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Novelty of the work: The use of these techniques can improve the development of ED-XRF results evaluation procedures that really is in a new phase.

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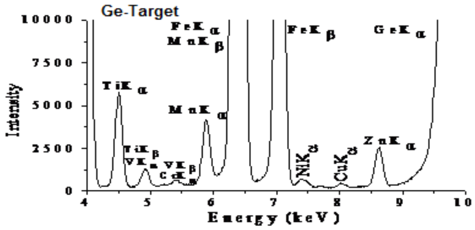

Validation of classical quantitative fundamental parameters method using multivariate calibration procedures for trace element analysis in ED-XRF

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Abstract

In this study, the X-ray intensities obtained from 76 soil samples were converted to concentration by means of the Epsilon software program applying the fundamental parameters method (FP). Various National Institute of Standards and Technology (NIST) standard reference materials (SRMs) were used to evaluate the accuracy of the analysis. The discussion was restricted to the analysis of only ten elements. The results have indicated that the soil samples contain V(10-93), Mn(313-7227), Co(3-18), Ni(47-281), Cu(1-32), Zn(20-86), As(30-236), Sr(131-592), Ba(78-7329), Rb(25-149) and Pb(17-67) between minimum and maximum values in a range of mg/kg. Partial Least Squares (PLS) and Principle Component Regression (PCR) models were used to predict the elemental concentrations. Cross-validation (CV) was used to calculate the Estimated Mean Square Predictive Error (*EMSPE*) values and to determine the optimal number of PLS and PCR components. Predicted concentrations were based on *EMSPE* values, utilizing 1 PLS and PCR components for V, Co, Cu, Zn, 3 PLS and PCR components for Mn, Ni, Pb, 5 PLS and 8 PCR components for As and Ba, 7 PLS and 10 PCR components for Rb and 3 PLS and 4 PCR components for Sr with minimum *EMSPE* values. It was observed that prediction errors and increasing factor numbers were depend on the reference material concentration intervals as much as the number of SRM's. On the other hand, when PLS and PCR models were compared among themselves, it was seen that PLS model had a strong relation with FP method as compared to PCR model with less prediction errors and component numbers.

Key Words: *ED-XRF; fundamental parameters method; multivariate calibration procedures**;** partial least square regression; principle component regression; method validation; trace element.*

Introduction

During the last decade, energy-dispersive X-ray fluorescence (ED-XRF) spectrometry has been experiencing a revival. Improvements in electronics, detector and X-ray tube technology combined with an ever increasing computer power has led to various new versatile, compact and reasonably cheap ED-XRF instruments. The nature of applications requires a fast processing of the gathered data. As such, a direct conversion of the obtained spectra into constituent concentrations without user interaction would be an ideal situation. However, the current data processing methods only partially fulfill this goal. The main drawbacks of ED-XRF are the spectral interference of element characteristic lines due to the limited resolution of the solid-state detector and the presence of matrix effects that make a straightforward conversion of peak intensities into element concentrations difficult.[1]

The fundamental parameters method is based on mathematical expressions first derived by Sherman and by Shiraiwa and Fujino.[2,3] The application of the fundamental parameters method requires certain conditions to be satisfied, e.g. homogeneous and flat samples. However, the major drawback is that the complete procedure and in particular the spectrum processing remains difficult to automate. The fundamental parameters method is especially interesting because it allows the semi-quantitative analysis of completely unknown samples. Unfortunately, the approach suffers from uncertainties in mass absorption coefficients and fluorescence yields of the individual elements. The implementation of expert systems to enable automation has been considered.[4]

Apart from fundamental parameters method a large variety of multivariate methods are used in combination with XRF results. Orthogonal multivariate regression models are those most employed for quantitative analysis, as well as principle components regression (PCR) and partial least square regression (PLS).[5] PLS combines spectral and analytical information of a number of samples to build predictive models by establishing a direct correlation between spectra of samples and properties of interest (generally concentration values) of the species contained in them. All these implementations have opened the possibility of usage of XRF as a rapid and low cost technique to obtain basic information of total concentration of metals in the assessment of potentially polluted soils and sediments.[6] Compared with the classical method, PLS and PCR embody both the spectrum evaluation and the quantitative analysis. The analysis merely consists of a multiplication of matrices and does not require much computer power and time. PLS and PCR methods end by pointing out the major drawback when applied to XRF, i.e. the need for a large number of calibration samples. A good agreement between calculated and experimental results is critical for a successful implementation of the PLS and PCR methods.[1]

PCR method has a significant drawback with respect to ED-XRF. The PCR is the standard formulation for which the PCs defining score matrix are in accordance with the size of their corresponding eigen values alone and not on their predictive value. This procedure neglects low variance components that may have predictive value. The PCs solely describe the largest variance components of the spectral data, X, and it is not necessarily true that this is the most informative variance to model the concentration data, $\mathbf{y}$. This is particularly the case for ED-XRF. Suppose PCR is used for the quantitative analysis of Pb in soil samples. It is obvious that the Pb signals are only responsible for a small part of the total variation in the ED-XRF spectra. Other elements such as Si, Fe, Ca and K contribute much more to the total variation in X and though it is captured by the first PCs, it is of secondary importance to describe the Pb concentration. Yet, PCR will primarily use the first PCs to model the Pb concentration. Therefore, several authors suggest retaining, in the final PCR model, only those PCs that show a good correlation with the y-variable.[7,8,9] Another solution is to derive the eigenvectors in such a way that the more predictive information is placed in the first PCs.

In 1995 only two publications on the use of PLS for XRF analysis were reported. Wang et al.[10] applied the PLS method for the analysis of Nickel alloy samples employing

WD-XRF. The first application of PLS to ED-XRF was reported by Swerts et al.[11] who used the combined method for the analysis of Sulfur-Graphite mixtures. After 1995, Urbanski and Kowalska applied the PLS method to various low-resolution ED-XRF analyses.[12]

This study aims to provide an alternative validation method for the quantitative analysis of ED-XRF results. The first part of this work focuses on the fundamental parameters calibration procedure to calculate the concentrations of heavy metals in soil samples and then principles of PLS and PCR and their tailoring for ED-XRF results will be discussed, followed by application of the methods.

PCR and PLS regression models

1. Methodology

The matrix **X** is used exclusively to contain the ED-XRF intensity data. For example **X** ($n \times p$) is a matrix containing *n* samples each of which consist of *p* elements. Usually, *n* is the number of objects or samples for which the spectrum is recorded. Likewise, **Y** is used exclusively to contain the element concentrations. **Y** ($n \times m$) is a matrix containing the concentrations for each *m* element in *n* samples.

The idea in principle component analysis (PCA) is to construct successive linear combinations so that each one accounts for as much of the total variation as possible subject to the constraint that it is orthogonal to the linear combinations already extracted.[13] After PCA is carried out, the original data contained in **X** and described by *p* variables is represented by score matrix, if one is satisfied with the rank *m* approximation. By doing so, the number of variables is also reduced from *p* to *m* without a significant loss of information. The PCR method uses the linear combinations or PCs (Principle Components) of **X,** derived using PCA, to model the relationship between **X** and *p*. The derivation of the PCs is independent on *p* and therefore different *y*-variables are all modeled by means of the same subset of PCs. In an improved approach, only those PCs are used that show a good correlation with the *p*-variable of interest but often, and especially in ED-XRF, this is not sufficient. In contrast to PCR, the subspace retained in PLS is constructed with reference to the vector of observations. Moreover, the PLS method is not restricted to one variable and several dependent variables can be modeled simultaneously.

