted from it. To check the uniformity of sample, a wheat target was cut at the middle and weighed one by one on a weighing machine. The weights of the two parts were 0.0479 and 0.0472 g, giving uniformity of the sample within 1.5%. Further, these two parts were cut at their centers, and the four parts of the single target were weighed, which came in as 0.0225 g 0.0224, 0.0218, and 0.0226 g with variance 1.29167E-07.

To monitor potassium and calcium macronutrients in wheat plants and soils, the formulations were first tested with synthetic samples of K and Ca and then applied on wheat/soil samples from the pot experiment.

Measurements on synthetic samples for K and Ca contents. Synthetic samples of borax+KCl and borax+CaO with fix proportion 10:1 were used to study the K X-ray peak of K and Ca respectively. Three targets from each mixture were prepared, with weights 0.009, 0.018, and 0.0225 g of borax+KCl and 0.0045, 0.0135, and 0.0225 g of borax+CaO. In the experimental setup of the side window X-ray tube [11], samples were selectively excited at anode voltage/filament current 4 kV/0.35 mA for potassium K X-rays with *K*-edge energy 3.607 keV and 5 kV/0.2 mA for calcium K X-rays with *K*-edge energy 4.034 keV in the single reflection geometry with dead time losses <10%.

The emitted fluorescent X-rays and scattered photons of the tube from the target were recorded in a Si-PIN detector of an Amptek X-123 spectrometer with 0.5 mil Be window and of dimensions 6 mm²/500 μ m having a resolution of 145 eV at 5.95 keV Mn X-rays. The fluorescent X-ray spectra for potassium and calcium excitation are shown in Fig. 2.

Plots of counts under KK_{α} (Fig. 3a) and CaK_{α} photo peaks versus sample weights for two synthetic sets were made, and straight line fits were applied to the plots.



Fig. 2. Spectra of borax+KCl(0.0225 g) at 4 kV/0.35 mA (a) and borax+CaO (0.022 5g) at 5 kV/0.2 mA (b).



Fig. 3. Straight line fit for KK_{α} counts vs. weights of borax+KCl samples (a) and plot of evaluated K amounts from counts at t_S and $2t_S$ (with scattered t_S and $2t_S$ selections on straight line fit (a)) and further straight line fit to K amounts vs. t_S weights (0.0101–0.0112 g) (b).

The fit justifies the linear variation of X-ray counts with sample weights. With a pair of counts at selected t_s and $2t_s$ sample weights in the linear region, β_s were evaluated and corresponding elemental fractions x of K/Ca were determined with relation (7) (plot of x for potassium at different t_s values is shown in Fig. 3b). Calculated x were found varying with t_s and slightly less than the expected fractional amount of

potassium. The plot showed the dependence of x on t_s . A cross check on relation (7) revealed the inverse proportionality of x with t_s . Thus, to compensate for the inverse linear dependence on t_s , straight line fits were applied on x vs. t_s data for K and Ca on the end weights side (Fig. 3b) and x were evaluated at $t_s = 0$ where the β_s factor (denominator bracket terms in Eq. (7)) becomes 1 and the target behaves as a single atomic layer in the true sense. Thus, x at $t_s = 0$ is the actual value and came to 0.053 for K and 0.079 for Ca.

To check the reproduction of results, the range of selected t_S values was arranged in five different groups with six values in each group after permutation and combination of x and t_S data. The generated values (Table 1) were almost constant with variance, 9.52479E-07 for K content and 1.91485E-06 for Ca. All this supported the methodology and formulation used. The errors in evaluated values culminated in 10% because of the errors 0.1-2% in counts, 5% in β and ~10% in t_S .

TABLE 1. Evaluated x Results from Five Different (x, t_s) Data Groups				
for Each KK_{α} and $CaK_{\beta}X$ -Rays				

Groups	Borax+KCl		Borax+CaO		
	x value		<i>x</i> value		
	Generated	Actual	Generated	Actual	
1	0.052 ± 0.005	0.047	0.076 ± 0.008	0.065	
2	0.052 ± 0.005		$0.076 {\pm} 0.008$		
3	0.052 ± 0.005		$0.076 {\pm} 0.008$		
4	0.052 ± 0.005		$0.076 {\pm} 0.008$		
5	0.052 ± 0.005		$0.076 {\pm} 0.008$		
Variance	1.192E-08		2.882E-08		

Experiment on wheat plants and soil samples. Wheat plants were grown in different pots with an equal number of wheat grains in each pot in a spacious airy laboratory room of dimensions $\sim 24 \times 21 \times 12$ ft with proper daylight and no artificial luminance at night. The growing medium, i.e., soil, was collected from three different places, Ajrawar (village) Pond, Patiala (city) River, and Moonak (town) River side places in Punjab, and a homogeneous mixture of the each soil along with clay/sand was prepared. After full growth, wheat plants were cut from above the soil level and washed under running water to remove the soil and foreign material (if any) on the plants.

