

An Investigation of Bursa-Uludağ Wolfram Ore By NAA And EDXRF Methods*

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Abstract

In this study 4 wolfram ore samples obtained from Bursa-Uludağ wolfram deposit, together with concentrated scheelite sample, that was enriched in Scheelite mineral (CaWO_4), obtained from the ore samples, were analysed for their major and minor constituents by radioisotope excited energy dispersive X-ray fluorescence (EDXRF) and neutron activation analysis (NAA) techniques. The concentrations of Na, Mg, Al, Si, P, S, Ca, Sc, Ti, Cr, Mn, Co, Fe, Cu, Ni, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Mo, Ru, Ba, La, Ce, Nd, Eu, Ag, Sb, Cs, Yb, Hf, Ta, W, Th, U elements have been determined.

Özet

Bu çalışmada Bursa-Uludağ wolfram yatağından alınan 4 wolfram maden örneği ile maden örneklerinden Şelit minerali içeriği bakımından (CaWO_4) zenginleştirilmiş şelit konsantrasyonunun içeriklerindeki major ve minor elementler, enerji dağılımlı X-ışınları floresans analizi (EDXRF) ve nötron aktivasyon analizi (NAA) teknikleri ile saptanmıştır. Örneklerin Na, Mg, Al, Si, P, S, Ca, Sc, Ti, Cr, Mn, Co, Fe, Cu, Ni, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Mo, Ru, Ba, La, Ce, Nd, Eu, Ag, Sb, Cs, Yb, Hf, Ta, W, Th, U konsantrasyonları belirlenmiştir.

Keywords: *Wolfram ore, neutron activation analysis, XRF, energy dispersive x-ray fluorescence.*

Introduction

Wolfram (W, tungsten) is an important metal with a wide range of uses. Most of the unusual properties are due to half-filled 5d-electron shell $\{_{74}\text{W}; (\text{Xe}) 4f^{14} 5d^3 6s^2\}$ with a very high binding energy of the wolfram metal lattice. Based of these properties, wolfram and wolfram allows and some wolfram compounds have many important applications in different fields of modern technology [1]. It is widely used as wolfram carbides (WC , W_2C) in cemented carbides. Cemented carbides (also called hard metals) are wear-resistant materials used by the metalworking, mining and construction industries. Wolfram metal wires, electrodes are used in lighting electrical, heating and welding applications. It is also used in the production of some special steel. High-speed tool steels, and many other alloys contain wolfram. It has excellent corrosion resistance. The thermal expansion is about the same as borosilicate glass, which makes the metal useful for glass-to metal seals. Wolfram composites are used as a substitute for lead in bullets and shot. W chemical compounds are used in catalysts, inorganic pigments and high temperature lubricants. It is also used for radiation shielding.

The aim of this study is to determine the concentrations of the wolfram ore deposit of Bursa-Uludağ (Turkey). Analyses were performed by NAA and EDXRF methods.

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Experimental

The main ore of wolfram is Wolframite $\{(Fe, Mn)WO_4\}$ and Scheelite $(CaWO_4)$. In this study scheelite ore was concentrated by gravimetric methods combined with froth flotation from the ore samples obtained Bursa-Uludağ wolfram deposit and this enriched in scheelite ore sample was also analysed together with the other ore samples. In this study 4 wolfram ore samples obtained from the different areas of the Bursa-Uludağ wolfram ore deposit together with the ore sample enriched in Scheelite mineral were analysed by using NAA and EDXRF techniques.

In the case of thermal neutron activation analysis, about 0.4g sample powders was placed in polyethylene sample tube and irradiated at the thermal neutron flux of about 8.10^{12} neutron. $cm^{-2}.s^{-1}$ in the TRIGA-II research reactor of Istanbul Technical University for one hour (The power of the reactor is 250 kW). A fast pneumatic system was used to transfer the irradiated samples. The gamma spectra were measured using a Canberra S-100 gamma ray spectrometer with HPGe detector (GC 2020). The resolution was 2 keV at 1332.5 keV for ^{60}Co , and 1 keV at 122 keV for ^{57}Co . The detector was shielded by a cylindrical lead shield with an average thickness of 10 cm, in order to achieve a background level as low as possible. The gamma spectra obtained have been analysed using Canberra S-100 acquisition and analysing system. The details of this technique were given in references [2-4].