2. Validating the regression models

Validating the models essentially concerns the selection of the optimal number of PLS and PCR components. In addition, the validation method provides a value for the prediction error enabling the assessment of the predictive capacity of the model. The determination of the optimum number of PLS and PCR components is mainly done by calculation of the Estimated Mean Square Predictive Error (*EMSPE*) with cross-validation (CV)[14];

$$EMSPE = \sqrt{\frac{\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2}{n}} \qquad (1)$$

in which n denotes the number of observations, y is the given (or 'true') value of the analyte of interest and y is the value predicted by the PLS and PCR model. Given a certain data set, the EMSPE values are calculated for different numbers of components included in the PLS and PCR model. Normally the *EMSPE* reduces with increasing number of PLS components until a minimum or constant value is reached and the corresponding number of components is regarded as optimal. The predicted error is composed of two contributions, the remaining interference error and the estimation error. The former is the systematic error due to unmodeled interference in the spectral data and the latter is caused by random measurement noise of various kinds or of systematic error not relevant for the modeled analyte y. The interference error decreases with an increased modeling of the systematic variance by including more PLS or PCR components. However, at the same time the statistical uncertainty error increases. Including too few PLS or PCR components results in under fitting and one risks that important phenomena are not modeled. Including too many components results in over fitting and this is equivalent to the modeling of noise.

Materials and methods

1. Sample preparation and analytical method

The powder certified reference materials with 0.63 µm particle diameters were pressed into thin pellets of 40 mm diameter. It was required a substrate material, thus 0.46 g of wax (high purity cellulose binder with 20 µm particle diameters) was pressed with a compression of 5 kN and then the mixture (0.48g of specimen and 0.09g of wax) was pressed together with substrate material with a compression of 10 kN. Samples for EDXRF analysis are usually prepared as powder pellets with the use of a binder.

The measurement parameters were set up using the Epsilon 5 EDXRF (PANalytical, Almelo, the Netherlands) system’s in-built software. Samples were irradiated by X-rays **from** a Gd tube under vacuum, equipped with a liquid nitrogen cooled PAN-32 Ge X-ray detector having a Be window thickness of 8 µm. The maximum power, typical current and voltage of the instrument were 600 W, 24 mA and 100 kV, respectively. The instrument has a 3D (Cartesian) optical geometry in which the primary beam from the X-ray tube first irradiates a polarizing target before striking the sample placed at 90°. The sample spectrum is recorded by a detector placed at 90° to the sample in a third plane, thus eliminating the effect of scattered X-ray tube radiation by polarization and considerably reducing spectral background level.[15] The schematic set-up is as given in Figure 1. This method is a nondestructive which requires little sample preparation and gives reliable results within almost analysis time. The Epsilon 5

EDXRF spectrometer has been used significantly for the analyses of macro, micro and trace elements in environmental samples such as soil, rock, coal, oil, plastics, moss and sediment.[16] The detection limits of several kinds of XRF apparatus are not good enough for trace elements, but the environmental concentrations of trace elements are much higher than the trace values. Spectral interferences between peaks can affect detection limits and accuracy for XRF analysis.

FIGURE-1

The system's software (Epsilon 5 software) automatically analyzed the sample spectrum and determined the net intensities of element peaks as soon as the measurement was completed. When elements overlap one another, accuracy is essential for the trace element analysis. Representative spectra are illustrated in Figure 2.

FIGURE-2

Lower Limits of Dedection (LLDs) were calculated using 3 times the square root of the background (count rates obtained by deconvolution) as shown in the following equation:

$$\frac{N_p}{\sqrt{N_b}} \geq 3 \qquad (2)$$

where N_p is the number of counts measured on the peak and N_b the number of counts measured on the background.[17]

For the study, five measurement conditions were defined. Measurement parameters and detection limits for each element are presented in Table 1 and Table 2.

TABLE-1 and TABLE-2

2. System calibration using FP method

Pellets (solid) of 40 mm diameter with 1.2g Standard Reference Materials (SRM) with different elemental contents (for geological materials) were measured to calibrate the spectrometer. The SRMs and their elemental context are shown in Table 3. Determination of the concentrations of the other elements, coefficients (intercept and slope) was calculated by using regression statistic based on concentration and intensity values for each element. Linear calibration curves for all elements were accomplished. After determination of coefficients, concentrations of unknown elements in the samples could be calculated using linear equation related to their intensity values. Regression equation was given as below;

$$y = D(slope)x + E(intercept) \quad (3)$$

where y and x represent from concentration of element and intensity of analysts line, respectively. Calibration parameters such as intercept, slope, R^2, estimated standard uncertainties of the method, and 95% confidence levels for coefficients were calculated using regression statistics as given in our previous paper by Cevik et al.[1]

TABLE-3

3. Computation procedure

All calculations were performed using Matlab R2011b [The Math Works Inc, Natick, USA and the Chemometrics Toolbox (Eigenvector Research, USA)]. This application is first to test the suitability of the PLS and PCR methods for quantitative ED-XRF analysis using fundamental parameters method validation. This particular example concerns the analysis of 76 soil samples. The results of the analysis were used to evaluate the calibration procedure. For this purpose, PLS and PCR calibration procedures by using the concentration and intensity values were performed. In order to symbolize of the sample matrix, an independent variable matrix **X**(76x38) was built using dominant intensity values of 38 elements (Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Nb, In, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sn, Yb, Hf, Ta, W ve Pb) in the soil matrix. On the other hand, dependent variable matrix **Y**(76x1) was created with n=76 and m=1 values (*n* is the number of samples, m is represent from concentrations for each *m* element in *n* samples). The results predicted by PLS and PCR model were then used for the comparison of the measured ED-XRF results. Since this application was primarily used to verify of classical quantitative fundamental parameters method using multivariate PLS and PCR calibration procedures, the discussion was restricted to the analysis of only V, Mn, Co, Ni, Cu, Zn, As, Sr, Ba, Rb and Pb.

Results and discussion

When the optimum component number is identified, the PLS and PCR models are used to determine (predict) the concentration of the elements. This prediction is also performed for an increasing number of PLS and PCR components included in the model and the Estimated Mean Square Predictive Error (*EMSPE*) is calculated and plotted together with the validation curves. The true predicted error can be calculated and compared with the predicted error ascertained via the validation techniques. *EMSPE* curves are observed starting at 1 PLS and PCR components. The *EMSPE* curve has a minimum at 1 or 3 PLS and PCR components while the *EMSPE* curve keeps going down even further until 5 or 8 PLS and PCR components. Based on this observation, a model including 1 or 3 PLS components; is probably the most parsimonious choice. As seen from the plot, it is clear that *EMSPE* curve gives too optimistic predicted errors for all numbers of PLS and PCR components for 76 soil samples. The *EMSPE* curves with PLS and PCR components were given for V, Mn, As, Sr, Ba and Pb in Figure 3.

FIGURE-3

As concentration values were calculated depending on the SRMs and according to FP model of examples, PLS and PCR models have been limited at the certain intervals because they depend on the high correlation set among the different concentrations. In Figure 4, graph showing each element stating the number of components and the concentration results that plotted with FP models are shown.

