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An Optimized Method for Characterization and Verification of Nano Sized Uranium and Thorium Particles for Safeguards Purposes

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Abstract

An optimized method that depends on preparation of nano-sized samples using ball mill technique (PM 400) and mounting it on cupper coated carbon grid was applied for microanalysis of particles to verify uranium and thorium existence. Five uranium and thorium bearing samples were analyzed by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) to verify the presence of uranium and thorium particles. High Resoluation Transmission Electron Microscope (HR-TEM) was used to image samples in order to verify the presence of different nano-sized particles. All samples were scanned by SEM at optimum conditions before and after applying the developed procedure; working distance =10 and 11 mm, voltage =30 kV, magnification value = X500, spot-size = 50, to screen the samples. The developed method is not time consuming and gives reliable results in case of heterogeneous samples and samples of low content of uranium and thorium.

Keywords: Scanning Electron Microscope (SEM), Nano particles, Safeguards, Uranium, Thorium.

1. Introduction

Safeguarded nuclear material (uranium, thorium and plutonium) are of great interest not only for the International Atomic Energy Agency (IAEA) but also for the States due to their wide range of applications and also for their considerable threat to be used in nuclear weapons manufacture. States which have signed the Non Proliferation Treaty (NPT) have the responsibility to establish and maintain a system of accounting for, and control of, all nuclear materials any where under its authority (IAEA 1972). Both for accountancy and control purposes, mass and composition of nuclear material are mainly determined by measurements performed by destructive and non-destructive methods. Destructive Assay (DA) involves measurements on samples taken from a larger quantity or batch; typically samples are altered by their preparation such that the sample is not returned to the batch. Non Destructive Assay (NDA) is a measurement in which no physical or chemical change occurs for samples during analysis. Energy dispersive spectrometer depends on the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis (Agarwal 1991). All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements ($Z < 10$). Qualitative analysis involves the identification of the specific lines in the X-ray spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration standards of known composition. By scanning the beam in a television-like raster and displaying the intensity of a selected X-ray line, element distribution images or 'maps' can be produced (Agarwal 1991). Also, images produced by electrons collected from the sample reveal surface topography or mean atomic number differences according to the mode selected. The scanning electron microscope (SEM), which is closely related to the electron probe, is designed primarily for producing electron images but can also be used for element mapping and even point analysis, if an X-ray spectrometer is added. SEM accompanied by X-ray analysis is considered as relatively rapid, inexpensive, and basically non-destructive approach to surface analysis. It is often used to survey surface analytical problems before proceeding to techniques that are more surface-sensitive and specialized. Since the electron probe an analysis is done to a shallow depth (Goldstein *et al.* 2003) , specimens should be well polished so that surface roughness does not affect the results. Sample preparation is essentially as for reflected light microscopy, with the provision that only vacuum compatible materials must be used. Opaque samples may be embedded in epoxy resin blocks. For transmitted light viewing, polished thin sections on glass slides are prepared. In principle, specimens of any size and shape (within reasonable limits) can be analyzed (Goldstein *et al.* 2003).

Holders are commonly provided either for 25mm diameter round specimens or for rectangular glass slides. Standards are either mounted individually in small amounts or in batches in normalized mounts (Scott & Love 1983). Many samples are electrically non-conducting so a conducting surface coat must be applied to provide a path for the incident electrons to flow to ground. The usual coating material is vacuum-evaporated carbon or gold (~10nm thick) (JEOL LTD 1998; Goldstein *et al.* 1981). Energy-dispersive spectrometers (EDXs) employ pulse height analysis (Goldstein *et al.* 2003): A silicon drift solid state detector is used because of its better energy resolution, the detector giving output pulses proportional in height to the X-ray photon energy is used in conjunction with a pulse height analyzer (in this case a multichannel type). Incident X-ray photons cause ionization in the detector, producing an electrical charge, which is amplified by a sensitive preamplifier located close to the detector. Both detector and preamplifier are cooled with liquid nitrogen to minimize electronic noise. Si(Li) or Si drift detectors (SDD) are commonly in use. Dynamic light scattering (DLS) also known as photon correlation spectroscopy or quasi-elastic light scattering is a technique can be used to determine the size distribution profile of small particles in suspension or polymers in solution (Berne & Pecora 2000). It can also be used to probe the behavior of complex fluids such as concentrated polymer solutions. When light hits small particles, the light scatters in all directions (Rayleigh scattering) as long as the particles are small compared to the wavelength (below 250 nm). If the light source is a laser, and thus is monochromatic and coherent, the scattering intensity fluctuates over time. This fluctuation is due to the fact that the small molecules in solutions are undergoing Brownian motion, and so the distance between the scatterers in the solution is constantly changing with time. This scattered light then undergoes either constructive or destructive interference by the surrounding particles, and within this intensity fluctuation, information is contained about the time scale of movement of the scatterers. Sample preparation either by filtration or centrifugation is critical to remove dust and artifacts from the solution (Berne & Pecora 2000).