The EDXRF analysis of the pelletised samples were performed by using either tube excited KEVEX-0700 XRF spectrometer with Rh target or radioisotope excited EDXRF spectrometer. Tube excited EDXRF spectrometer has also Ti, Fe, Ge, Mo, Ag, Sn, Gd, Al and Au secondary targets. In the case of tube excited EDXRF spectrometer the analyses were performed by comparison with the standards. The standards of Geological Survey of Japan and Mineralogical Institute of Turkey were used.

In the case of radioisotope excited Energy Dispersive X-Ray Fluorescence (EDXRF) analysis, samples were excited using an ^{241}Am source (10 mCi) and a HPGe detector or a ^{109}Cd source (25 mCi) and a Si(Li) detector for 50,000 s with resolutions of approximately 350 eV and 185 eV FWHM, respectively, at 5.89 keV and the analysis were performed by using the fundamental parameter technique (FPT), in order to minimise the matrix effects. The details of this technique were given in references [5-8]. For the FPT, the geometric factors, G_i , for each element i {that were related to the incident-exciting X-ray intensity, the geometric factor of the spectrometer and the detection efficiency for the fluorescence radiation from element i }, were first determined experimentally, by using uniform thin standard samples, according to reference [8], and then a calibration graph for the spectrometer was drawn. The geometric factors for the other elements of the sample investigated were calculated by using this graph. Finally, the absorption corrections of the elements and then the concentration of each element i of the sample was determined. The analyses were performed in triplicate.

The precision and accuracy of the analyses have been checked with the United States Geological Survey and Japon Geological Survey standarts (USGS and GSJ). Our results are found to be in confidence interval of SRMs. The analytical precision was better than 10%.

Results

The Radioisotope excited EDXRF spectrum of the concentrated scheelite ore sample is given in Figure 1. The decay γ -ray spectra of W-sample 4, recorded 7, 27 and 33 days after irradiation are given in Figures 2-4. The quantitative results of the concentrated scheelite ore and W-ore samples are given in Tables 1 and 2. Analytical results indicate that samples contain Na, Mg, Al, Si, P, S, Ca, Sc, Ti, Cr, Mn, Co, Fe, Cu, Ni, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Mo, Ru, Ba, La, Ce, Nd, Eu, Ag, Sb, Cs, Yb, Hf, Ta, W, Th, U elements, in different concentrations.