FIGURE-4

According to results, for the elements (except As Rb, Ba and Sr) concentration predictions were done with PLS and PCR models using only either 1 or 3 components. In an application that was used the results of 76 samples, 1 and 3 components numbers were marvelous. PLS and PCR models for V, Co, Cu and Zn could predict a strong correlation with only one component. As it is stated above, SRMs number used in the application of calibration and reference intervals had an important role among the parameters that was applied in algorithm. The number of reference materials used for V, Co and Zn were 17, 12, and 19, respectively. The number of reference materials used for these elements were appropriate for getting a calibration curve and it could be concluded that the reason why prediction errors were a little bit high as compared to others could be attributed to the concentration intervals of SRM. As it is seen in R^2 values, PLS model has shown a more strong correlation than PCR model among most of the elements (R^2 values are given on Table 4).

TABLE-4

For Ni and Pb, PLS and PCR models have proved the coherence with a low predicted error using 3 components. The numbers of SRMs for both elements were 17. As many number of reference materials will keep the limited concentration interval wide, models predicted low error with a few component. On the other hand, according to application of Mn with 3 components, it was predicted the concentration with a 100 % coherence for each of the models without any error. The numbers of reference materials used in calibration were 18 and it showed that SRMs have the same characteristics in which 100 % coherence was used.

While PLS regression for Sr was applied with 3 and 4 components, PCR regression was used with 4 components. PLS regression was showed to be a meaningful correlation with 3 components. On the other hand, PLS regression with 4 components showed a stronger correlation than PCR model using 4 components. During the calibration process, although the numbers of reference materials were 7, these correlations were quite strong. This situation showed that reference material compositions were rather different.

New concentration values were predicted using 7 components in PLS regression for Rb and 10 components in PCR regression. Because the sample numbers used for 7 and 10 are high, component numbers are acceptable. Uncertainties were decreased with increasing components numbers. If we consider the best of components numbers and low error, it could also be attributed to the SRM numbers and concentration intervals used during the process of calibration.

For Ba, 9 SRMs were used during the calibration process and PLS with 5 components and PCR with 8 components were done with a little predicted error. PLS regression was tested with 5 and 6 components and 6 components showed less error in correlation. However; as 5 components clarified the issue sufficiently, components with 6 factors were not showed in the graphics.

PLS and PCR models were applied using 5 and 8 components for As, respectively. As SRMs and concentration intervals used in EDXRF calibration gave rise to a set of limitations and if lots of reference materials was used, reliable concentration intervals would increase on calibration. Reference materials concentration intervals were important as much as the number of reference material. For this reason, the calibration that was set carefully with same characteristic SRMs give result in less error.

Conclusion

The most general evaluation that was gotten from the application; PLS and PCR models that were developed over the results of calibrated ED-XRF spectrometer used classical quantitative fundamental parameters method (FP). The method has successfully proved for many trace elements of interest. As it was seen from the results, decreasing number of reference materials has increased the most appropriate component numbers including the information belongs to samples (As, Rb, Sr and Ba). It was observed that prediction errors and increasing factor numbers were depend on the reference material concentration intervals as much as the number of SRM’s. In this way, correctness of elemental analysis results that was carried out for ST-EDXRF spectrometer was validated by means of setting of PCR and PLS regression models simulation. On the other hand, when PLS and PCR models were compared among themselves, it was seen that PLS model had a strong relation with FP method as compared to PCR model with less prediction errors and component numbers.

Acknowledgement

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Figure Captions

Figure 1: Schematic representation of a three-dimensional polarizing optics. The original tube beam is scattered over 90º on the target (A) and before reaching the detector (C), this beam is scattered a second time over 90º on the sample (B).

Figure 2. Representative spectra using Ge target on IAEA 7 (top soil) Standard Reference Material.

Figure 3. Represented *EMSPE* curves of the PLS and PCR models for V, Mn, As, Sr, Ba and Pb based on EDXRF data.

Figure 4. CV predicted versus given elemental concentrations determined by the PLS and PCR models based on *Estimated Mean Square Predictive Error*, (The model relies on 1, 3,4,5,7 and 10 PLS or PCR components for V, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Ba and Pb).

Table 1. Measurement parameters of the standard samples

Element	**Conditions**	**Secondary Target**	**Studied Line**	**Measuring Time**	**Excitation Conditions**
V, Mn,	Mn	Co	K_α	500	50kV-12mA
Co, Ni, Cu, Zn	Ge	Ge	K_α	500	75kV-8mA
As	As	KBr	K_α	1000	100kV-6mA
Rb, Sr, Pb	Sr_Y_Pb_U	Mo	K_α, L_α(Pb)	1000	100kV-6mA
Ba	B_4C	B_4C	K_α	1000	100kV-6mA

Tablo 2. Dedection Limits for each elements (mg/kg)

Element	Mn	V	Co	Ni	Cu	Zn	As	Rb	Sr	Pb	Ba
LLD	1.76	4.40	0.31	1.09	0.53	0.61	0.39	0.23	0.18	0.96	2.18

Table 3 Standart reference samples used (mg/kg)

SRM	**Mn**	**V**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Rb**	**Sr**	**Pb**	**Ba**
SARM18	22	23	6.7	10.8	5.9	5.5	-	8.1	44	5	78
SRM1645	785	23.5	-	45.8	109	1720	66	-	-	714	-
SRM1632a	28	-	-	-	16.45	-	-	-	-	-	-
IAEASL_1	3460	170	19.8	44.9	30	223	-	113	80	37.7	639
SRM1635	21.4	5.2	0.65	1.74	3.6	4.7	-	-	-	1.9	-
BCR40	139	-	7.8	25.4	-	30.2	-	-	-	24.2	-
SRM1648	860	130	18	82	609	4760	-	-	-	-	737
BCR038	479	334	-	194	176	581	48	-	-	262	-
BCR182	195	24.3	-	-	-	33.3	-	-	-	-	-
NBS_1633	493	214	-	98	128	210	61	-	-	70	-
BCR277t	1600	102	17	43.4	101.7	547	47.3	-	-	146	329
NIES_02	770	250	27	40	210	343	-	42	110	105	-
IAEA_7	631	66	8.9	26	11	104	-	51	108	60	159
SRM2711	638	81.6	10	20.6	114	350.4	105	110	245.3	1162	726
SRM1646a	40.9	6.46	2.08	5	23	10.01	-	6.23	38	11.7	210
SARM19	157	35	5.6	16	13	12	-	9	126	20	304
SARM20	80	47	8.3	25	18	17	-	10	-	26	372
BCR180	34.3	19.3	-	-	-	27.4	-	-	-	17.5	-
BCR176	1.5	-	-	123.5	-	-	93.3	-	-	-	-
BCR181	-	12	-	-	-	8.4	27.7	-	-	2.59	-
BCR143	-	-	-	99.5	2365	1272	-	-	-	1333	-

Tablo 4. PLS, PCR and FP method application reports for each element. Unit was in a range of mg/kg,

Element	**PLS**			**PCR**			**Measurement Calibration Using FP Method**		
	Component Number	***(EMSPE)***	***R^2***	***Component Number***	***(EMSPE)***	***R^2***	***SRMs numbers for calibration***	***Relative Error***	***R^2***
V	1	10	0.9058	1	10	0.9049	17	0.027	0.9578
Mn	3	0	1	3	0	1	18	0.080	0.9899
Co	1	0.81	0.9380	1	0.81	0.9260	12	0.003	0.9122
Ni	3	30	0.8891	3	30	0.8841	17	0.019	0.925
Cu	1	4.12	0.8785	1	4.12	0.8777	16	0.019	0.9913
Zn	1	13.74	0.8398	1	13.74	0.8388	19	0.059	0.9924
As	5	22	0.9480	8	3	0.9905	7	0.008	0.9574
	6	2.75	0.9939	8	3	0.9905	7	0.008	0.9574
Rb	7	5.72	0.9931	10	5.83	0.9892	8	0.007	0.9867
Sr	3	21	0.9741	4	4	0.9972	7	0.018	0.9614
	4	4.29	0.9983	4	4	0.9972	7	0.018	0.9614
Ba	5	42	0.9585	8	2.32	0.9999	9	0.038	0.9748
	6	1.17	0.9978	8	2.32	0.9999	9	0.038	0.9748
Pb	3	13	0.9214	3	11	0.9202	17	0.036	0.9903