X-ray fluorescence (XRF) is another useful tool, can be used in both qualitative and quantitative of uranium and thorium. The difference between EDS and XRF is the type of radiation hitting the sample. EDS uses an electron beam while XRF uses an x-ray beam. Due to the small beam size possible with electrons, elemental analysis can be obtained for volumes as small as one µm in diameter. EDS specimens must be sputtered with a conductive coating to avoid charging issues with the electron microscope. Specimens are often cross-sectioned at the area of interest on the component-board to provide an internal view of solder joint at both the component and board level. The elemental composition can be analyzed for the solder joint and the surface finish/plating thicknesses can be measured. Also, the intermetallic layer can be analyzed for composition as well as thickness. Thicknesses can be directly measured by electron microscopy. Both XRF and EDS can be used in performing qualitative and quantitative analysis. XRF can provide non-destructive qualitative and quantitative analysis but is limited to surface analysis and by coating uniformity for thickness measurement. EDS with electron microscopy provides enhanced x-ray microanalysis, direct thickness measurement, and imaging under higher magnification for examining bulk solder and intermetallic layer.

Transmission Electron Microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a Charge Coupled Device (CCD) camera. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail even as small as a single column of atoms, which is thousands of times smaller than the smallest resolvable object in a light microscope. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging (Wikipedia ; Reimer 1997; Williams & Carter 1996).

In this study, SEM combined with EDX analysis, was applied as a semi-quantitative technique to the characterization of U and Th particles. The aim of this work is to show how the SEM-EDX method may be helpful to identify, characterize and quantify uranium and thorium in real non-homogenous samples from Egyptian ores.

2. Experimental

2.1 Samples

Five uranium and thorium bearing samples with low content of uranium and thorium were used in the present study to assay their uranium and /or thorium content. Samples (TS.1) and (TS.4) are carbonaceous fossil wood fragments while (YS.3), (YS.8) and (YS.33) are rock samples collected from different lithologies (sandstone) (Eman 2011).

2.2 *Samples preparation*

Assayed samples were grinded to 200 mesh and sieved in order to increase homogeneity for analysis by SEM and EDX, small quantities (about 0.5g) with reasonable size and shapes were taken to get representative specimen which should not exceed holder diameter. The specimen was fixed on a carbon tape pasted on the holder using spatula. All samples were prepared in nano-size using Ball mill which is an effective technique for getting small size particles these particles may be present in nano-size that can be verified by other techniques like DLS and TEM. The Planetary Ball Mill PM 400 pulverizes and mixes soft, medium-hard to extremely hard, brittle and fibrous materials. Dry and wet grinding can be carried out. The high speed of 30 to 400 min^{-1} in combination with the very large sun wheel diameter of 300 mm guarantee extremely high fineness in a short time. The PM 400 is a robust, compact floor model with 4 grinding stations for grinding jars with a nominal volume of 12 to 500 ml. It can grind up to 8 samples simultaneously down to the sub-micron range (Florez-Zamora 2008). Samples were prepared by another procedure in which ball mill type PM 400 is used to decrease sample size in order to get very tiny particles and so increase the homogeneity to what extent. Samples were milled or grinded for (16 hr) at (350 rpm) then DLS Malvern zetasizer MAL 10/1664 was used to determine the average size.

