

EVALUATION OF ANALYSIS METHOD STANDARDLESS BY WDXRF AND EDXRF OF ALUMINUM POWDER USED IN MTR TYPE FUEL

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ABSTRACT

The nuclear fuel used in IEA-R1m reactor at the Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP) is the MTR type. This fuel is compound of a core (U₃Si₂-Al dispersion briquette) wrapped in an aluminum plate with two cladding (superior and inferior) both in aluminum. The fuel element efficiency depends on the quality control of U₃Si₂ and aluminum. For aluminum should be checked the impurities levels such as Si, Mn, Fe, Co, Cu, Zn and others and Al_{total}. Aiming to provide a quick method, multielemental and non-destructive, the performance of the wavelength dispersive (WDXRF) and energy dispersive (EDXRF) X-ray fluorescence techniques, using the curve instrument sensitivity curve method, also known like standardless analysis, was evaluated. This method allows the determination from the element boron (Z=5) to uranium (Z=92) with concentrations ranging from 0.001 to 99.99% without the need for individual calibration curve and chemical pretreatments in the sample preparation. The results were compared with calibration curve method data, using statistical tests tools. By multivariate analysis of all the experimental data, especially by the discriminant analysis (DA) and cluster analysis (CA), respectively, it was possible to evaluate a correlation between variables of the applied analytical methods could be interpreted in context to qualify the fuels by XRF technique and method standardless. The results showed that the proposed method is satisfactory for both spectrometers; however it was found that the WDXRF presents the greatest conformity degree.

1. INTRODUCTION

The MTR type dispersion fuel element (Material Testing Reactor) is constructed with plates compound by a core of uranium-aluminum alloy. It is manufactured by rolling a set of core, frame and cladding [1]. IPEN has been manufacturing fuel element with silicide (U₃Si₂) powder dispersed in Al (predetermined proportions). This mixture is compacted in the briquettes form and degassed under vacuum. Afterwards, it is assembled a set for rolling, compound of U₃Si₂-Al dispersion briquette. Aluminum alloy was used for the frames and covers in fuel plate assemblies. The IEA-R1 research reactor power capacity was increased from 2 to 5 MW, by using MTR type dispersion fuel. This, it was necessary because of a significant increase in the radiopharmaceuticals consumption in Brazil and also for the production of new radioisotopes [2]. The quality control of U₃Si₂ as the Al powder is very important because ensures the fuel element efficiency. According to the Nuclear Fuel Center (CCN-IPEN/SP) should be checked the levels of impurities such as B, Cd, Co, Cu, Fe, Si, Mn, Zn, Li and others, Al₂O₃, volatile materials, carbon, aluminum total, surface area and particle size in the aluminum. In this context, the X-ray fluorescence (XRF) spectrometry has

been detached once; it allows non-destructive chemical analysis, sample preparation without previous chemical treatments such as dissolution, digestion, and others. Furthermore, multi-elemental determinations from boron (B) to uranium (U) in concentrations percentages and/or milligram per kilogram (mg kg^{-1}) without the use of individual calibration curve. Due favorable characteristics already mentioned, the XRF provides incontestably great advantages in routine chemical analysis when compared to other spectroscopic techniques (examples atomic absorption spectrometry (AA) and inductively coupled plasma atomic emission (ICP), mainly in relation to samples physical characteristics (solid or highly viscous liquid), these techniques need a preliminary process of opening and treatment. However, there are two major factors that can limit the XRF to an analytical technical of first magnitude: the low sensitivity (light elements detection, $Z < 22$) and matrix interference (interelemental effect), they are caused by absorption or attenuation phenomena of signal emission, due to other elements that sample matrix compound [3].

As a result of matrix effects, the measured characteristic X-ray emission intensity of an interest element is not linearly correlated with its concentration. The matrix interelemental effects are systematic and predictable analysis by XRF, several methodologies for correction have been proposed since the 50s. The most important methods are: a) standard addition and dilution, b) radiation scattering, c) calibration with certified standards of similar composition to samples, d) mathematical methods (influence coefficients, fundamental parameters, multivariate calibration and neural networks) [3, 4].