The washed plants were then dried first at room temperature for 2–3 days, then in an oven at 60–70°C for 5–6 h for a consecutive 3–4 days. Similarly, the soil samples were collected from individual pots at a depth of 0–5 cm and dried at 60–70°C for 5–6 h for 4–5 days. Dried soil samples were sieved through sieve mesh No. 300 having aperture width of 53 μ m. Further, dried plant samples were ground in an electric grinder and electric agate pestle mortar. The sample preparation procedure used for synthetic samples was followed for targets of soil and plant from three pots.

Each soil and plant target from pot-AP (Ajrawar Pond), pot-PR (Patiala River) and pot-MR (Moonak River) for K and Ca excitations was, in turn, excited with selective anode voltages 4 kV/0.35 mA and 5 kV/0.20 mA, respectively. The spectra were recorded for 500 s thrice to reduce statistical error. The typical spectra for wheat and soil samples are given in Fig. 4b.

Due to the limited resolution of the detector, photo peaks K_{β} of K and K_{α} of Ca overlap in calcium excitation (Fig. 4b). Thus, for analysis, only K_{α} of potassium and K_{β} of calcium (being free from interference) were considered. Plots between number of counts and sample weights were applied straight line fits, and fractions x were evaluated with counts at thicknesses t_S and $2t_S$ from interpolated straight lines N_S^{el} vs t_S and are listed in Table 2.



Fig. 4. Background subtracted spectra for 0.0200 g Pot-AP wheat/soil sample at 4 kV/0.35 mA (a) and 5 kV/0.2 mA (b), spectrum of plant (1) and soil (2).

Wt., g	Plant sample			Soil sample		
t_S	POT-AP	POT-PR	POT-MR	POT-AP	POT-PR	POT-MR
	Calculated K fractions for KK_{α} counts					
0.005	0.192	0.254	0.149	0.101	0.096	0.085
0.0051	0.188	0.249	0.146	0.098	0.094	0.083
0.0052	0.185	0.243	0.144	0.096	0.095	0.081
0.0053	0.182	0.238	0.142	0.094	0.050	0.080
0.0054	0.179	0.233	0.14	0.092	0.088	0.078
0.0063	0.158	0.197	0.124	0.077	0.074	0.066
0.0065	0.154	0.191	0.121	0.074	0.071	0.064
0.0067	0.150	0.185	0.118	0.072	0.069	0.062
0.0069	0.147	0.179	0.115	0.069	0.067	0.060
0.0071	0.144	0.174	0.113	0.067	0.064	0.058
0.0091	0.120	0.135	0.096	0.051	0.049	0.045
0.0093	0.119	0.132	0.094	0.05	0.048	0.044
0.0095	0.117	0.129	0.093	0.049	0.047	0.043
0.0097	0.115	0.127	0.092	0.047	0.046	0.042
0.0099	0.114	0.124	0.091	0.046	0.045	0.041
	(Calculated C	a fractions f	br Ca K_{β} co	ounts	
0.0050	0.045	0.060	0.074	0.044	0.058	0.038
0.0051	0.045	0.058	0.074	0.043	0.057	0.037
0.0052	0.044	0.057	0.073	0.042	0.056	0.036
0.0053	0.043	0.056	0.072	0.041	0.054	0.036
0.0054	0.042	0.055	0.071	0.04	0.053	0.035
0.0063	0.036	0.046	0.065	0.034	0.045	0.03
0.0065	0.035	0.044	0.064	0.033	0.044	0.029
0.0067	0.034	0.043	0.063	0.032	0.042	0.028
0.0069	0.033	0.041	0.062	0.031	0.041	0.027
0.0071	0.032	0.04	0.062	0.031	0.04	0.026
0.0091	0.026	0.03	0.055	0.024	0.031	0.021
0.0093	0.025	0.03	0.055	0.024	0.03	0.02
0.0095	0.025	0.029	0.054	0.023	0.029	0.02
0.0097	0.024	0.028	0.054	0.023	0.029	0.02
0.0099	0.024	0.028	0.053	0.022	0.028	0.019

TABLE 2. Calculated Amount of K and Ca in Sample at Different Sample Weights ts.

Further, calculated fractions x at different sample thicknesses t_S were straight line fitted near end points and extrapolated to zero thickness ($t_S = 0$). The process was repeated for different combination of (x, t_S) data values in each case, and evaluated x values are listed in Table 3, which represent the collection of the results with variance lying in the range $10^{-5}-10^{-7}$ for fractional amounts.