2.3 *SEM and EDX measurements*

The SEM used in this study is a JEOL JSM-6510LV model with resolution of 1pA^0 to 1µA^0 (Jeol.com 2014). SEM equipped with EDX spectrometer was employed for the measurements. The major parts of a SEM/EDX are: vacuum specimen chamber, electron column with electron source, electromagnetic lenses, scanning coils and signal detectors (Jeol.com 2014). A number of signals, such as secondary electrons (SE), backscattered electrons (BSE) and X-rays, result from interactions of a focused scanning electron beam with the atoms of a specimen, thus providing different information about the sample (Jeol.com 2014). The specimen was placed inside the holder and it was fixed inside the instrument at working distance 10 or 11 mm (WD10 mm), voltage=30 kV, magnification value = X500 and spot-size = 50. A standard-less semi quantitative method (Quant method) was used for analysis (Jeol.com 2014). This type of analysis is performed without recording spectra from standard materials for all the elements.

Usually, 30 kV accelerating voltages were used in the EDX analysis enabling excitation of both uranium and thorium L and M electrons.

2.4 *TEM measurements*

TEM of type JEM – 2100 is another technique that was used to verify the presence of nano-size particles through imaging and estimating particles size by nanometer bar. TEM images assure the existence of nano-particles in the studied samples. Samples were tested again to detect uranium and thorium by two different procedures, the first in which the prepared nano-particles were placed on the holder and fixed by carbon paste then analyzed by EDX, In the second procedure anti solvent (water) was added to small portion of the prepared nano-particles in a test tube then tube was shaked well to get suspension. The tube is then placed in ultrasound instrument BRANSON 1510 for 15 min to increase homogeneity after the specified time. A small volume of the suspension was withdrawn by pipette and distributed in cupper coated carbon grid and left for drying then analyzed by EDX. The second procedure was used for samples preparation in case of imaging by TEM and analysis by EDX (Reimer 1997; Williams & Carter 1996).

3. Results and discussion

X-ray spectrometry is one of the analytical methods used for safeguards and accountability measurements of nuclear materials. Scanning electron microscopy is extensively applied to characterize the morphology of the uranium particles (Ciurapinski *et al.* 2002). The particles' form, size, surface structure, and composition can give complementary information on their history and source (Stebelkov 2005; Pidduck *et al.* 2006). SEM-EDX analyzing system can be particularly useful in the initial identification of uranium in swipe samples, and might be appropriate to identify and characterize uranium particles (Rafael *et al.* 2013).

X-ray spectrometry is used for qualitative and semi-quantitative analysis in which the sample is analyzed in order to identify the existing elements, by looking at and identifying the peaks in the X-ray spectrum, while semi-quantitative analysis, the proportion of each element present was measured as accurately as possible, by measuring the areas under the X-ray peaks. Electron-probe microanalysis, with its capability of qualitatively or quantitatively analyzing a point as small as 1 µm in diameter on a polished mineral surface, has wide application in identifying uraniferous minerals and also in determining their uranium content (Henley et al. 1972). Also, different monazite and pyrochlore generations in deeply weathered ores, containing minor concentrations of uranium and other trace elements, was standard-less quantified (Salge et al. 2013).

SEM-EDX equipped with Si(Li) X-ray detector was used to analyze elemental composition of the given samples. The X-ray spectra generated were analyzed with data handling system. Quantitative information was obtained by comparing the areas of the peaks in the spectra with the area of single element standard peaks; the ratio obtained was corrected with a standard ZAF computer program. For the SEM-EDX measurements, identification of the particles was based on the presence of the uranium Mά X-ray line at 3.17 keV, the Mβ line at 3.34 keV (Kips *et al*. 2007) and For thorium Mά X-ray line at 2.99 keV in the EDX spectrum. The previously mentioned uranium and thorium bearing samples were analyzed using EDX spectrometer and the obtained results in view of uranium and thorium concentrations were listed in Table (1). EDX results for samples TS.1(carb.1) and TS.4 (carb.4) were obtained from Shaban et al (Shaban *et al*. 2013).

As can be seen from Table (1) uranium and thorium cannot be determined in all examined samples. As in samples YS.3, YS.8 and YS.33, there is no evidence for uranium and thorium existence.
However, in a previous work (Shaban *et al*. 2013; Gascon 1994 ; Holden 2003 ; Vesterbacka *et al*. 2009) used in the current study were analyzed for uranium and thorium investigation using gamma spectroscopy and the obtained results affirmed the presence of both elements in the all tested samples.