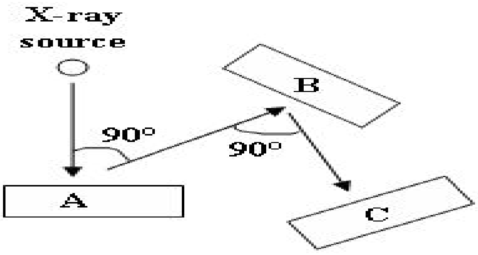
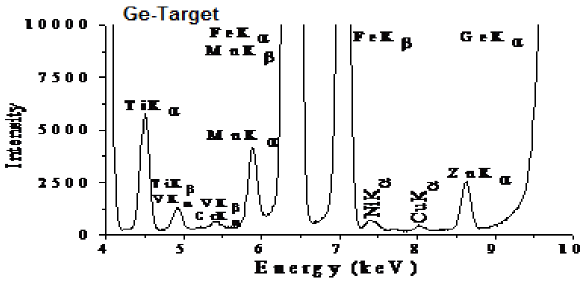
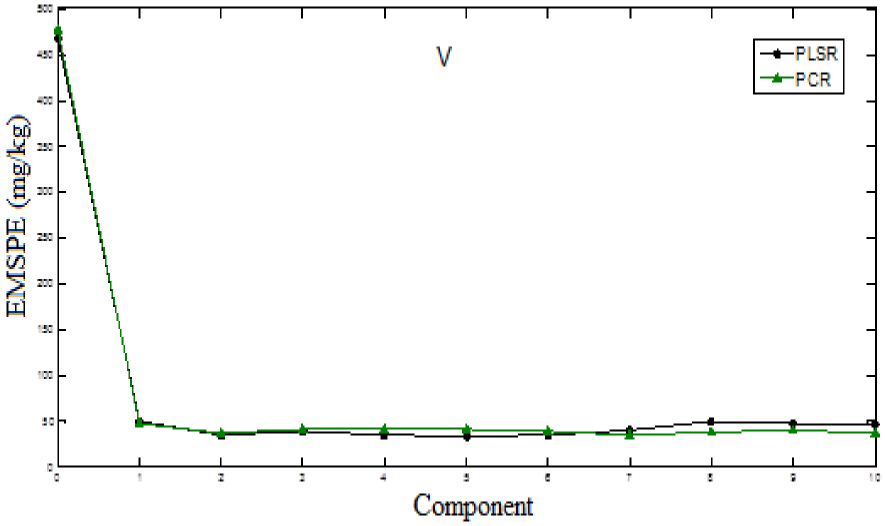


Figure 1: Schematic representation of a three-dimensional polarizing optics. The original tube beam is scattered over 90º on the target (A) and before reaching the detector (C), this beam is scattered a second time over 90º on the sample (B).



365 **Figure 2.** Representative spectra using Ge target on IAEA 7 (top soil) Standard Reference 366 Material.


V
PLSR
PCR
EMSPE (mg/kg)
Component
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400
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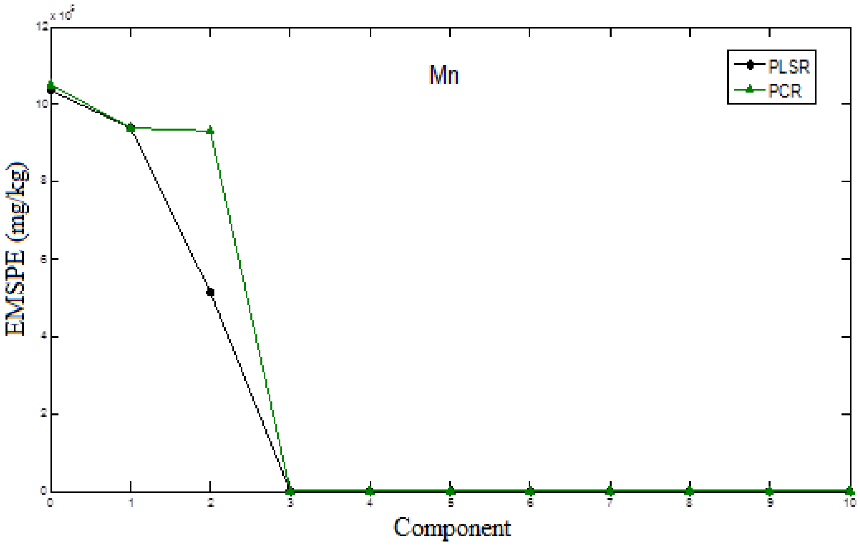
Mn
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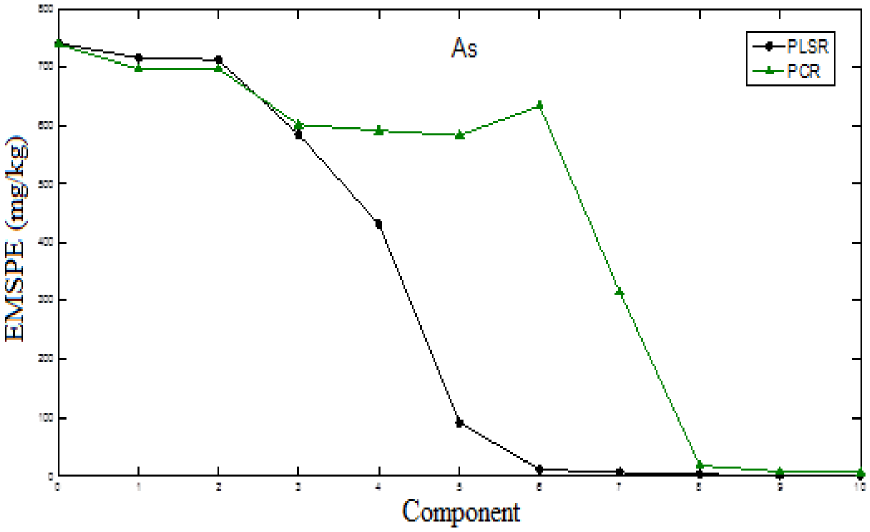
As
PLSR
PCR
EMSPE (mg/kg)
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200
300
400
500
600
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800
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9
10

