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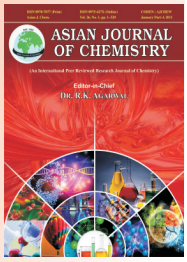

Comparison of Atomic Absorption Spectroscopy and Energy Dispersive X-Ray Fluorescence Spectrometer Methods for Chemical Analysis

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This study aims to find out which method can obtained the most accurate results in less time and at the lowest cost on the basis of element. At the beginning of the study, worldwide researches about this subject are investigated. As a result of this investigation, two of the chemical analysis methods which are widely used in the elemental analysis of the inorganic raw materials used in mining were compared. Then, 15 test samples which have different compositions and generally investigated main element content were determined in order to compare. The samples were analyzed in parallel with atomic absorption spectroscopy (AAS) and energy-dispersive X-ray fluorescence spectrometer (EDXRF). The compatibility and the deviations were determined by comparing the results of the analysis statistically from both methods. It was tried to determine which method can be used for which type of elements. It is observed that the material composition effects choosing appropriate method.

Keywords: AAS, Quantitative analysis, Energy-dispersive X-ray fluorescence spectrometer, Semi-quantitative analysis.

INTRODUCTION

The chemical analysis of inorganic materials used as raw materials nowadays can be made in different ways. Some of the analysis methods are quite expensive; others reach the result at the end of a long struggle. Previous studies have focused on just one element or they have made comparison between the application techniques of the same method[1,2]. But in this study, different methods are compared with the different elements. First method is atomic absorption spectroscopy and it is used principally for the quantitative determination of metal elements in aqueous and solid samples from a wide range of fields including medicine, food and geology since 1950s[3-5]. Second method is the analyse that is relatively low cost and uses energy-dispersive X-ray fluorescence spectrometer (EDXRF) which makes analyses without standards. Also with EDXRF method there is no need to be experienced on using device and sample preparation process. Although in this method the analysis is completed in a short time gives the semi-quantitative results with theoretical read[2,6-10].

The wet chemical and atomic absorption spectroscopy method is quantitative but EDXRF method is semi-quantitative. So in this study, the wet chemical and atomic absorption spectroscopy analytical results are accepted as reliable.

This paper, aims to show the relation of the results which obtained from two different analytical techniques. It is hope that this paper will shad a light to researches that begins analyze on their subject of choosing a method.

EXPERIMENTAL

Examples were selected from a wide scale ranging from rocks with a complex metallic content to more simple rocks with non-metal content. The variability showed in the different compositions of the same kind of elements will be made to differentiate in this way. Both of the analysis systems are using samples milled to powder size. Firstly, 15 of the samples were reduced to an average 0.5 mm grain size by the crushing process. After breaking the samples the natural moisture of the samples were removed by being allowed the samples milled to powder size to stand at 105 °C until getting the constant weight. The dehydrated samples were stored in a dry environment.

Traditional chemical analysis and atomic absorption spectroscopy device: After the examination of the working principles and analyze phases of atomic absorption spectroscopy it is determined to giving priority to this device[3,4]. The conventional chemical analysis methods; composed by the wet analyzes techniques was used for the analyses of high concentration compounds (such as SiO_2) which cannot be read by atomic absorption spectroscopy. Atomic absorption spectroscopy has high costs and longer processing time, but gives more reliable result with Pinaacle 900H (Perkin Elmer) atomic absorption spectroscopy (AAS) device.

Energy-dispersive X-ray fluorescence spectrometer (EDXRF) device: Semiquantitative analysis, or standardless analysis, in its basic form is based on some mathematical methods also used to proceed matrix correction, in X-ray fluorescence spectrometry. Among these mathematical methods there is one, based on fundamental parameters, which uses some physical parameters along with the instrument parameters to calculate the instrumental sensitivity. It is a mathematical method of calibration, in which all the matrix-effects are accounted for, using physical theory only[8]. In the study, standardless analysis-will be used for different sample matrices and content- was deemed appropriate with minipal 4 (Pananlytical) energy-dispersive X-ray fluorescence spectrometer (EDXRF) device.