Table 1 NAA Analysis results of the wolfram ore samples

$\mu\text{g/g}$	W1, concentrated in Scheelite	W2	W3	W4	W5
Cs	46.42 \pm 0.69	3.00 \pm 0.53	6.58 \pm 0.29	20.07 \pm 0.41	89.69 \pm 1.15
Co	1.21 \pm 0.12	8.75 \pm 0.28	2.16 \pm 0.18	0.60 \pm 0.10	1.60 \pm 0.14
Eu	1.11 \pm 0.06	3.17 \pm 0.08	1.12 \pm 0.05	2.74 \pm 0.05	0.39 \pm 0.05
Zr	189.7 \pm 61.1	231.3 \pm 45.4	487.9 \pm 102.1	1033.8 \pm 100.7	105 \pm 11.0
Ag	24.9 \pm 1.01	103.57 \pm 2.41	3.75 \pm 0.70	1.95 \pm 0.64	24.50 \pm 1.08
Zn %	9.01 \pm 0.13	3.03 \pm 0.02	0.67 \pm 0.01	0.32 \pm 0.01	3.23 \pm 0.05
Ta	0.28 \pm 0.13	9.97 \pm 0.40	2.15 \pm 0.18	2.03 \pm 0.16	0.23 \pm 0.15
Sc	0.45 \pm 0.02	0.85 \pm 0.02	1.81 \pm 0.04	2.05 \pm 0.04	0.62 \pm 0.03
Th	0.82 \pm 0.42	28.93 \pm 0.83	8.73 \pm 0.34	14.16 \pm 0.40	0.45 \pm 0.03
U	4.35 \pm 0.56	27.63 \pm 1.46	17.83 \pm 0.60	41.23 \pm 1.08	2.55 \pm 0.44
Cr	143.16 \pm 4.95	64.32 \pm 1.83	60.33 \pm 2.72	130.52 \pm 3.53	38.56 \pm 3.73
Hf	nm	6.50 \pm 0.44	1.20 \pm 0.17	2.31 \pm 0.18	0.28 \pm 0.18
W %	23.68 \pm 0.67	5.94 \pm 1.21	0.11 \pm 0.01	0.55 \pm 0.07	0.25 \pm 0.05
Ca %	9.08 \pm 0.43	2.20 \pm 0.25	1.14 \pm 0.42	6.58 \pm 0.30	8.12 \pm 0.79
Ru	nm	62.96 \pm 9.03	27.70 \pm 4.24	46.14 \pm 3.87	nm
Sb	7.85 \pm 0.89	23.47 \pm 1.99	4.30 \pm 0.57	6.80 \pm 0.93	44.46 \pm 1.90
Rb	0.54 \pm 0.02	0.03 \pm 0.01	0.08 \pm 0.01	0.14 \pm 0.02	1.37 \pm 0.05
Ce	4.37 \pm 1.13	70.23 \pm 2.48	30.29 \pm 1.26	46.48 \pm 1.38	7.04 \pm 1.36
La	11.93 \pm 1.10	197.65 \pm 8.76	56.77 \pm 2.27	136.54 \pm 5.03	14.52 \pm 0.85
Se	nm	3.91 \pm 0.47	9.95 \pm 0.24	6.57 \pm 0.20	nm
Yb	0.54 \pm 0.33	7.37 \pm 0.33	1.74 \pm 0.34	3.01 \pm 0.34	nm
Mo	0.11 \pm 0.02	4.06 \pm 0.16	0.16 \pm 0.02	0.34 \pm 0.03	0.05 \pm 0.01

nm= not measured.