This paper aim at to evaluate the dispersive wavelength (WDXRF) and energy dispersive (EDXRF) X-ray fluorescence spectrometers, using the calibration curve methods (similar reference materials) and fundamental parameters, according to NBR ISO 17025 legal requirements. Besides, to support the CCN-IPEN/SP in aluminum powder characterization used in the fuel element manufacture and to provide a fast analytical procedure, low cost and less waste post-analysis.

2. EXPERIMENTAL

2.1 Instrumentation

2.1.1 WDXRF

The measurements have been performed on a dispersive wavelength X-ray fluorescence spectrometer (WDXRF) model RIX 3000, by RIGAKU, Co. The accessories to establish the better instrumental conditions for each element analyzed were used: rhodium X-ray tube (3.0 kW), six diaphragms for the X-ray beam (35, 30, 25, 20, 10 and 5 mm), four filters (Zr, Ti, Al, and Ni), three collimators (160, 460 and 520 μm), seven diffraction crystals (LiF -200, PET-002, Ge-111, TAP RX-70, RX-80 and RX-4) and two detectors (scintillation (SC) and proportional flow (CSF)). Besides, a software managed by a microcomputer (PC) that perform matrix effect corrections such as absorption, attenuation and absorption/attenuation by the fundamental parameters method (FP), that can also be associate to Thomsom scattering, Compton and Continuous Spectrum methods.

The methodology evaluation with calibration and sensitivity curves was used.

The calibration curves for Mg, Si, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sn and Pb were obtained by replicates from three measures of six certified reference materials (G900J2 55X, 55X G900J4, G05H1 511x, 511x G05H3, G3000B1 511x, 54x G25D4 from MBH Analytical LTD), in the metallic disk form. The correlation coefficient parameters, angular and intersection by linear regression method, available in the spectrometer software were calculated.

The instrumental sensitivity curve by replicas from three measures of the characteristic X-rays intensities (B→U), using metallic materials (purity between 99.99 to 99.999%) was obtained. The high purity inorganic compounds for non-metals elements were used. The Fig. 1 shows the relation between instrument sensitivity (measured and calculated X-ray intensities ratio by method FP) and atomic number for K and L emission lines [5].