Simple linear regression analysis: Firstly scatter chart was made in order to reveal whether there is parallelism or diversity among the data obtained during the study. With the scatter chart (X-Y graph) a general perspective was obtained about the direction of the relationship and whether there is a linear relationship between two sets of variables or not. In addition to this, the results of the measurement were subjected to regression analysis was conducted in order to examine the more consistent and precise measurement about the structure of the relationship. The purpose of the linear regression analysis is to establish a relationship between the dependent and the independent variables. The selected regression model shows the dependent variable directly as the ratio of the independent variable's value. By using the value of the independent variable (X) with a model which assumes that the dependent variable (Y) is in a linear relationship with the independent variable (X), the value of the dependent variable is estimated. The value of R^2 can be found by calculating the squares of the difference between the estimated values and the Y values.The R^2 value takes a value between 0 and 1, when it gets closer to 1 its deviation decreases from the Y regression curve and the relation between the two variables is strengthened. The risk in the regression analysis was measured by P value test. Before starting the regression analyses the α-value was determined to be 0.05 due to the safety factor of the regression analyses being 95 %. According to this, the P-value is less than α, the risk of error in the regression analysis will decrease. While the P-values being bigger then alpha suggests that the risk of error is high.

RESULTS AND DISCUSSION

All the samples after the suitable preparation process were subjected to chemical analysis.The values of the results of EDXRF read by a measurement without standards were given in Table-1. In the same way the Table-2 was created by using the methods of wet chemicals and atomic absorption spectoscopic analysis together. In both tables the values of the lost ignition were given which were obtained by calculating the carbon dioxide lost in the muffle furnace.

First, the element concentrations obtained from both methods groups regardless of composition were compared and the relationship between them was tried to be investigated.

The results of EDXRF analysis represent the X independent variable. The results of wet chemicals and atomic absorption spectroscopy analysis represent the Y dependent variable. The relationship between X and Y was tested in compliance with the linear regression model. The obtained results were showed by the R^2 values associated with the slope of the regression curve on the distribution graphics (Fig. 1). Additionally, the values of the regression test were given in Table-3.

The values of Si element revealed a very high relationship with the correlation coefficient and R^2 values. Besides this, the reliability in the calculation for the P value showed to be high. There is no similarity between measurement results except Si element. Therefore after questioning the relationship in general the samples were examined in terms of the main elements and the Figs. 2 and 3 were formed by calculating the cumulative frequency distribution of the main elements in each of the samples.

When analyzing the Figs. 2 and 3 besides the silica and calcium groups of the sample composition a mixed silica-calcium group which was accompanied by different elements was distinguished and were divided into the following three groups according to the sample numbers.

TABLE-1
CONCENTRATION OF ELEMENTS (%) WITH EDXRF

EDXRF Analysis									
Sample No	Lost of Ignition	Elements (%)							
		Mg	Al	Si	Ca	Cr	Mn	Fe	Cu
1	19.000	0.972	0.420	8.756	26.742	0.094	16.620	0.521	0.022
2	8.000	1.159	10.269	21.706	7.758	0.023	0.150	7.678	0.023
3	1.667	1.947	10.716	26.759	0.817	0.037	0.040	7.024	0.018
4	1.000	0.463	0.995	42.300	0.235	0.061	0.015	1.095	0.637
5	2.000	3.587	8.502	23.168	6.276	0.087	0.229	10.070	0.000
6	32.000	4.859	0.000	5.178	29.869	0.112	0.063	4.560	0.000
7	36.000	2.803	0.000	2.533	35.574	0.105	0.154	2.495	0.000
8	44.000	0.101	0.127	0.313	39.088	0.013	0.000	0.110	0.000
9	2.000	3.116	7.310	23.214	8.886	0.219	0.184	10.462	0.000
10	2.000	2.293	4.909	36.480	0.987	0.027	0.068	3.403	0.070
11	43.000	0.000	0.211	0.321	39.656	0.000	0.000	0.173	0.000
12	44.000	0.386	0.062	0.061	39.036	0.004	0.010	0.015	0.000
13	14.000	18.008	0.359	16.613	0.392	4.924	0.231	7.868	0.000
14	44.000	0.289	0.065	0.221	39.072	0.000	0.028	0.071	0.000
15	44.000	0.215	0.092	0.229	39.100	0.013	0.002	0.102	0.000