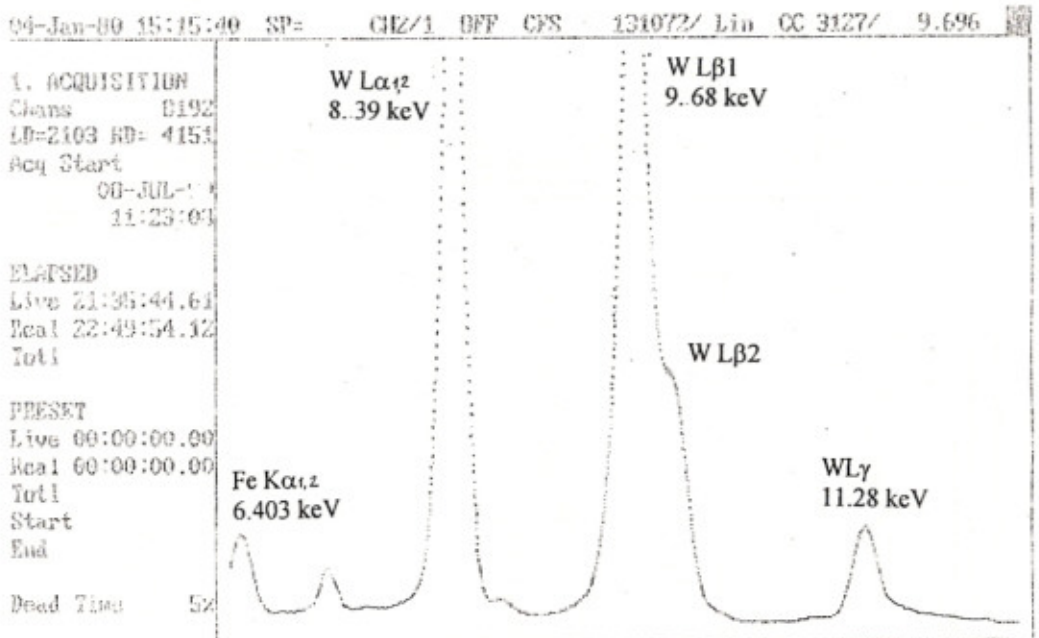
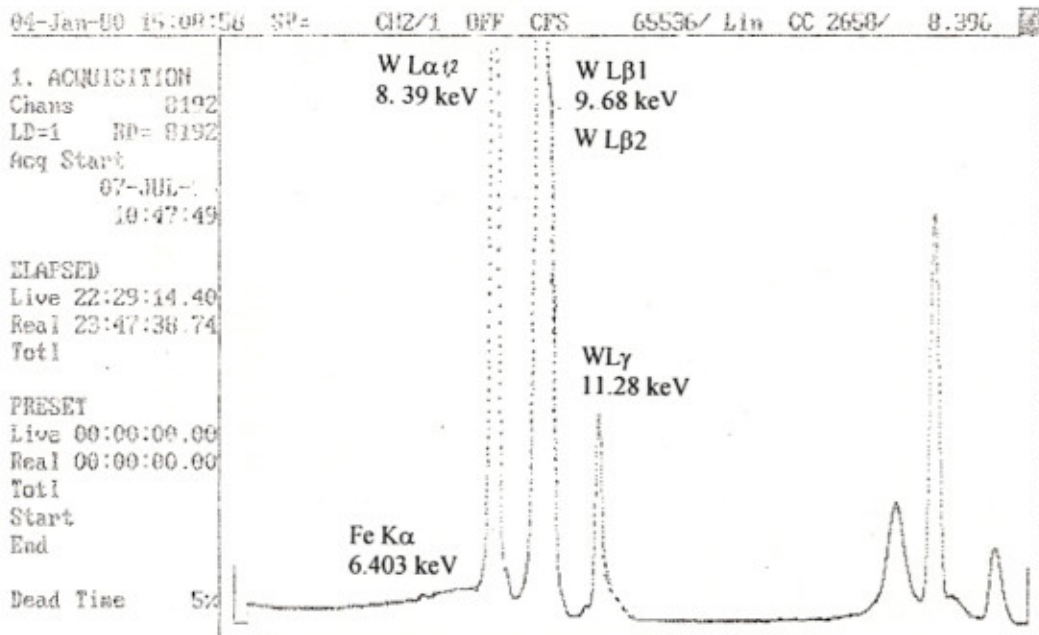
Table 2 EDXRF Analysis results of some W samples

%	W1,scheelite	W2	W3	W4	W5
ΣFe	19.2	20.0	17.5	19.5	18.3
Si	9.0	26.0	28.0	26.5	24.0
Al	1.5	1.7	1.6	1.6	1.7
S	4.0	4.0	4.1	5.5	4.0
Na	1.0	1.3	1.3	1.3	1.4
Mg	1.5	1.5	1.6	1.7	1.8
Ti	1.3	1.4	1.4	1.3	1.4
P	0.3	0.4	0.4	0.3	0.4
Cu	0.3	0.4	0.3	0.4	0.4
Ga	0.01	0.01	0.01	0.02	0.02
As	0.3	0.4	0.4	0.4	0.4
Ba	1.4	1.5	1.6	1.6	1.7
Mn	0.9	1.0	1.1	1.2	1.3
Nd	0.01	0.01	0.01	0.01	0.01
Y	0.0020	0.0018	0.0020	0.0019	0.0020
Sr	0.5	0.6	0.7	0.7	0.7
Rb	0.02	0.03	0.04	0.05	0.05
Ni	0.01	0.01	0.02	0.02	0.02

The accuracy of the values is found to be better than $\pm 12\%$.