The difference between gamma and EDX results may be attributed to the samples heterogeneity, since EDX quantitative analysis results are considered only if the sample has a uniform composition over the area that to be examined, i.e. the areas that X-rays pass through. The noise from the background and the dead time can add small systematic contribution also.

Since EDX can provide rapid qualitative or with adequate standards, quantitative analysis of elemental composition with a sampling depth of 1-2 microns, the obtained results for the last three sampled indicates that, either uranium or thorium exist on the outer surface of the samples investigated. SEM-EDX method is a microanalysis and semi-quantitative, so some differences in the quantitative results may appear when moving from area to another in the case that the sample is not uniform or heterogeneous. It is well known that in SEM-EDX analysis only a portion of the tested sample is fixed a specimen with a few centimeter diameter which means that only a portion of gram scale is analyzed, however in gamma spectroscopy the whole sample is being analyzed. This means the accuracy in quantitative analysis acquired by those two different techniques is different especially for this type of samples.

Since SEM-EDX analysis scan only a limited depth of the surface on specimen and provided only the spatial resolution that was needed to characterize these materials in the micro scale, the granule structures of uranium deposit with elements distributed in the inner part of the sample can not be detected by SEM-EDX assay. This motivated us to prepare the tested samples in a manner to be uniform and homogeneous. This was done through conversion of these samples to the nano-size using Ball mill technique. The prepared nano-sized samples were characterized using DLS and TEM techniques, in order to examine existence of nano-sized particles. DLS technique was used to measure the average size of particles to assure the existence of nano-sized particles (Berne & Pecora 2000). Results obtained from DLS assured that samples were in nano-size. The average size obtained from DLS for the samples is ranging from 312.9 nm to 524.8 nm and the PdI is around 0.5.

TEM was also used as a different technique for assuring the existence of nano-sized particles. Samples were imaged at different magnifications using HR-TEM at 200 kV, and the obtained TEM images of samples TS.4 and Y.8 using digital micro graph software were represented in Figure 1. These images indicate the presence of nano-particles with different shapes and sizes, which is attributed to the different tested matrices. TEM image for TS.4 sample shows nano-sized (100 nm) with a needle shape particles, meanwhile, TEM image for Y.8 sample shows nano-sized spherical particles (50 nm) with a particle size greater than that of TS.4 sample.

In order to examine the applicability of the developed procedure, the prepared nano-sized samples were further analyzed by SEM-EDX spectrometer using two different procedures. The first procedure involving fixation of a reprehensive sample portion on carbon paste, while the second one involving usage of anti-solvent (water) and cupper coated carbon grid as showed in the experimental section.

Uranium and thorium content were assayed and EDX results for all samples obtained by applying the first and second procedures are listed in Tables (2 and 3) respectively. Tables (2 and 3) clearly indicate the presence of uranium and thorium in all tested samples with different concentrations. These qualitative analyses were found to be in a good agreement with those data obtained by gamma spectrometry. It is also clear from Tables (2 and 3) that, uranium and thorium content obtained by the second procedure is fairly higher that that obtained by the first one, which indicates that the second procedure is better that the first one. This can be explained on the basis of the more uniformity and homogeneity of the samples offered by the second method.

The micrographs of the prepared nano-sized samples were also obtained by SEM. SEM images of samples Y.8 obtained by applying the first and second procedure are shown in Figures (2-a and 3-a) while their corresponding EDX spectra are shown in Figures (2-b and 3-b) respectively. On the other hand, the micrographs of the prepared nano-sized samples were also obtained by SEM. SEM images of samples TS.4 obtained by applying the first and second procedure are shown in Figures (4-a and 5-a) while their corresponding EDX spectra are shown in Figures (4-b and 5-b) respectively. It is obvious from these figures that the morphology of the same sample prepared by these two different methods is greatly different. EDX spectrum of the sample Y.8 showed many elements such as (C, O, K, Mg, Fe, Si, Ca, Mn, U and Th), while, EDX spectrum of the sample TS.4 showed (C, O, Mg, Al, Si, Fe, Mn, Zn, U and Th). The Cu peaks which appear at Figures (3b and 5b) are attributed to the cupper grid used in the second procedure of analysis. It is known that analysis of soil or ore samples without chemical treatment is not an easy work, however, chemical treatment of such type of samples greatly improve the obtained results. This is will be considered in our future work.