TABLE-2
CONCENTRATION OF ELEMENTS (%) WITH WET CHEMICAL AND ATOMIC ABSORPTION SPECTROSCOPY ANALYSIS

Wet chemical and atomic absorption spectroscopy analysis									
Sample No	Lost of Ignition	Elements (%)							
		Mg	Al	Si	Ca	Cr	Mn	Fe	Cu
1	19.000	3.60	0.0003	8.844	7.530	0.000	0.019	3.700	0.000
2	8.000	0.27	0.0019	10.744	2.460	0.000	0.000	4.550	0.000
3	1.667	0.87	7.7000	15.310	0.452	0.000	0.000	7.600	0.000
4	1.000	0.70	0.0002	21.005	0.680	0.000	0.000	0.410	0.000
5	2.000	0.94	0.0033	12.413	7.960	0.020	0.048	0.980	0.000
6	32.000	1.14	0.0000	2.972	13.350	0.004	0.030	1.650	0.000
7	36.000	0.06	0.0000	1.843	16.250	0.006	0.510	0.640	0.000
8	44.000	18.01	0.0000	0.220	4.240	0.000	0.000	0.013	0.000
9	2.000	0.00	0.0042	11.458	30.600	0.000	0.006	0.030	0.001
10	2.000	0.05	0.0030	18.567	0.000	0.004	0.030	1.080	0.015
11	43.000	0.94	0.0001	0.220	24.900	0.005	0.002	0.060	0.000
12	44.000	4.53	0.0000	0.220	31.950	0.003	0.004	0.005	0.000
13	14.000	3.80	0.0002	5.688	5.170	0.014	0.040	1.050	0.000
14	44.000	0.00	0.0001	0.220	9.480	0.008	0.025	0.032	0.000
15	44.000	0.12	0.0002	0.220	17.840	0.009	0.000	0.000	0.000