Figure Caption

1. Radioisotope excited EDXRF spectrum of concentrated scheelite ore sample.
 2. Gamma-ray spectrum of W-sample 4, recorded 7 days after irradiation.
 3. Gamma-ray spectrum of W-sample 4, recorded 27 days after irradiation.
- Gamma-ray spectrum of W-sample 4, recorded 33 days after irradiation.



E (keV)

Figure 1.

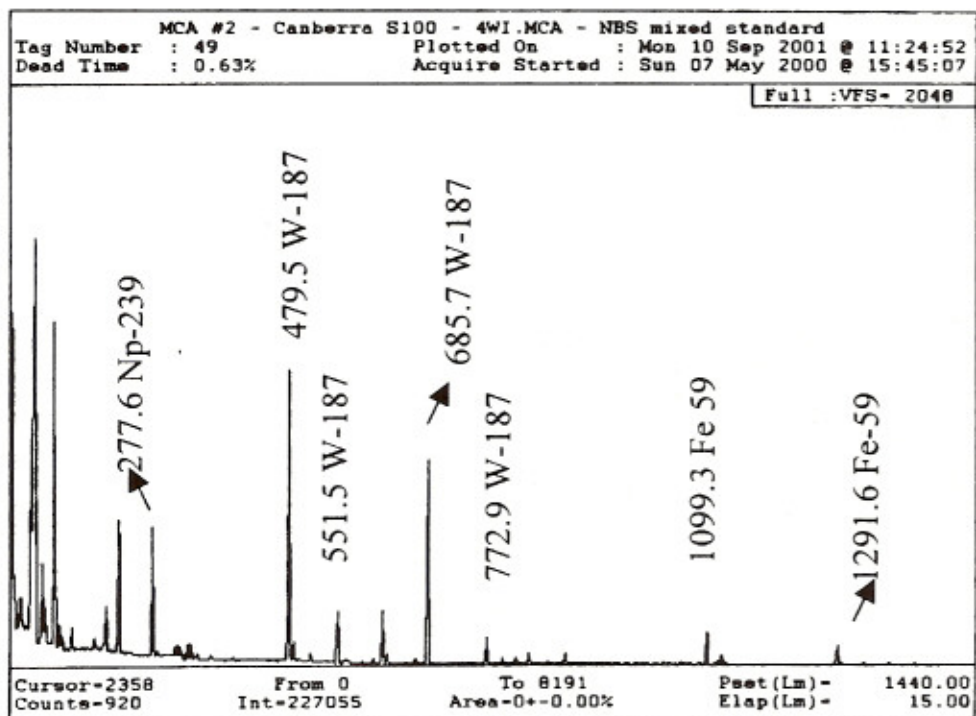
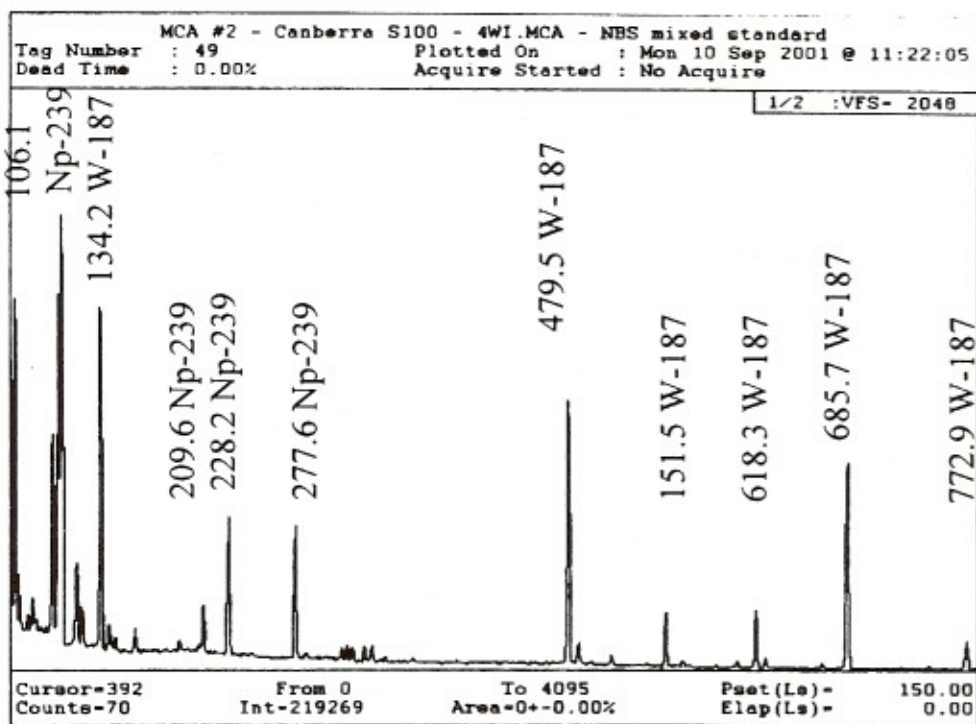