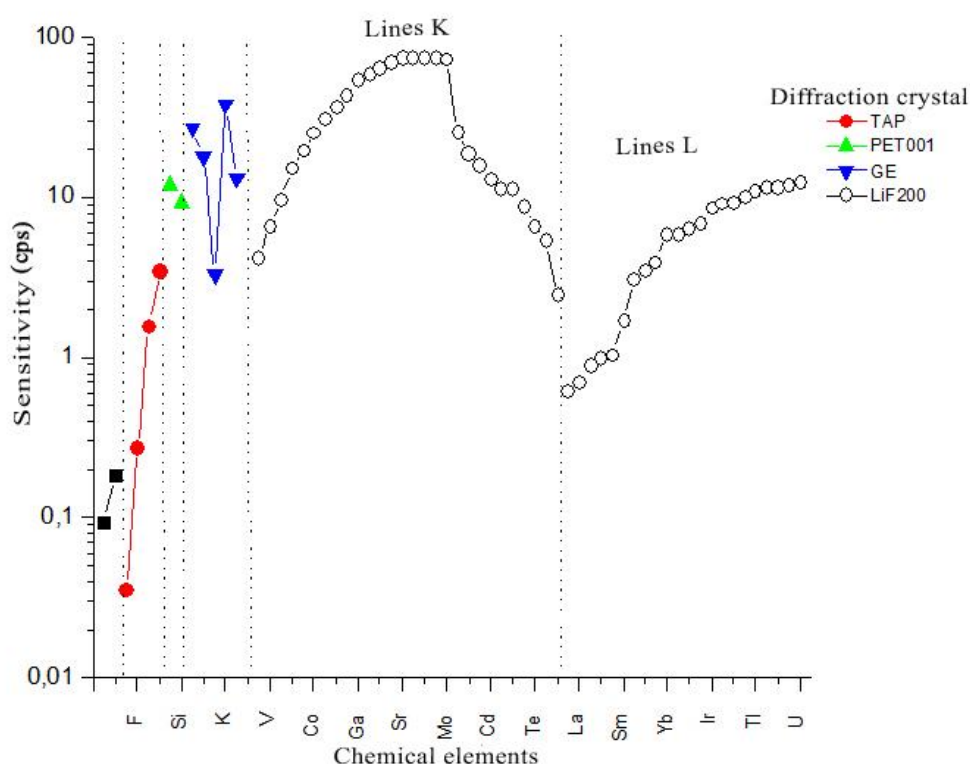


Figure 1. Instrumental sensitivity curve for the emission lines K and L from the WDXRF RIGAKU Co., 3000 RIX.

2.1.2 EDXRF

A Shimadzu Co., model EDX-720 X-ray fluorescence spectrometer was used, using the following accessories: rhodium X-ray tube (250 W), current automatically adjusted maximum 1 mA, a collimator (5 and 10 mm), Si (Li) detector cooled with liquid N₂.

The calibration curves by replicas from three measures for the same elements and certified reference materials cited in the item WDXRF were obtained. The correlation coefficient parameters, angular and intersection by linear regression method, available in the spectrometer software were calculated. The instrumental sensitivity curve by replicas from

three measures of the characteristic X-rays intensities (Na→U), using metallic and compounds materials high purity (99.999%) was obtained. The elements not measured such as H, Li, He, B, C, N, O and others in the instrumental sensitivity curve were interpolated (Fig. 2).

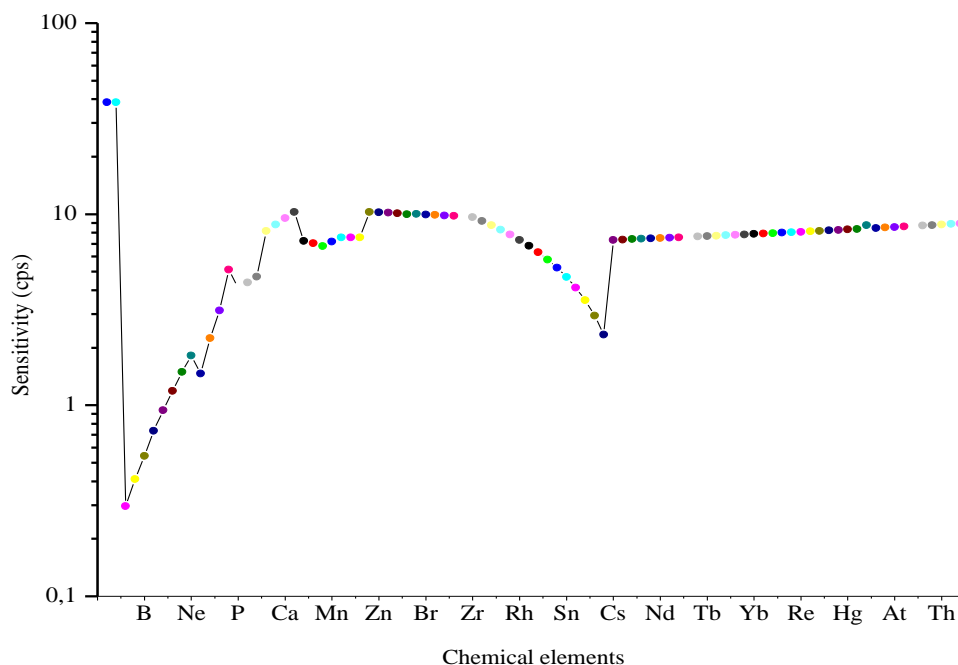


Figure 2. Instrumental sensitivity curve for the emission lines K and L from the EDXRF Shimadzu EDX 720.