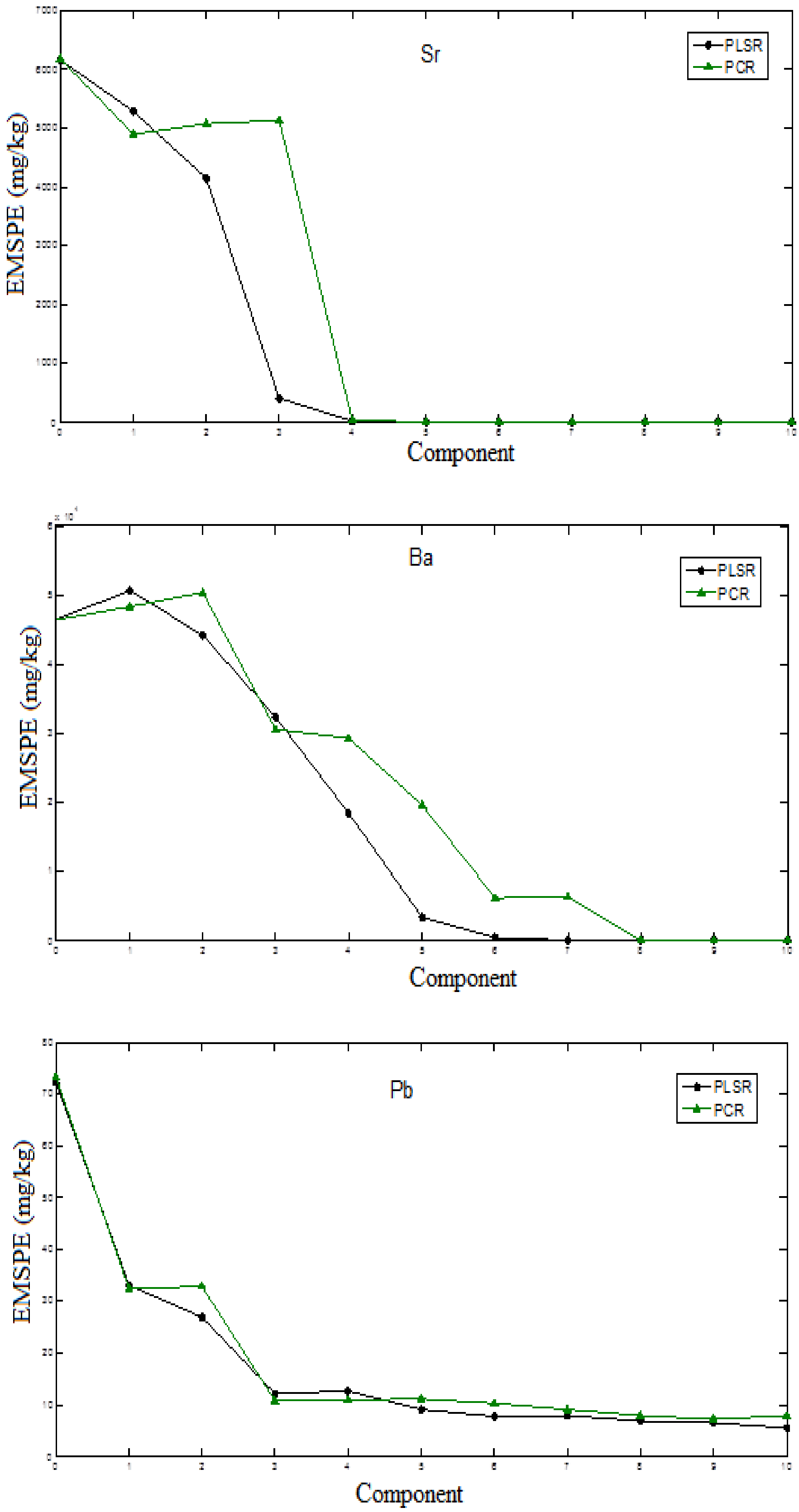
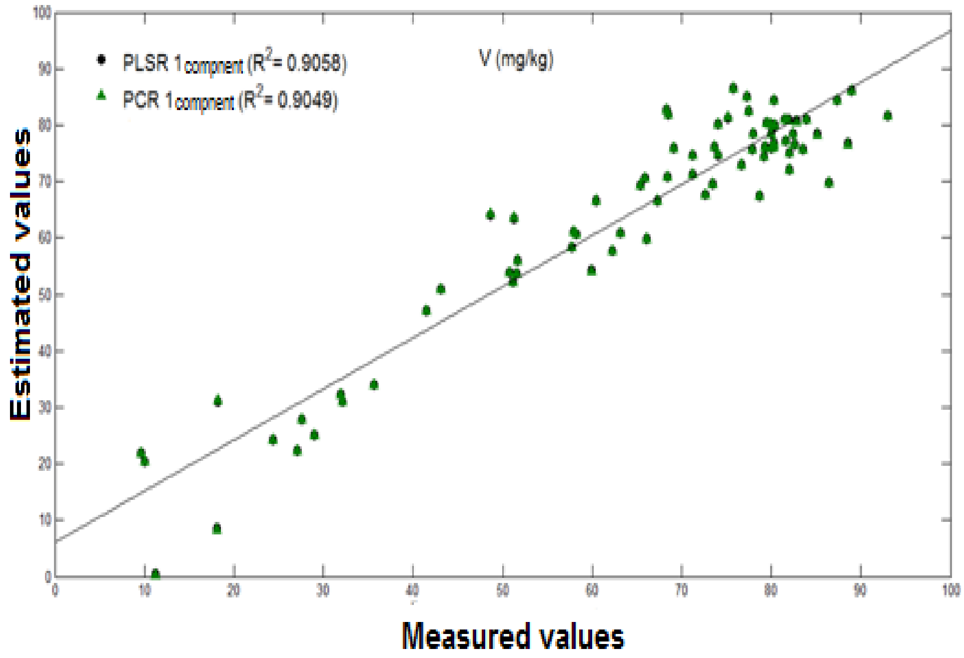
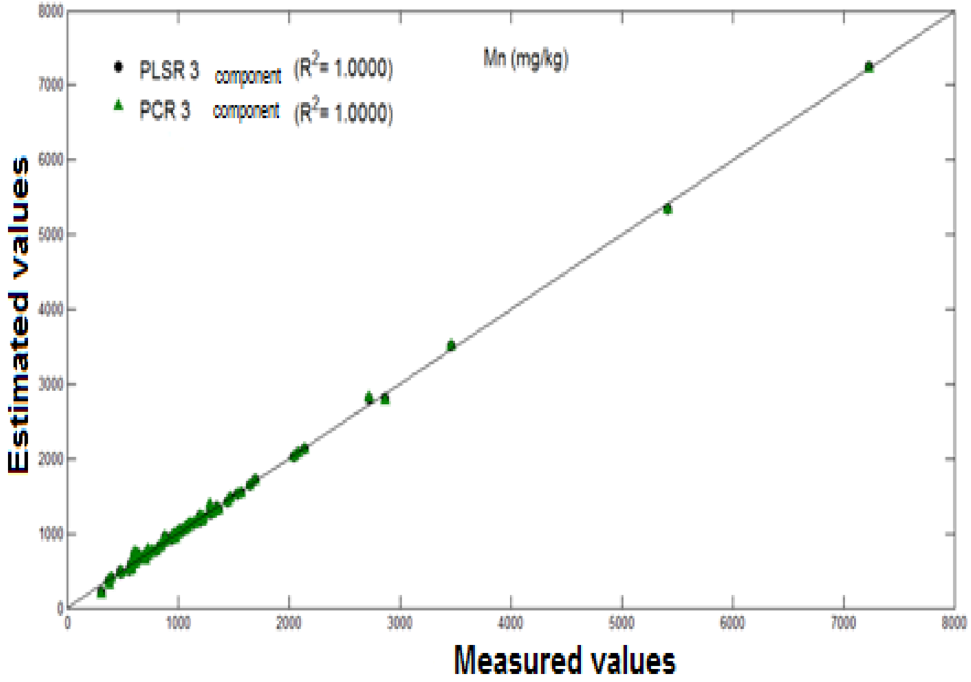
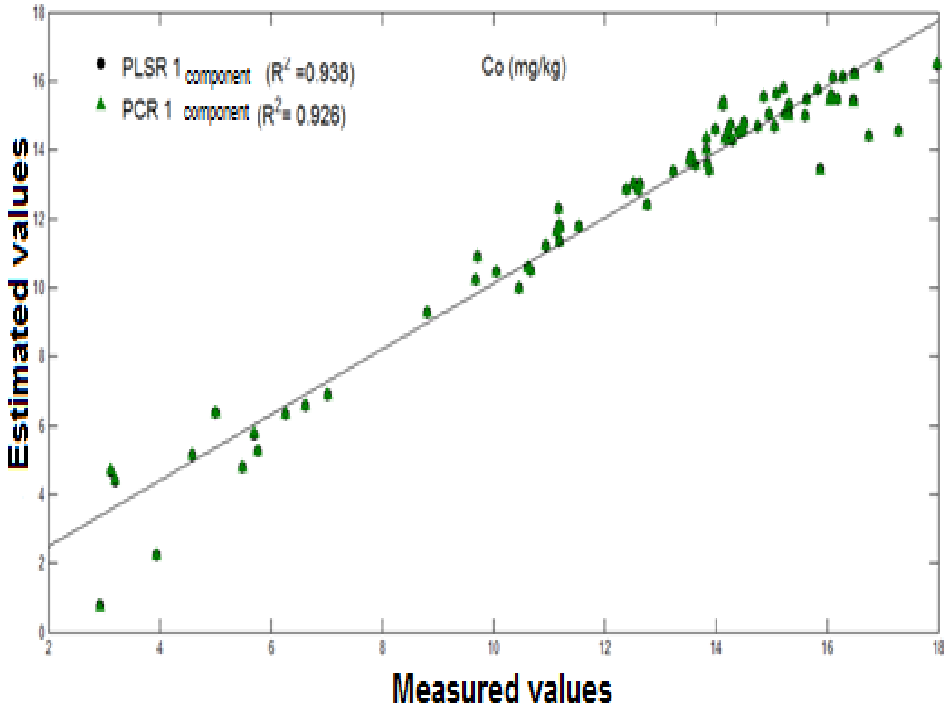
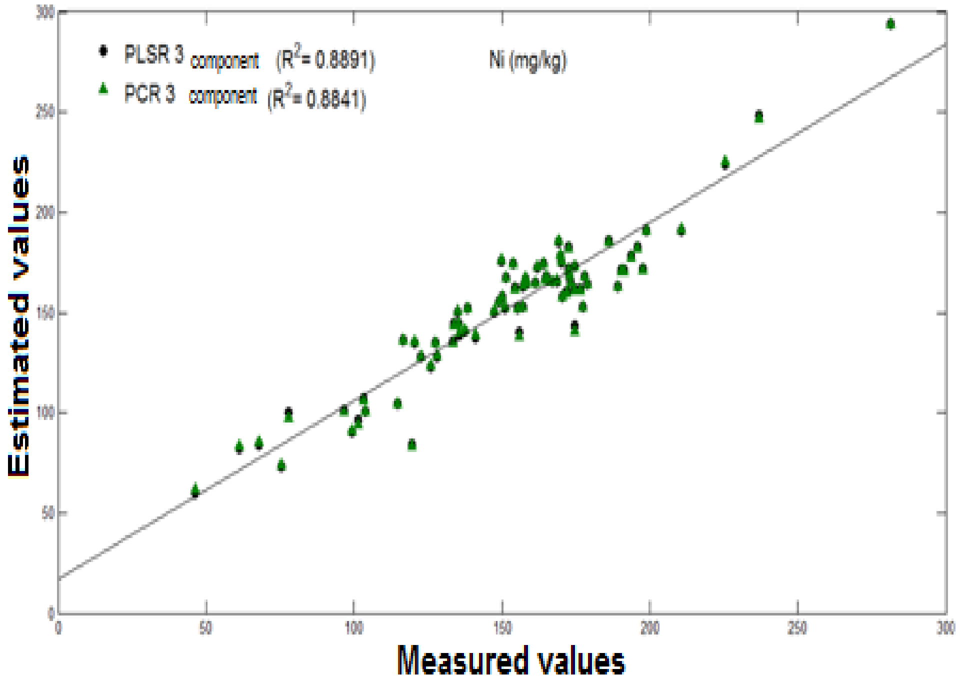