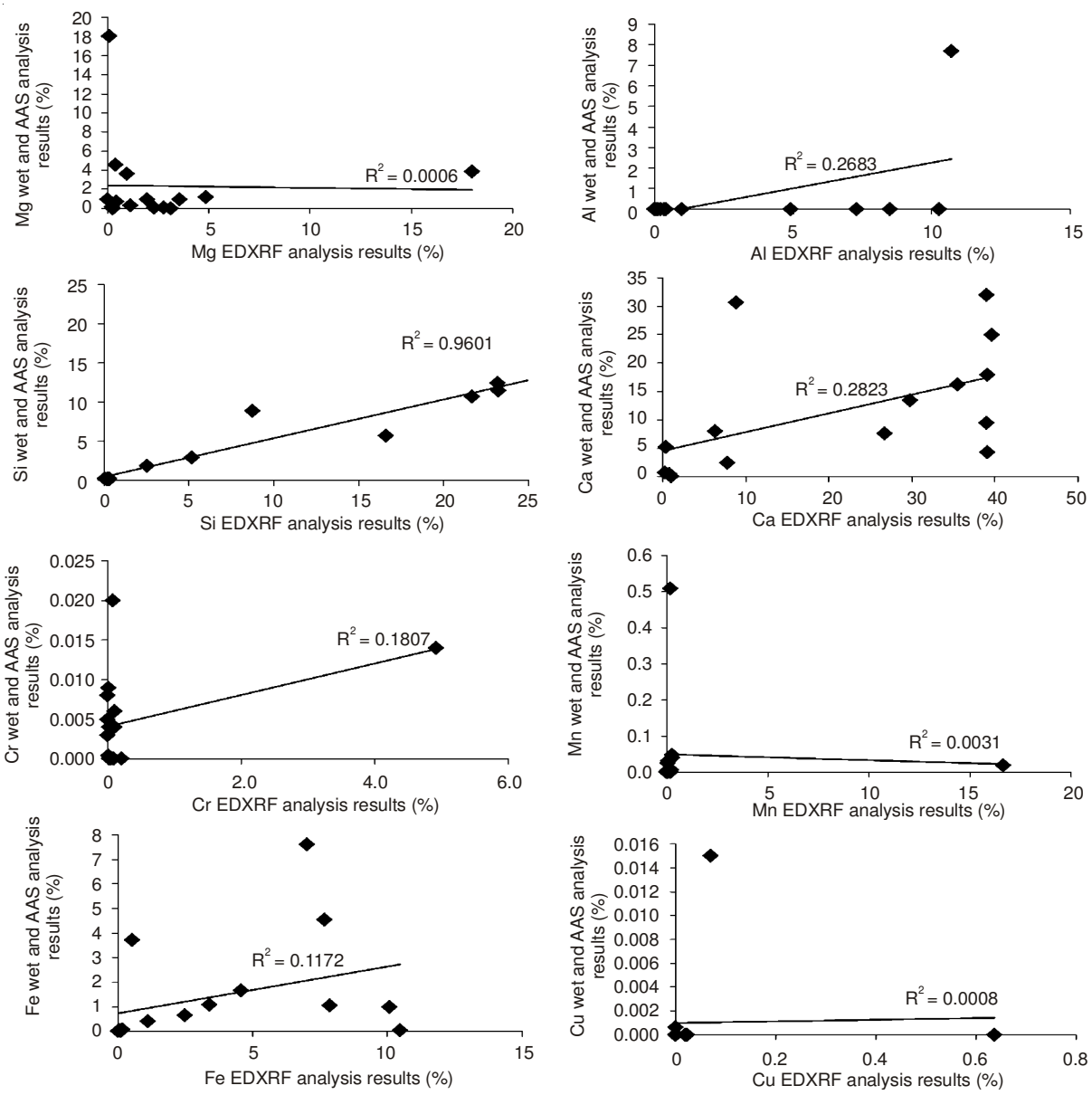

Fig. 1. Scatter chart graphs of all samples

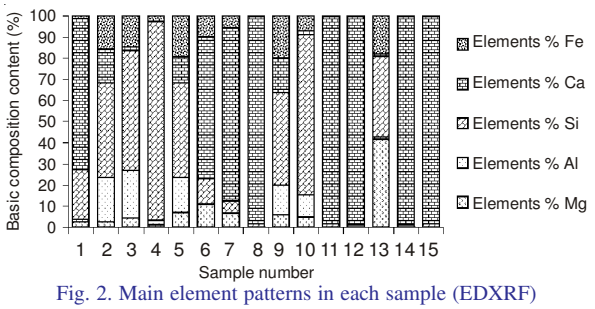

Fig. 2. Main element patterns in each sample (EDXRF)

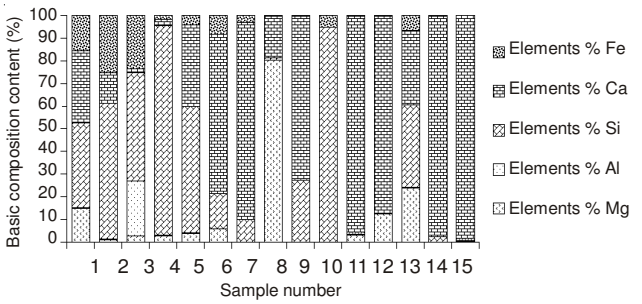

Fig. 3. Main element patterns in each sample (Wet chemical and atomic absorption spectroscopy)

- Group Number 1: Silicon group (sample number 3, 4, 10, 13)
- Group Number 2: Silica-calcium (sample number 1, 2, 5, 6, 7, 9)
- Group Number 3: Calcium group (sample number: 8, 11, 12, 14, 15)

The regression analysis of the Group 1 including sample pairs where the elements of Si group are intensive and the elements of Ca group are negligibly small are given in Table-4. The scatter graphs belonging to Group 1 are represented by Fig. 4.