2.1.3 Methodologies evaluation

Methodologies evaluation by replica from ten measures of certified reference material aluminum/magnesium 511x GO5 H2 MBH Analytical LTD was performed.

The outliers by Chauvet's test were eliminated, according to Eq 1 [6]:

$$|X_i - \bar{X}| > k_n * s \quad (1)$$

X_i ≡ measured value;

\bar{X} ≡ average;

k_n ≡ Chauvet's coefficient;

s ≡ standard deviation.

The method determination limits (MDL) were calculated, according to Eq. 2. This expression allows obtaining more realistic values that detection limits [7, 8]:

$$LDM = 2 * \sqrt{\frac{\sum_{i=1}^N (c_i - \bar{C})^2}{N - 1}} \quad (2)$$

- 2 \equiv coverage factor (0.05 significance level);
 C_i \equiv measured value;
 \bar{C} \equiv measured replica average value;
 N \equiv replica numbers.

The precision (U) at 0.05 significance level was calculated (Eq 3) [9]:

$$U = \pm t_{n-1}\left(\frac{\alpha}{2}\right) * \frac{s}{\sqrt{n}} \quad (3)$$

- n \equiv repetition numbers;
 s \equiv standard deviation;
 $t_{n-1}\left(\frac{\alpha}{2}\right)$ \equiv Student's t-test.

The accuracy in term of percentage relative error (RE%) was calculated and by Z-score (Z) was evaluated (Eq 5) [9]:

$$RE\% = \frac{\bar{x}_{lab} - x_v}{x_v} * 100 \quad (4)$$

- \bar{x}_{lab} \equiv experimental average;
 x_v \equiv certified value.

$$Z = \frac{\bar{x}_{lab} - x_v}{\sqrt{\sigma_{lab}^2 + \sigma_v^2}} \quad (5)$$

- σ_{lab}^2 \equiv experimental variance;
 σ_v^2 \equiv certified variance.

3. RESULTS AND DISCUSSION

In Tab. 1 the precision values calculated as percentage relative standard deviation (RSD%) and accuracy values as percentage relative error (RE%) are presented. In Tab. 2 the Z-score and method detection limit (LDM) values for the elements Mg, Si, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sn, Pb and Al, using the certified reference material MCR 511x GO5 H2 are given. The measurements by EDXRF and WDXRF using fundamental parameters (ED_{FP}) (WD_{FP}) and calibration curve methods (ED_{CC}) (WD_{CC}) were obtained.

Table 1. Percentage relative standard deviation (RSD%) and percentage relative error (RE%), calculated for the ED_{FP}, ED_{CC}, WD_{CC} e WD_{FP} methods in MCR 511X GO5 H2 certified reference material

| Elements | RSD% | | | | RE% | | | |
|----------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | ED _{FP} | ED _{CC} | WD _{CC} | WD _{FP} | ED _{FP} | ED _{CC} | WD _{CC} | WD _{FP} |
| Mg | 2.7 | 1.7 | 0.6 | 1.1 | 35.9 | 4.0 | 0.9 | 0.1 |
| Al | 0.2 | 0.05 | 0.03 | 0.04 | | | | |
| Si | 3.2 | 2.2 | 1.1 | 3.7 | 26.0 | 16.1 | 3.0 | 3.4 |
| Ti | 2.5 | 1.5 | 1.2 | 2.8 | 19.3 | 4.2 | 1.4 | 3.2 |
| Cr | 2.7 | 1.0 | 0.4 | 3.4 | 5.0 | 4.7 | 0.5 | 1.9 |
| Mn | 2.0 | 0.8 | 3.0 | 2.0 | 17.0 | 3.8 | 4.7 | 4.3 |
| Fe | 4.1 | 0.8 | 0.2 | 1.2 | 18.6 | 1.8 | 0.1 | 1.9 |
| Ni | 1.1 | 0.5 | 0.3 | 0.8 | 27.2 | 1.7 | 4.5 | 2.8 |
| Cu | 2.3 | 0.4 | 0.1 | 1.6 | 39.3 | 2.5 | 5.3 | 1.3 |
| Zn | 0.6 | 0.7 | 0.2 | 1.1 | 39.1 | 1.9 | 0.5 | 1.7 |
| Sn | 1.8 | 0.9 | 0.2 | 1.2 | 4.7 | 2.7 | 0.4 | 0.8 |
| Pb | 2.7 | 1.7 | 3.1 | 3.8 | 25.3 | 14.7 | 1.5 | 4.8 |