It is worth to highlight that the developed method is not only applicable to uranium and thorium bearing samples, but also to all types of solid samples within the operating conditions considered in this work.

4. Conclusion

In this work, SEM equipped with EDX spectrometer was used to verify the presence of uranium and thorium in the tested samples at both micro and nano-scale sized particles. Nano-scale uranium and thorium bearing samples were prepared by applying ball mill technique. The confirmation of the formation of nano-sized particles was made using DLS and TEM techniques. The results obtained in this work by SEM-EDX to verify the presence of uranium and thorium. The developed method may improve the accuracy of analysis especially for heterogeneous samples and samples of low concentration of uranium and thorium and could be applied to different types of solid samples within the operating conditions considered in this work.

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Tables

Table (1): Uranium and thorium concentrations for the tested samples obtained by EDX spectrometer (200 mesh size).

Sample ID	EDX results (Mass % ± σ_M)	
	Th	U
TS.1	0.100 ± 0.009	0.100 ± 0.007
TS.4	0.41 ± 0.012	0.32 ± 0.009
YS.3	0.00	0.00
YS.8	0.00	0.00
YS.33	0.00	0.00

Table (2): Uranium and thorium concentrations for the tested nano-sized samples obtained by EDX spectrometer and applying the first procedure.

Sample ID	EDX results (Mass % ± σ_M)	
	Th	U
TS.1	0.330 ± 0.016	0.250 ± 0.014
TS.4	0.060 ± 0.011	0.070 ± 0.010
Y.3	1.750 ± 0.021	0.380 ± 0.016
Y.8	0.450 ± 0.021	1.100 ± 0.017
Y.33	0.100 ± 0.024	0.330 ± 0.019

Table (3): Uranium and thorium concentrations for the tested nano-sized samples obtained by EDX spectrometer and applying the second procedure.

Sample ID	EDX results (Mass % ± σ_M)	
	Th	U
TS.1	0.890 ± 0.025	0.010 ± 0.019
TS.4	0.270 ± 0.014	0.060 ± 0.011
Y.3	0.840 ± 0.017	0.060 ± 0.013
Y.8	0.040 ± 0.026	1.170 ± 0.021
Y.33	0.070 ± 0.021	0.030 ± 0.027

Figures

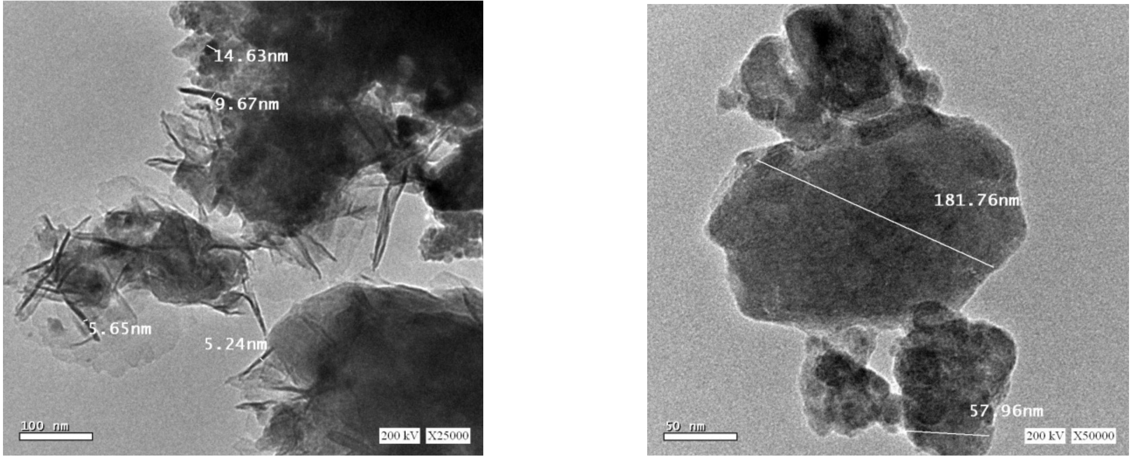

Fig.(1-a)

Fig.(1-b)

Fig.1. (a) TEM image of Y.8 sample at 200 KV and magnification value of X25000; (b) TEM image of TS.4 sample at 200 KV and magnification value of X50000.