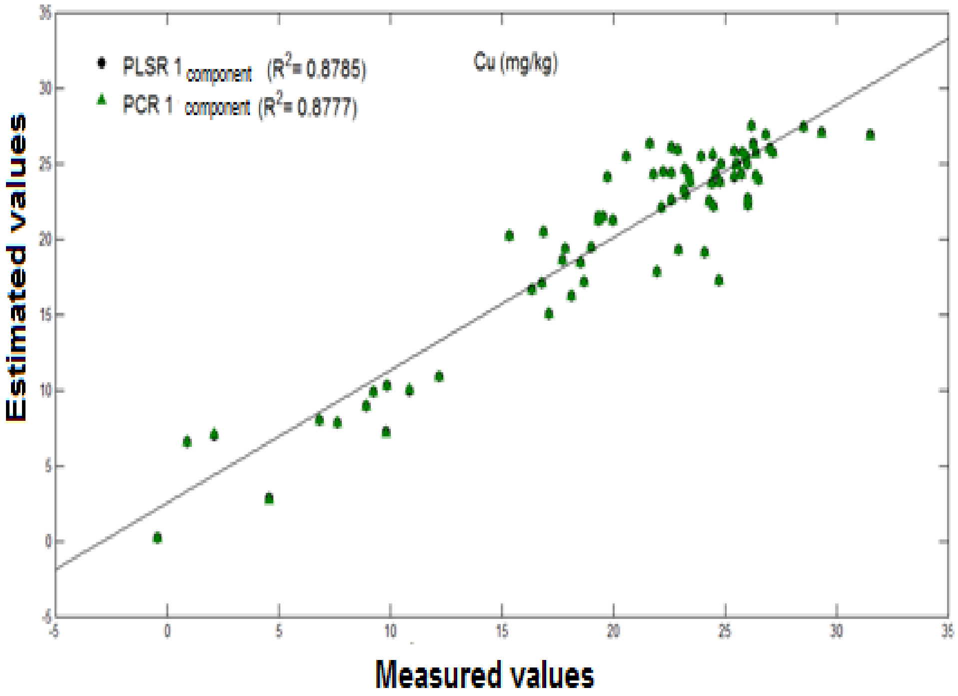
Figure 3. Represented *EMSPE* curves of the PLS and PCR models for V, Mn, As, Sr, Ba and Pb based on EDXRF data.