Table 2. Z-score values and method detection limit (MDL), calculated for the ED_{FP}, ED_{CC}, WD_{CC} e WD_{FP} methods in MCR 511X GO5 H2

| Elements | Z-score | | | | MDL | | | |
|----------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | ED _{FP} | ED _{CC} | WD _{CC} | WD _{FP} | ED _{FP} | ED _{CC} | WD _{CC} | WD _{FP} |
| Mg | 9.5 | 1.9 | -0.7 | -0.1 | 74 | 0.1 | 0.2 | 0.02 |
| Al | | | | | 70 | <0.01 | <0.01 | <0.01 |
| Si | 4.6 | 3.4 | 0.7 | 0.6 | 3.7 | 0.2 | 5.6 | 4.8 |
| Ti | -3.6 | 0.8 | 0.3 | 0.6 | 2.8 | 0.03 | 0.6 | 0.02 |
| Cr | -1.1 | -1.2 | 0.1 | 0.4 | 0.03 | 0.03 | 0.01 | 2.4 |
| Mn | -2.4 | 1.2 | 1.1 | -1.2 | 5.0 | 0.03 | 0.1 | 1.6 |
| Fe | -3.2 | -0.4 | 0.03 | -0.4 | 8.1 | 0.03 | 0.1 | 0.01 |
| Ni | -4.2 | -0.3 | -0.7 | -0.4 | 3.2 | 0.02 | 0.01 | 1.1 |
| Cu | -5.5 | 0.4 | 0.8 | 0.2 | 7.1 | 0.02 | 0.03 | 0.02 |
| Zn | -8.1 | -0.4 | 0.1 | -0.3 | 4.7 | 0.03 | 0.01 | 1.1 |
| Sn | -0.4 | -0.2 | 0.04 | -0.1 | 0.2 | 0.03 | 0.02 | 0.02 |
| Pb | -3.0 | 1.7 | 0.2 | -0.5 | 1.6 | 0.01 | 0.3 | 0.4 |

The precision assessment, in relation to RSD%, for all the elements using proposed four methods showed satisfactory repeatability, since a value <4% was obtained, except for Fe (4.14%) in the ED_{FP} method. Additionally, the WD_{CC} method showed better precision, mainly for the elements Mg, Al, Si, Ti, Fe, Cr, Ni, Cu, Zn and Sn with a value <0.6%, except

for Si (1.07%) and Ti (1.20%). The poor RSD% values for the ED_{FP} method were obtained, except for Ti (2.53%) and Zn (0.62%), showing that this method is less precise.

The results of accuracy evaluation, in relation to RE%, showed that the WD_{CC} and WD_{FP} methods are more accurate with values between -5 and 5%, except for Cu (5.31%) in WD_{CC}. The ED_{CC} method showed RE% values higher than 5%, showing that this method is less accurate. However, when the results were evaluated by Z-score, they showed that the ED_{CC} method presented |Z| values satisfactory (-2 < Z < +2). According to INMETRO the values |Z| ≤ 2 are considered satisfactory, 2 < |Z| ≤ 3 values are questionable and |Z| > 3 are considered unsatisfactory. The Z-score values also showed that the WD_{CC} method (-0.7 < Z < 0.8) is more accurate followed by WD_{FP} method (-1.1 < Z < 0.6).