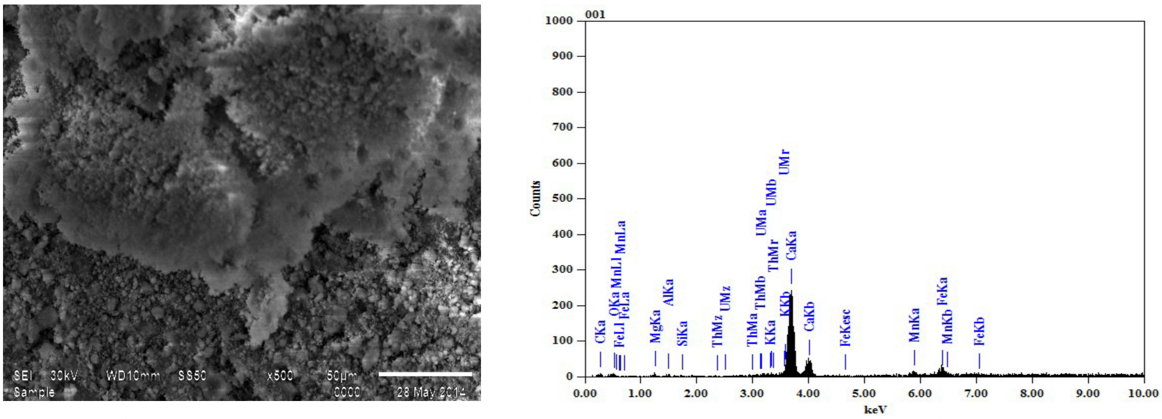

Fig.(2-a) Fig.(2-b)

Fig. 2: (a) SEM image (SEI) of Y.8 sample analyzed by first procedure scanned at (30kV-WD =10 mm – X500-SS= 50); (b) EDX spectrum for the same sample

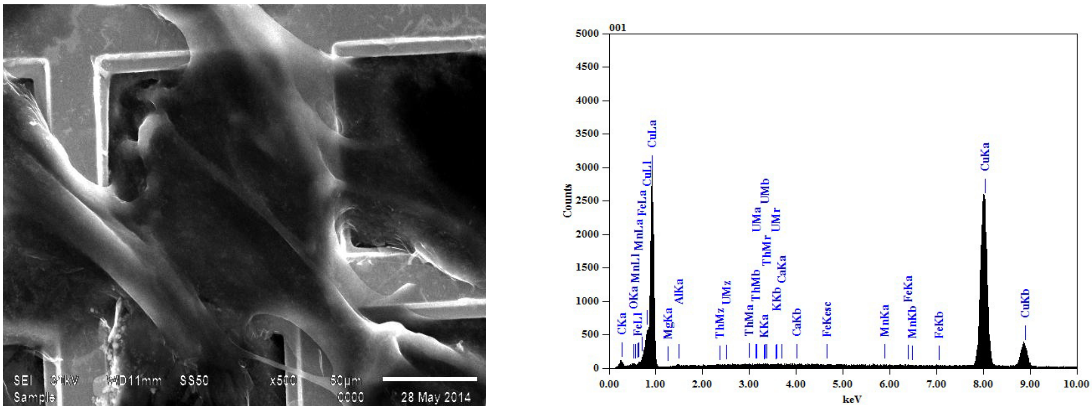

Fig.(3-a) Fig.(3-b)

Fig. 3: (a) SEM image (SEI) of Y.8 sample analyzed by second procedure scanned at (30kV-WD =10 mm – X500- SS= 50); (b) EDX spectrum for the same sample.