Figure 2.

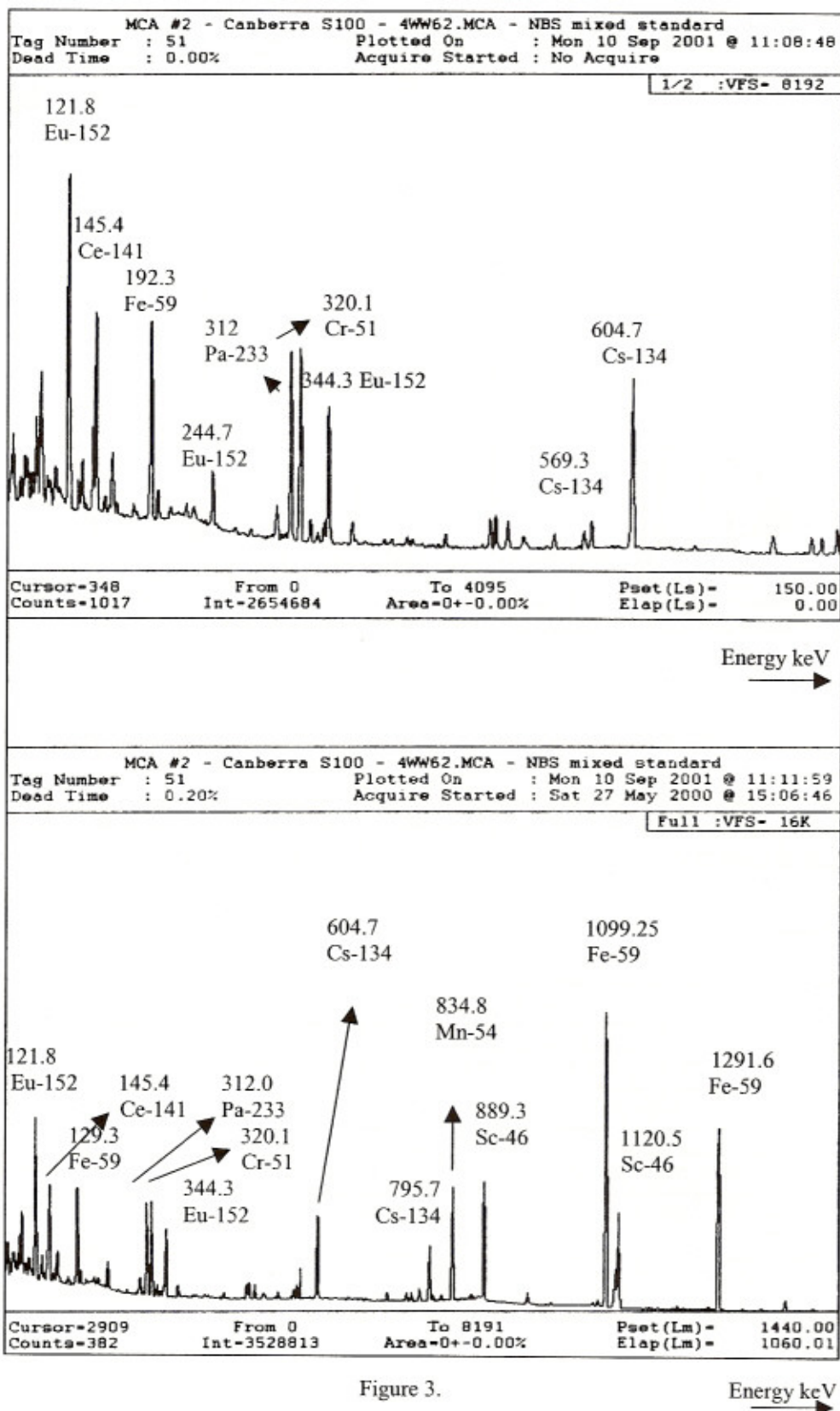


Figure 3.

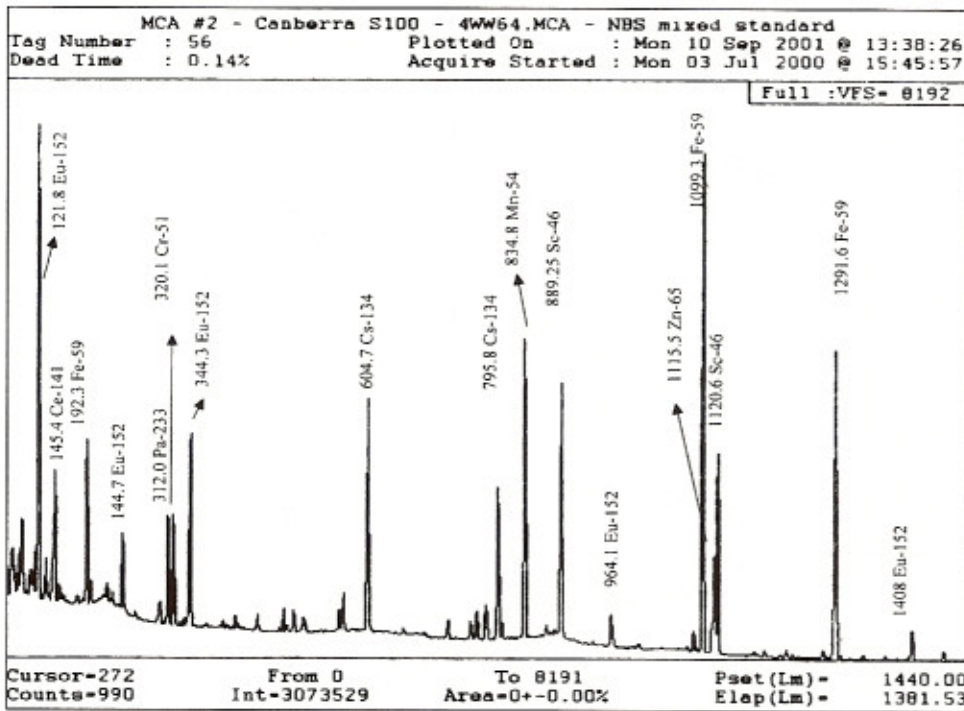


Figure 4.

We have demonstrated that use of EDXRF analysis method together with NAA is ideally suited to determine a wide range of impurities in W ore which has importance for the usage of the wolfram mineral. The concentration of workable wolfram ores is usually between 0.3 and 1.0% W. The wolfram concentration of the composite samples obtained from Bursa-Uludağ ore deposit is found to be 0.11-5.94%.

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