The LDM results showed higher values for WD_{FP} method, except for Si (5.5 mg kg⁻¹) in the WD_{CC}. Nevertheless, the values are satisfactory for the impurities determination in aluminum powder samples, since, according to CCN-IPEN/SP, the Si and Fe levels should be <9500 mg kg⁻¹, Mn <500 mg kg⁻¹ and other elements <1500 mg kg⁻¹ (classified as other).

Other statistical tools to evaluate the proposed methods efficiency in this paper, such as principal component analysis (PCA) and cluster (CA) were used [10]. Initially, the outliers by Mahalanobis distance (Eq. 6 and 7) were detected, using as critical value the Wilks lambda criterion, (Eq. 8). For the set of 40 data the critical value was 27.6. As a result, the samples had values below the critical, so there was no elimination of any sample.

$$D_i = \sqrt{(X_i - \bar{X})^T S^{-1} (X_i - \bar{X})} \quad (6)$$

$$S = \sum_{i=1}^n (X_i - \bar{X})(X_i - \bar{X})^T / n - 1 \quad (7)$$

D_i = Mahalanobis distance;

X_i = sample;

\bar{X} = sample average;

T = transposed matrix;

S = sample covariance.

$$\frac{p(n-1)^2 F_{p; n-p-1; \alpha/n}}{n(n-p-1 + p F_{n; n-p-1; \alpha/n})} \quad (8)$$

p = variable numbers;

n = sample numbers;

F = probability distribution F;

α = significance level (0.05).

Afterward, it was performed a preliminary classification using hierarchical cluster analysis (CA) to link the samples by their similarities, generating a dendrogram. The Fig. 4 shows the dendrogram by Euclidian distance as dissimilarity measure that formed of two well-defined groups subdivided into G1: WD_{CC} e WD_{FP} /G2: ED_{CC} e ED_{FP} .

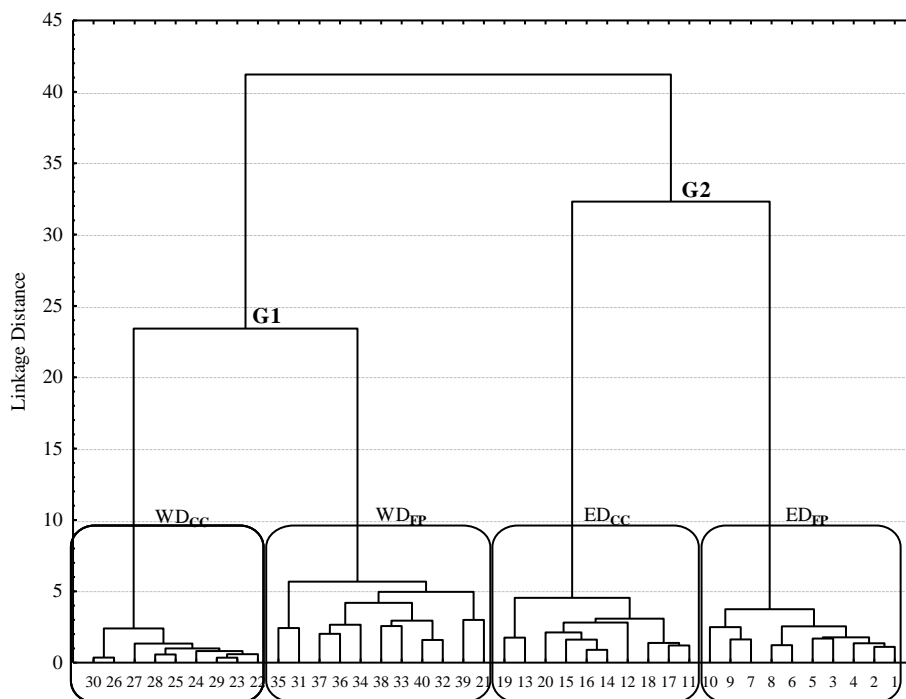


Figure 4. Dendrogram elemental analysis for WD_{CC} ; WD_{FP} ; ED_{CC} ; ED_{FP} .