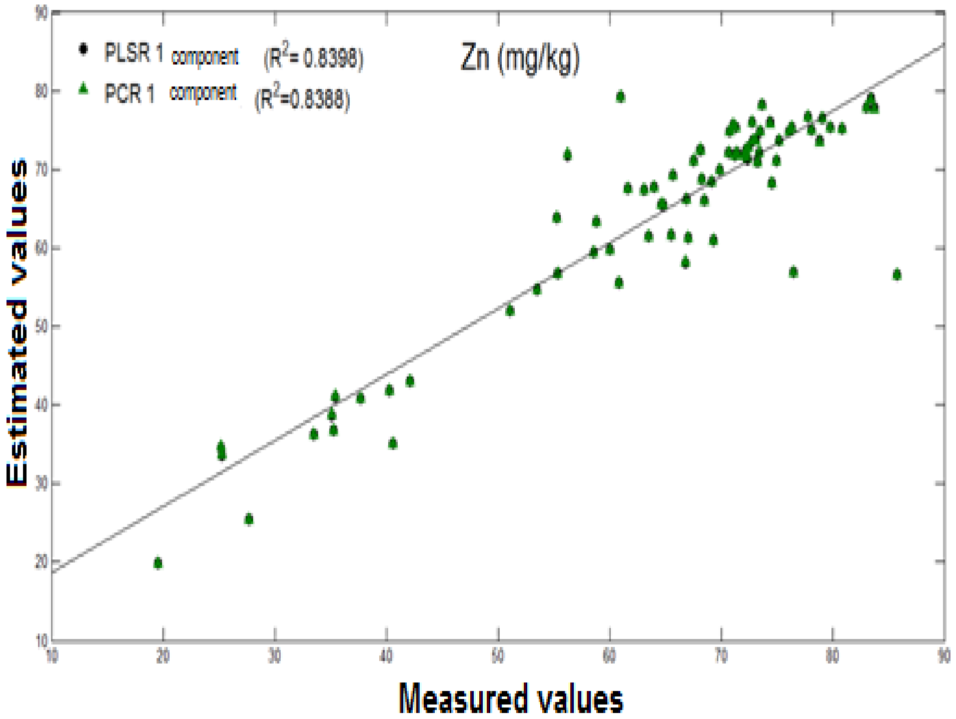

PLSR 1 compnent (R^2= 0.9058)
PCR 1 compnent (R^2= 0.9049)
V (mg/kg)
Estimated values
Measured values
0
10
20
30
40
50
60
70
80
90
100

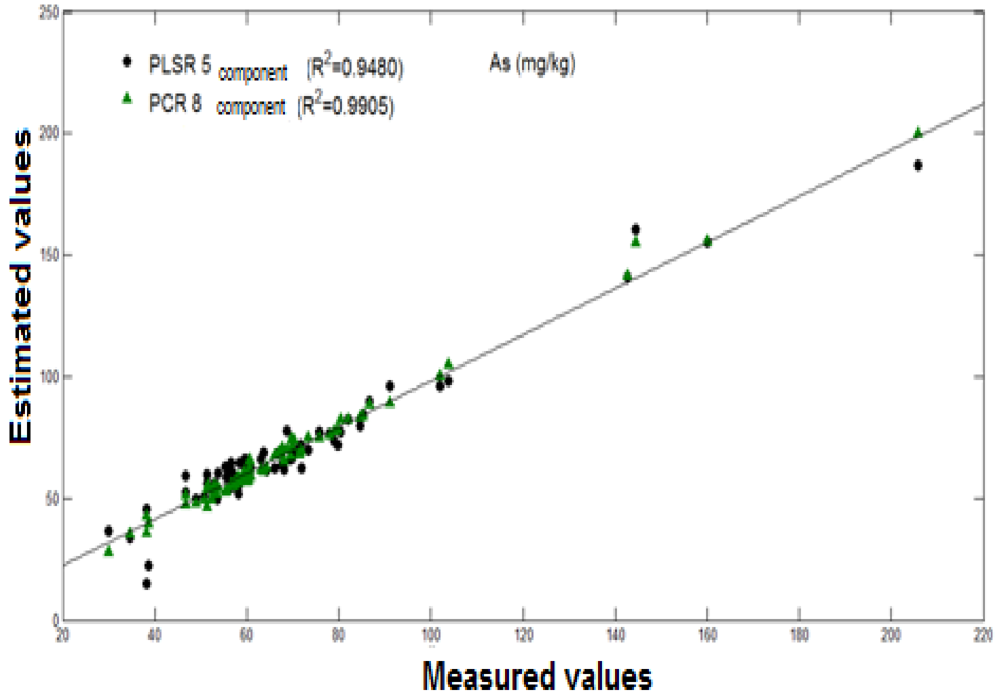

PLSR 3 component (R^2= 1.0000)
PCR 3 component (R^2= 1.0000)
Mn (mg/kg)
Estimated values
Measured values
0
1000
2000
3000
4000
5000
6000
7000
8000

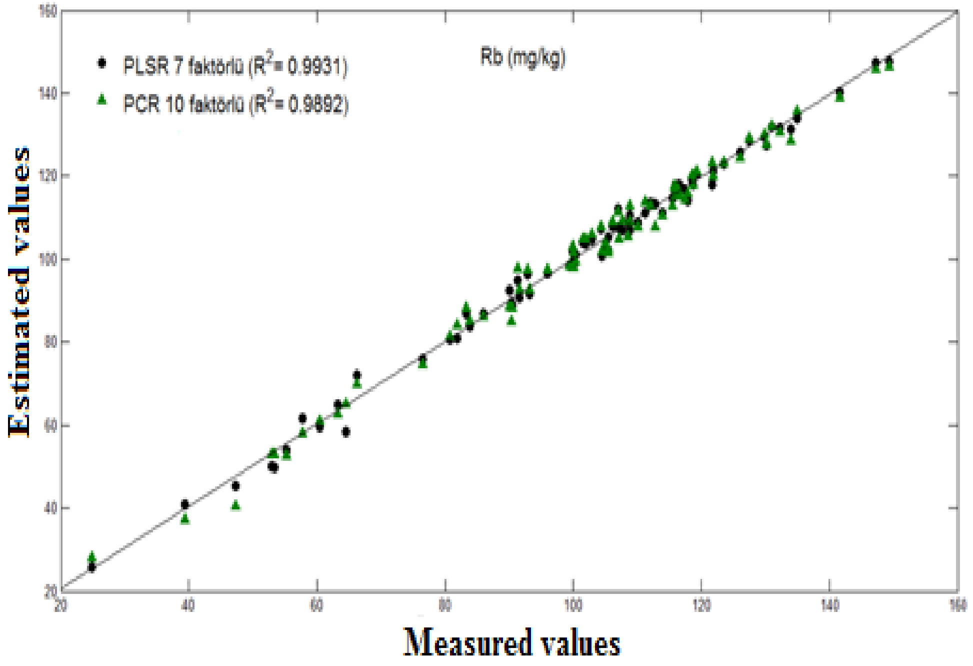

PLSR 1 component (R^2 =0.938)
PCR 1 component (R^2= 0.926)
Co (mg/kg)
Estimated values
Measured values
0
2
4
6
8
10
12
14
16
18
2
4
6
8
10
12
14
16
18