While examining the distribution graphs and the results of the regression analysis of the Ca, Cu and Fe elements it would not be correct to discuss about a relationship. On the other hand it was revealed that the concentration of Mg, Si and Cr elements among the pairs have meaningful and very high relation, also the reliability of this relationship was found in P-values. As for Al and Mn elements despite of the high correlation observed in terms of R^2 values it was pointed out that P-values were not within the acceptable limits of the reliability of these observation results. In the case, when the

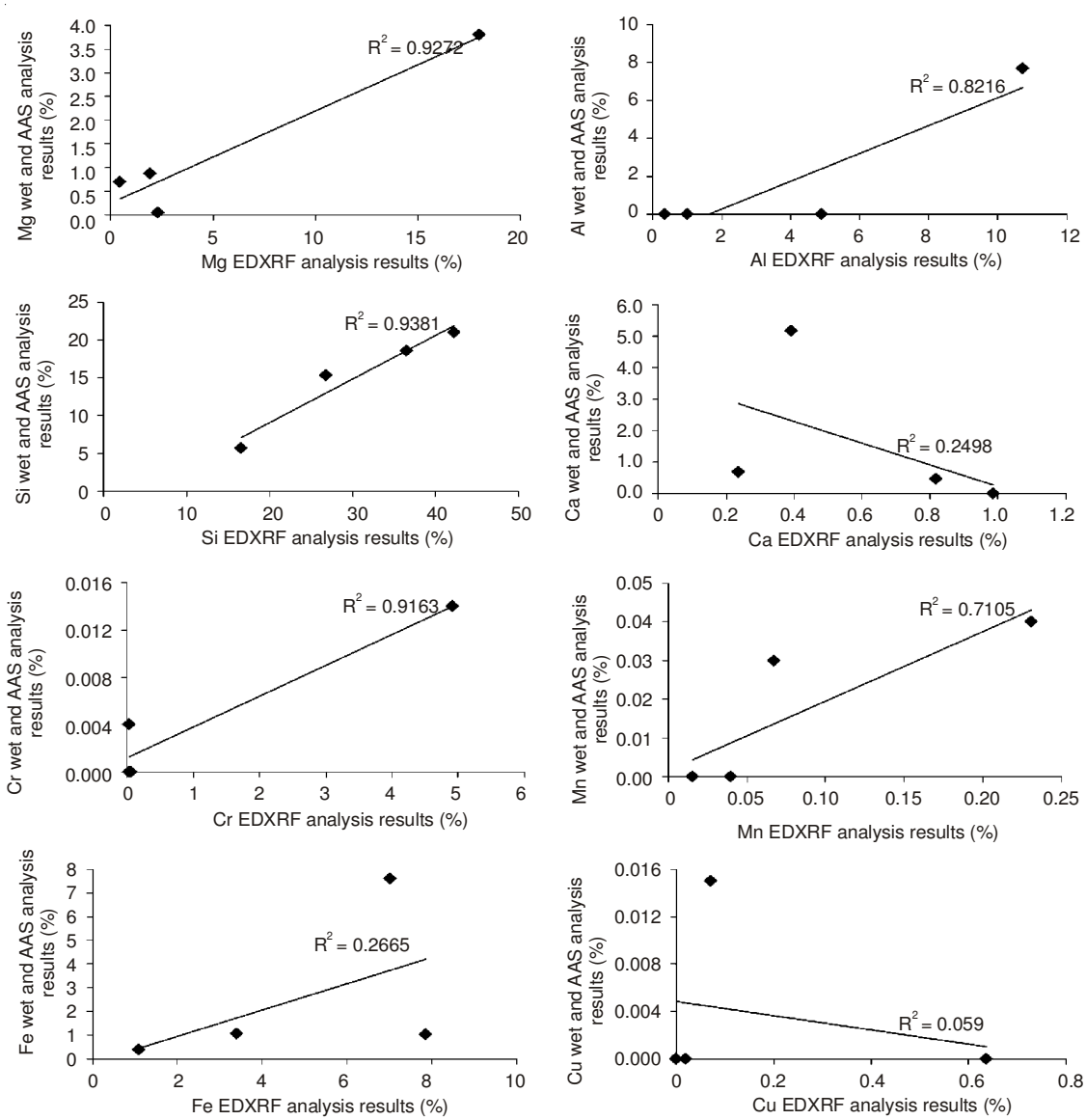

Fig. 4. Scatter chart graphs of group 1

TABLE-3
REGRESSION AND CORRELATION
ANALYSES RESULTS OF ALL SAMPLES

Elements	R^2	P Value
Mg	0.0006	0.933
Al	0.2683	0.048
Si	0.9601	0.000
Ca	0.2823	0.042
Cr	0.1807	0.114
Mn	0.0031	0.845
Fe	0.1172	0.212
Cu	0.0008	0.920

TABLE-4
REGRESSION ANALYSES RESULTS OF GROUP 1

Elements	R^2	P Value
Mg	0.9272	0.037
Al	0.8216	0.094
Si	0.9381	0.031
Ca	0.2498	0.500
Cr	0.9163	0.043
Mn	0.7105	0.157
Fe	0.2665	0.484
Cu	0.059	0.757

R^2 values are at the border and the numbers of pairs are found to be less, doubt should be constituted on the existence of a significant relationship which was encountered during the regression analysis.

In the number 2 sample group where the main concentration was concentrated at the Si, together with Mg, Al and Fe, Ca element also showed a presence of an average concentration. The distribution graph of group 2 was presented in Fig. 5. The results of the regression analysis were presented in Table-5. According to the distribution graphs a relationship can be mentioned for the Si and Al elements. The relationship status supported in the results of regression analysis for the Si was very high and significant, for Al it was powerful and significant. These calculations were within the safety limits based on the P-values. For the other elements it is not possible to discuss about a correlation or a meaningful relationship.