TABLE 3. K and Ca Fractions of Each Wheat Plant and Soil Samples Applying the Iteration	n Process
on Different Permutations and Combinations of Data Values of Table 2	

(x, t_S) data	KK_{α} contents					
value groups	Wheat sample			Soil sample		
	POT-AP	POT-PR	POT-MR	POT-AP	POT-PR	POT-MR
				O.247*	0.308*	0.346*
1	0.342	0.508	0.261	0.206	0.195	0.170
2	0.335	0.497	0.256	0.202	0.191	0.166
3	0.339	0.503	0.258	0.204	0.193	0.168
4	0.339	0.504	0.259	0.204	0.194	0.168
5	0.339	0.503	0.258	0.204	0.193	0.168
Mean	0.339	0.503	0.258	0.204	0.193	0.168
Variance	6.2E-06	1.60E-05	3.30E-06	2.00E-06	2.20E-06	2.00E-6
(x, t_S) data			CaK _β	contents		
value groups	Wheat sample			Soil sample		
	POT-AP	POT-PR	POT-MR	POT-AP	POT-PR	POT-MR
				0.104*	0.091*	0.016*
1	0.087	0.122	0.115	0.085	0.117	0.074
2	0.085	0.119	0.113	0.083	0.114	0.073
3	0.086	0.120	0.114	0.084	0.116	0.073
4	0.087	0.121	0.114	0.084	0.116	0.073
5	0.086	0.121	0.114	0.084	0.116	0.073
Mean	0.086	0.121	0.114	0.084	0.116	0.073
Variance	4.33E-07	1.03E-06	3.70E-07	4.24E-07	8.60E-07	3.24E-07

* K and Ca content in soil before planting.

Results and discussion. In synthetic samples, the repeatability of the results and the agreement between the actual and evaluated amounts openly support the present formulation and method of measurements. The repeatability/reproducibility of results in the case of wheat/soil further supports the reliability of the method for lesser amounts of sample analyzed using derived formulation. So, the determined potassium and calcium amounts in plants/soils collected from different locations are trustworthy. An overview of results shows more transmission of K from soils to wheat, and the Ca contents in plants of the respective soils are almost comparable, but the ratio of nutrient content in plant and soil (nutrient transmitted to plant to its residual contents in soil) is greater than 1 in all the cases.

To check the nutrient status of soils before and after the planting, the raw soils before planting were analyzed for K and Ca contents using our well established analytical method for thick samples [12] (listed with a star in Table 3). It is observed that after planting, K fractions in all the soils and Ca fractions in AP soil have decreased as plants extracted the nutrients from the soil. But in the case of MR and PR soils the Ca fraction after planting has increased along with good transmission of Ca to the plants. This is corroborated by the fact that for a system with high demand of nutrient by the plants and insufficient nutrient supply to the root surface by root interception or mass flow, continued uptake by the plant depletes the concentration at the root surface. A concentration gradient results from the bulk soil to the root surface, which causes nutrients to diffuse along that gradient towards the root surface [13].

A detailed interpretation of results listed in Table 3 follows. Comparatively minimum Ca and K contents left in MR soil correspond to \sim 1.5 times enhanced potassium and calcium transmissions in plant. AP soil with high residue of K corresponds to a nominal transmission of 1.5 times of K to the plant, while the Ca transmission is just at equilibrium level with soil Ca residue. Ca in PR soil and plant samples is almost at equilibrium level. Here K transmission to plants is enhanced too much (~2.5 times the K residue in PR soil, that is, in between the contents of AP and MR soils).

The pH testing of three soils after plantation showed the pH range \sim 7 for MR and AP soils and \sim 8 for PR soil. Therefore, the more alkaline nature of PR has enhanced K and Ca transmission in wheat sample [14] (pp. 450–452) and left comparatively Ca enriched soil due to higher Ca demand of the plant. Calcareous AP soil before plantation has suppressed transmission of Ca and left excess of K in the soil as more calcium in soil increases the potassium fixation in soils [14] (pp. 710–711) and, in turn, the higher level of potassium has depressed the calcium uptake in plants.

In addition to these explanations, there can be some other reasons for K and Ca transmissions in the plant samples, e.g., texture of soils, nature of plant and contents of pollutions etc., that require extra monitoring during experiment and are to be studied in future experiments.

Conclusion. Measurements on synthetic samples with repeatability of the results and the agreement between the actual and evaluated amounts openly support the present formulation and method of measurements for scanty amounts. A good demand of Ca by plant sets a concentration gradient from bulk soil to root surface that fetches the nutrient from deep in the soil to the upper part of the soil. The K and Ca nutrient contents from measurements on wheat plants grown on three soils and the soils justify the fact that alkalinity of soil (PR) has enhanced K and Ca transmission in wheat sample. Calcareous soil (AP) before plantation has suppressed transmission of Ca and left excess of K in the soil as more calcium in soil increases the potassium fixation in soils and, in turn, the higher level of potassium has depressed the calcium uptake in plants.

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