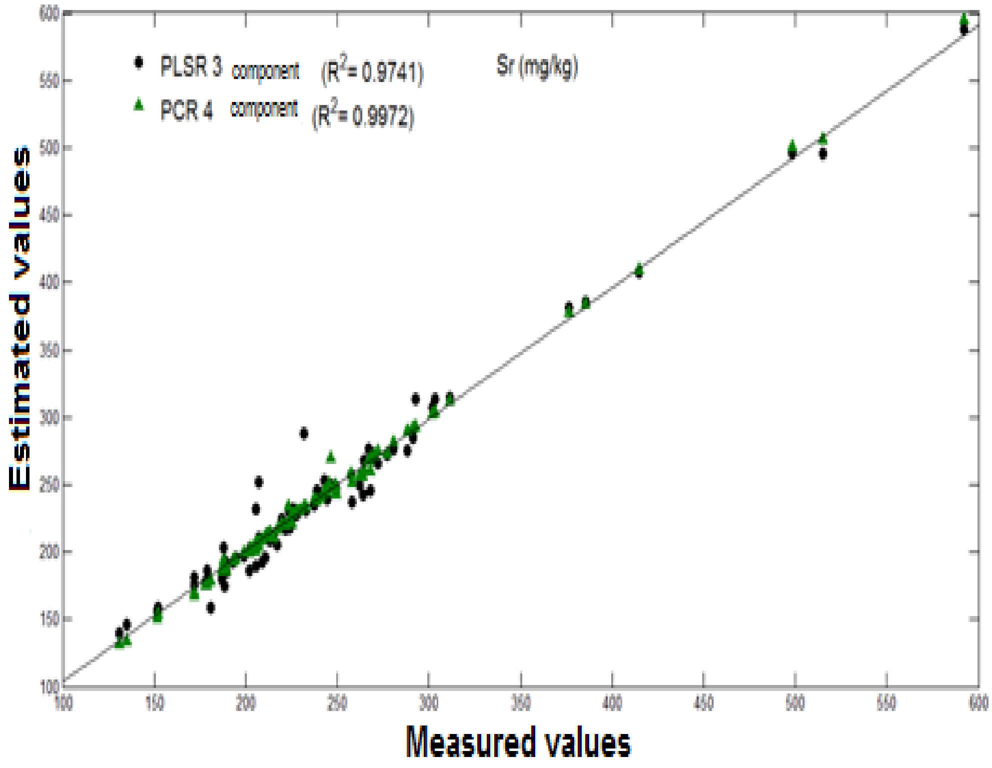

PLSR 3 component (R^2= 0.8891)
PCR 3 component (R^2= 0.8841)
Ni (mg/kg)
Estimated values
Measured values
0
50
100
150
200
250
300
0
50
100
150
200
250
300

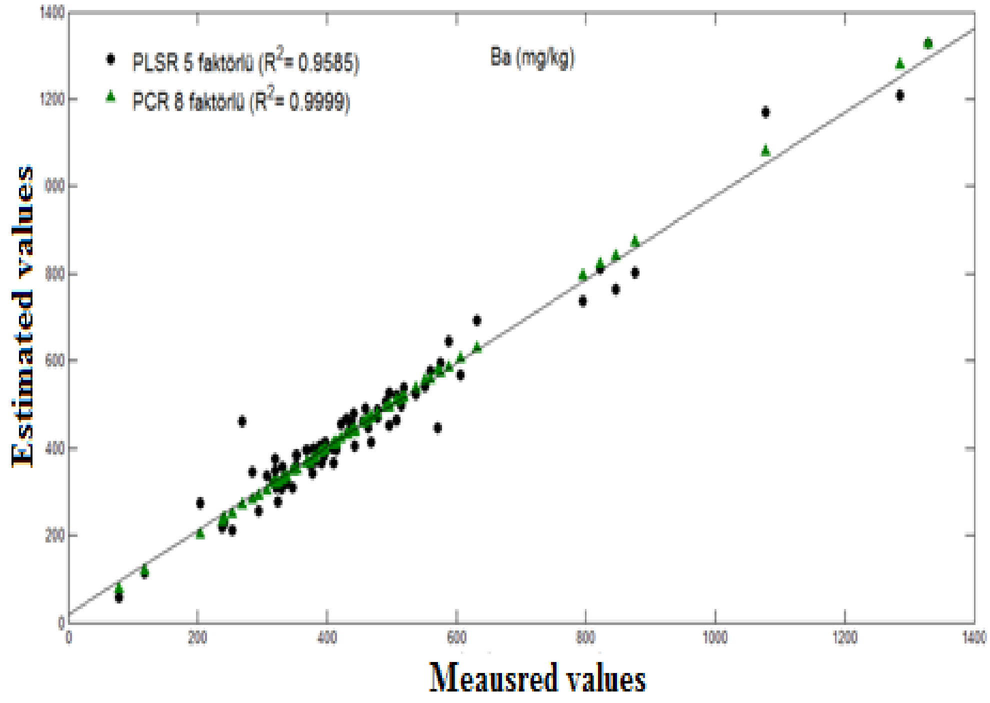

PLSR 1 component (R² = 0.8785)
PCR 1 component (R² = 0.8777)
Cu (mg/kg)
Estimated values
Measured values
35
30
25
20
15
10
5
0
-5
-5
0
5
10
15
20
25
30
35


PLSR 1 component (R² = 0.8398)
PCR 1 component (R² = 0.8388)
Zn (mg/kg)
Estimated values
Measured values
90
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90


PLSR 5 component (R^2=0.9480)
PCR 8 component (R^2=0.9905)
As (mg/kg)
Estimated values
Measured values
0
50
100
150
200
250
20
40
60
80
100
120
140
160
180
200
220


PLSR 7 faktörlü (R^2= 0.9931)
PCR 10 faktörlü (R^2= 0.9892)
Rb (mg/kg)
Estimated values
Measured values
20
40
60
80
100
120
140
160
20
40
60
80
100
120
140
160


PLSR 3 component (R^2= 0.9741)
PCR 4 component (R^2= 0.9972)
Sr (mg/kg)
Estimated values
Measured values
100
150
200
250
300
350
400
450
500
550
600


PLSR 5 faktörlü (R^2= 0.9585)
PCR 8 faktörlü (R^2= 0.9999)
Ba (mg/kg)
Estimated values
Meausred values
0
200
400
600
800
1000
1200
1400

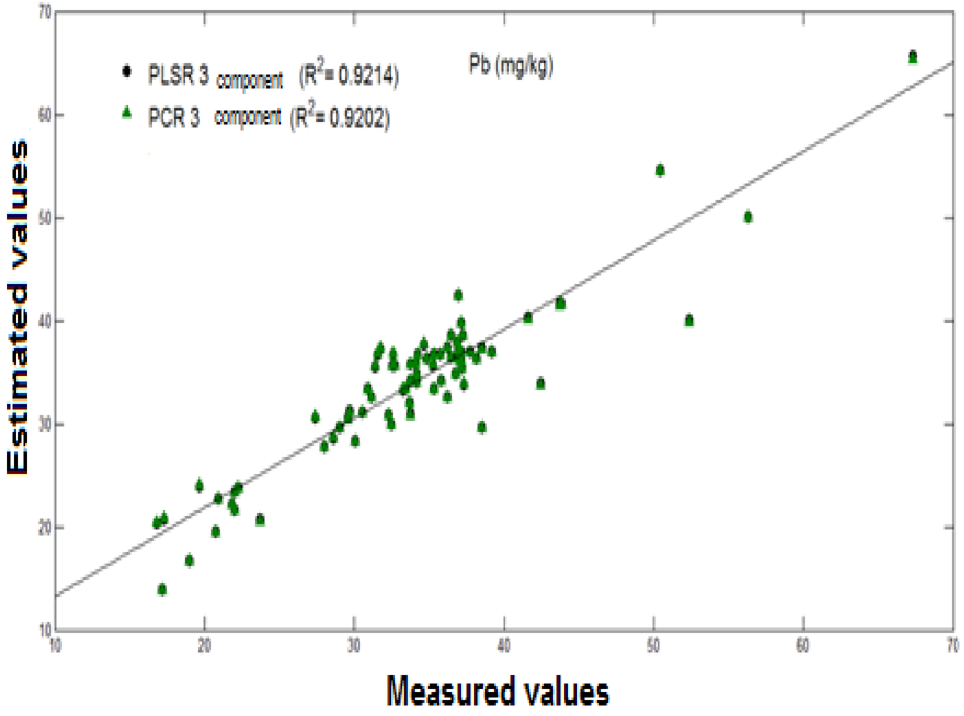


Figure 4. CV predicted versus given elemental concentrations determined by the PLS and PCR models based on *Estimated Mean Square Predictive Error*, (The model relies on 1, 3,4,5,7 and 10 PLS or PCR components for V, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Ba and Pb).