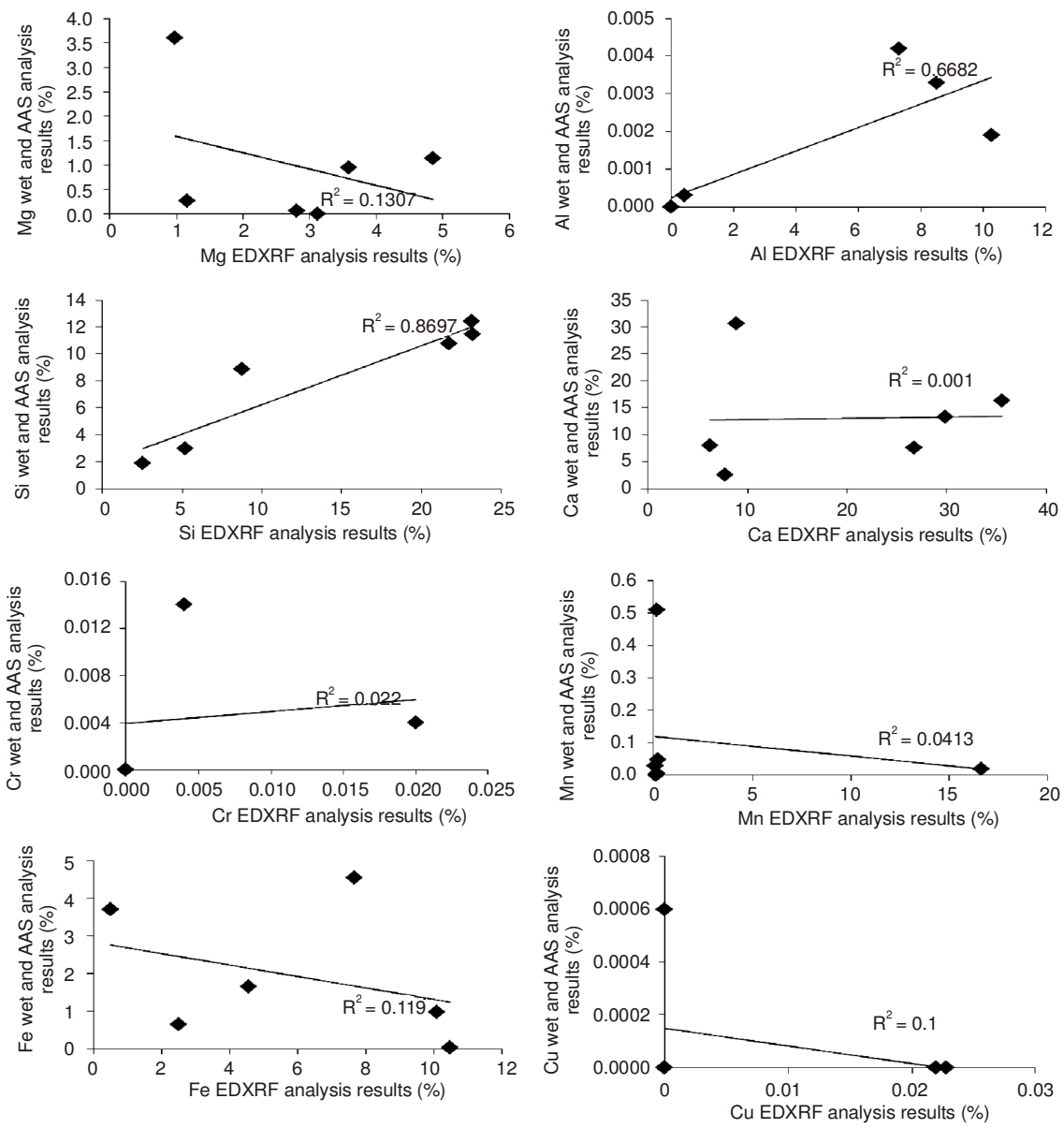

Fig. 5. Scatter chart graphs of group 2

TABLE-5
REGRESSION ANALYSES RESULTS OF GROUP 2

Elements	R^2	P Value
Mg	0.1307	0.481
Al	0.6682	0.047
Si	0.8697	0.007
Ca	0.001	0.953
Cr	0.022	0.773
Mn	0.0413	0.503
Fe	0.119	0.542
Cu	0.1	0.699

TABLE-6
REGRESSION ANALYSES RESULTS OF GROUP 3

Elements	R^2	P Value
Mg	0.054	0.706
Al	0.0045	0.915
Si	0.0087	0.902
Ca	0.0885	0.627
Cr	0.0241	0.803
Mn	0.9498	0.005
Fe	0.4485	0.216
Cu	-	-

In the group 3 samples of which basis element was the Ca there are elements including concentration in minor amounts (Table-6). When examining the scatter graphs for all elements in the group a significant relationship was found in Mn element. The group's the linear regression correlations support the scatter graph (Fig. 6). Any relationship was not concerned for all the remaining elements.