The results indicate a concordance between methods and techniques applied; the two techniques established the same formation of groups and agreed to identify the intra-group specific combination.

To complement the samples discrimination obtained by hierarchical cluster analysis, it was applied the principal component analysis (PCA) to the data matrix. The data decomposition obtained by PCA (Fig. 5) determines an orthogonal coordinate system such that the first principal components are those that most affect the data dispersion (variance). In this Fig. is showed the formation of three groups (WD_{CC} + WD_{FP} ; ED_{CC} ; ED_{FP}) for aluminum powder samples, the results obtained indicate the concordance for each proposed methodology.

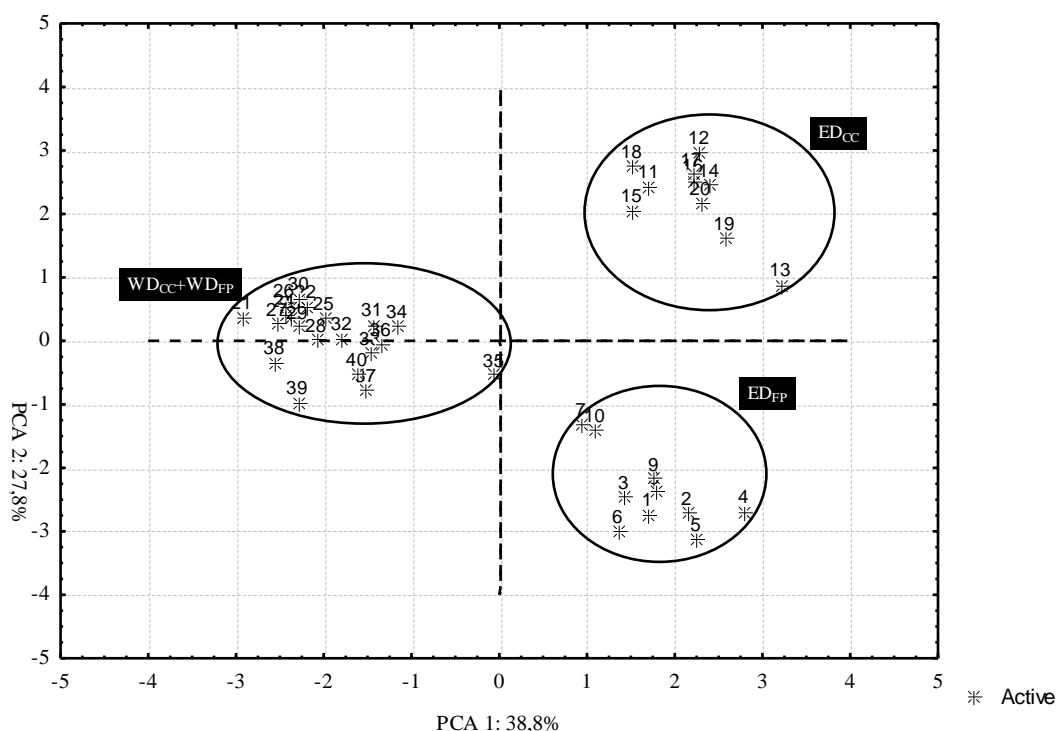


Figure 5. Principal component 1 versus principal component 2 for the set of 40 results of elemental analysis.

The group formed by WD_{CC} + WD_{FP} shows that the fundamental parameters method have the same efficiency as the calibration curve, however, it has the advantage to perform the analysis without the use of certified reference materials.

4. CONCLUSIONS

The X-ray fluorescence techniques, both dispersive wavelength (WDRXF) and energy dispersive (EDXRF) have precision, accuracy and quantification limit satisfactoriness for the Al_{total} impurities determination in aluminum powder used in the nuclear fuel manufacture type MTR. However, WDXRF, by available the instrumental sensitivity curve and this allows the determination of an impurities greater number shows be more appropriate.

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