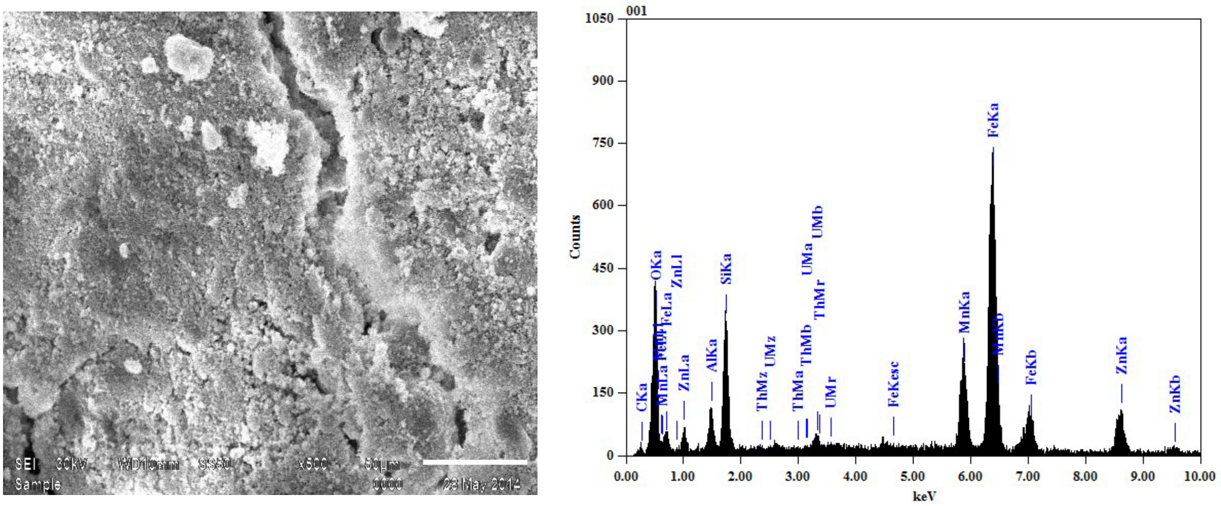

Fig.(4-a) Fig.(4-b)

Fig. 4: (a) SEM image (SEI) of TS.4 sample analyzed by first procedure scanned at (30kV-WD =10 mm – X500-SS= 50); (b) EDX spectrum for the same sample

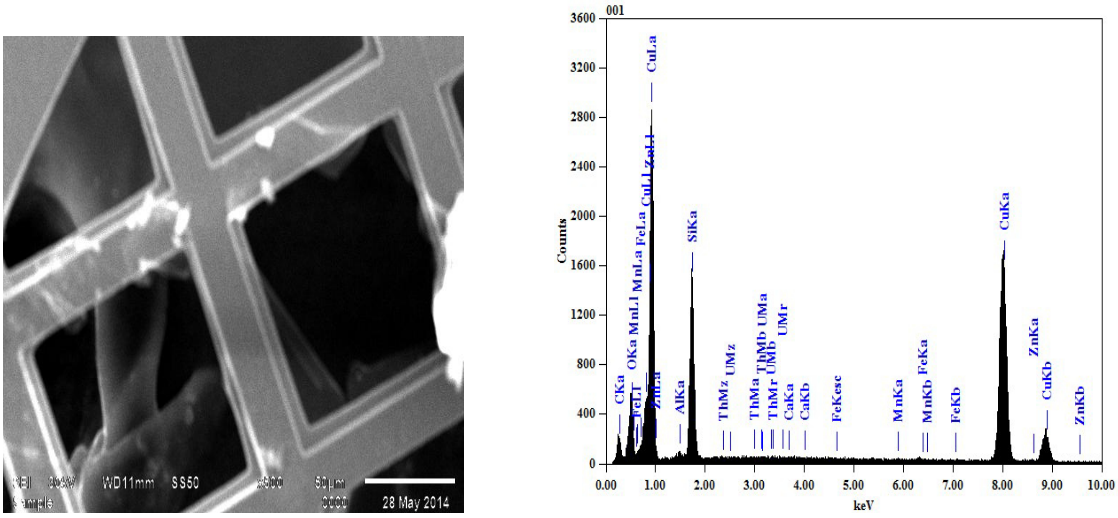

Fig.(5-a)

Fig.(5-b)

Fig. 5: (a) SEM image (SEI) of TS.4 sample analyzed by first procedure scanned at (30kV-WD =10 mm – X500- SS= 50); (b) EDX spectrum for the same sample.