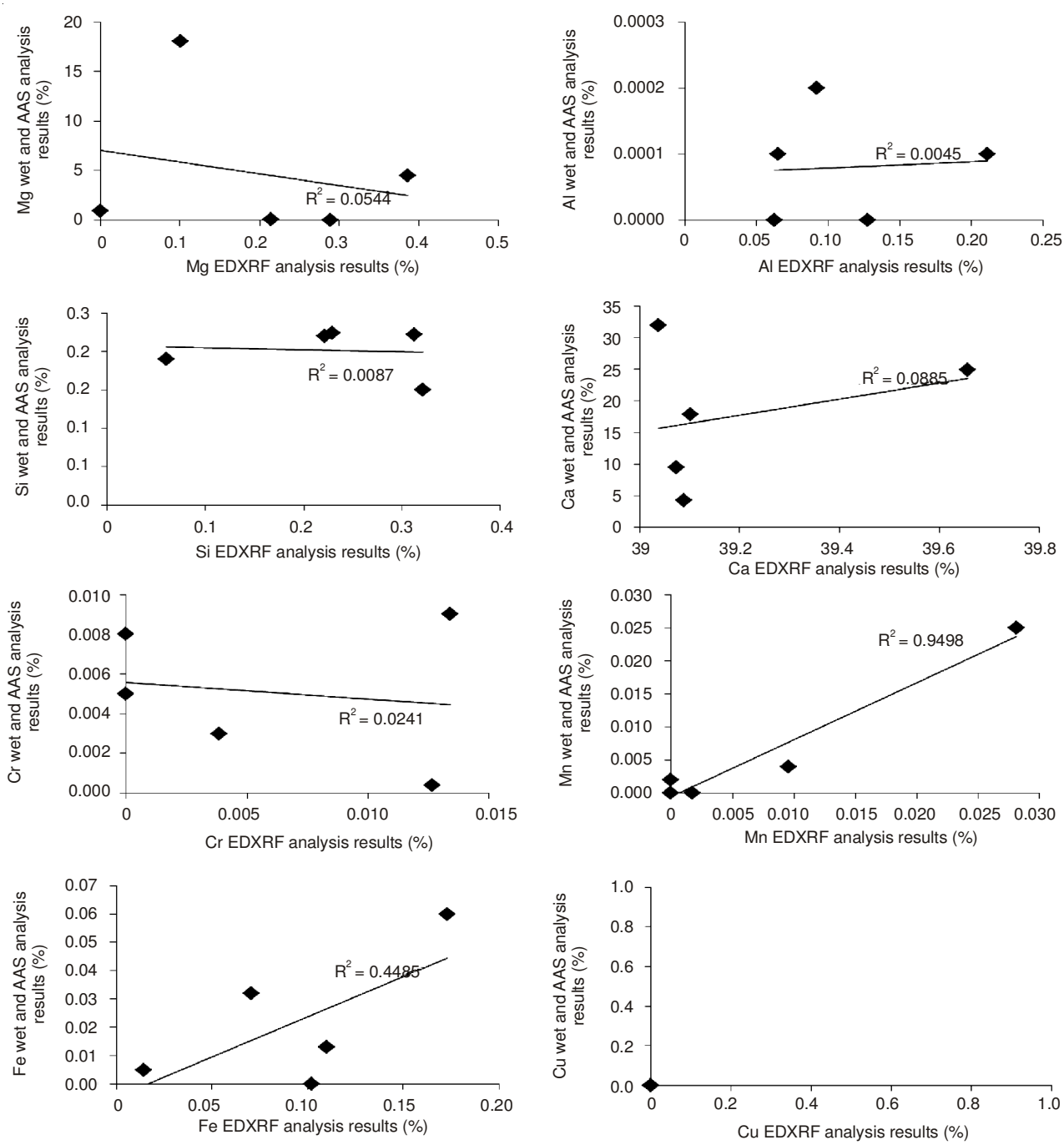

Fig. 6. Scatter chart graphs of group 3

Conclusion

The selection of the method which will be the basis of the study should be done by depending on the composition of the samples which will be analyzed. The study shows when the Ca concentration in samples rise, the deviation between EDXRF and atomic absorption spectroscopy (wet chemical analytical method) will rise. For this reason, EDXRF results should not be used in any condition while analyzing Ca element.

The concentration of Si can be examine with EDXRF, for instance, the laboratories working with standard of Si in the glass industry. At the same time, Al concentration measurement can be obtained from EDXRF with only samples in complex structured compositions containing Ca at an average level, *e.g.*, cement factories which use of own regional standards belonging to the compositions. Apart from these, EDXRF in other words semi quantitative analysis should not be used for direct results. In laboratories where a wide range of composition analyses are done in the university laboratories in order to avoid wasting time and effort the quantitative and semi-quantitative methods should be used together. The conducted study showed that readings without standards performed by EDXRF tend to show the concentration of the elements high. So this situation provides advantage. When investigating samples that have not been defined previously in the first step the general concentration scale can be revealed easily with a measure without standards with EDXFR. The element concentrations which presence was probably determined should be determined by a second analysis with targeted quantitative methods.

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