

# Preparation of Natural Standard Reference Material (SRM) for El-lajjun Oil Shale/Jordan

Mousa Magharbeh<sup>a</sup>, Manar Fayyad<sup>a</sup>, Mufeed Batarseh<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, University of Jordan, Amman - Jordan

<sup>b</sup> Department of Chemistry and Prince Faisal Center for Dead Sea Environmental and Energy Reserach, Mutah University, PO Box 7, 61710 Karak-Jordan.

## Abstract

The standard reference materials (SRMs) represent a key tool for the quality control of chemical analyses and the demand on these materials is constantly increasing worldwide. A standard reference material of oil shale (SJL-1) collected from El-lajjun area in Jordan was prepared and certified to be used for quality control of analyses and calibration particularly for the oil shale characterization and testing laboratories. This work was a part of the Arab collaborative projects initiated by Arab Atomic Energy Agency (AAEA) during the period from 2007 to 2009.

The paper describes the certification procedure and the inter-laboratory comparison study results, which was carried out through participation of twelve national and international laboratories applying eleven different analytical techniques used to determine the analytes concentration. Details of the production, homogeneity and stability of SJL-1 standard reference material were reviewed as well as the results of certification. The Certificate of Analysis for SJL-1 provides assigned certified values for almuinium oxide, phosphorus pentoxide, calcium oxide, titanium dioxide, magnesium oxide, potassium oxide, ferric oxide, sodium oxide, manganese oxide, sulfur, uranium, vanadium, chromium, zinc, nickel, copper, and strontium. Reference values are provided for Loss on Ignition (LOI), silicon oxide, cadmium, molybdenum, cobalt, lead, barium and arsenic. Finally, range values are assigned for other thirty-seven constituents of oil shale.

© 2012 Jordan Journal of Earth and Environmental Sciences. All rights reserved

**Keyword:** SJL-1; Standard Reference Materials; Oil Shale; El-Lajjun; Jordan.

## 1. Introduction

The lack of quality control of chemical analyses carried out particularly in industrial testing laboratories may lead to inaccurate data and wrong assessment of the product quality. The oil shale mining is a promising industry in Jordan. However, in the Middle East region few studies were concerned with preparation of natural Certified Reference Materials (CRMs) that can be used for quality control and calibration (Al-Masri, et al. 2006).

Recently, the Arab Atomic Energy Agency (AAEA) sponsored a project entitled "Standard Reference Materials (SRMs)" aiming for encouraging cooperation between researchers in Arab World for preparation of CRMs to be used as reference materials for quality assurance in laboratories testing, methods validation and instruments calibration. The overall project efforts lead for the following: Egyptian team prepared two materials: Olive leaves and black sand as SRMs, Syrian team prepared sewage sludge and Jordan team prepared Oil Shale and Phosphate. Additionally, an in-house reference soil sample containing high level of naturally occurring radioactivity was prepared by Syrian Atomic Energy Agency (Al-Masri, et al. (2006).

The National Institute of Standards and Technology (NIST), United States Geological Survey (USGS) and the institute of Geochemistry SB RAS (IGI) prepared and purchased several number of standard reference materials (SRMs) for oil shale worldwide. Most of these SRMs are used for validating and calibrating analytical methods with certified oxide, metals and organic components, while others oil shale constituents reported as averages or ranges only. However, limited numbers of SRMs were prepared for quantification of trace level of organic compounds such as polycyclic aromatic (PAHs) (Heidelberg, 1988). There are thirty-six organic SRMs have been prepared in natural matrix and forty-four solutions for instruments calibration. Future goals include certifying more organic constituents such as polychlorinated Biphenyls (PCB), dioxins, and emerging contaminants such as brominated flame retardant (Wise, 2002).

The numbers of SRMs prepared worldwide for shale and accordingly assigned for some certified values are limited. The Green River Shale (SGR-1) has been certified for nine oxides and twenty six elements, while others constituents such as total carbon, ash and moisture content were neither certified nor measured (Gladney et al, 1988). Devonian Ohio Shale (SDO-1) was certified for ten oxides

\* Corresponding author. e-mail: Batarseh@mutah.edu.jo.

and twenty five elements, while total carbon, organic carbon and moisture content were reported as measured values only, ash was not measured (Kane et al. 1990). Cody Shale (SCO-1) has been certified for ten oxides and twenty seven elements, but organic carbon and total carbon were reported as measured values, ash and moisture were not measured (Gladney et al, 1988). Sukhoy Log Shale (SLg-1) was certified for ten oxides and twenty six elements, while, organic carbon and total carbon reported as measured values, only (Petrov et al. 2004). Finally, Khomolkho Shale (SCHS-1) certified for eleven oxides, thirty nine elements and LOI but again organic carbon and total carbon reported as measured values (Petrov et al. 2004).

The present work describes the preparation, analysis and certification of oil shale standard reference materials called (SJL-1), which can be valuable on the national and international levels for laboratory testing, analytical method validation, quality assurance, and instruments calibration. It can be used also on industrial level for economical studies related to oil shale exploitation and performing interlaboratory comparison studies. The SJL-1 material constituents including carbon content, ash, moisture, macro- and microelements, minerals and metal oxides concentrations were measured according to standard certification procedure using different analytical techniques at national and international accredited laboratories.

## 2. Methods and Materials

### 2.1. Sample Collection and Pre-treatment

An oil shale test material was collected from the El-lajjun deposits, located 120 km south of Amman city, Jordan, Figure 1. The sampling was carried out at a new mining area that was established recently by Jordanian Natural Resources Authority (NRA). About 100 kg of oil shale rocks material was collected and pooled together. The sample had a composition adequately representative of oil shale and containing measurable quantities of major and minor constituents similar to the candidate standard reference material (SRM).

The sample preparation was including crushing using a Jaw crusher and removal of the coarse material ( $> 2$  mm). Then sample was ground using an Agate Ball Mill to pass 200 mesh ( $75\mu\text{m}$ ). The fine material was homogenized in a polyethylene-lined mixing drum. Finally, the sample was left to settle down and packed in sealed polyethylene bottles each of 100 g. About 200 sample bottles were produced as a candidate SRM of oil shale and ready for analysis. A sophisticated protocol for testing the homogeneity and stability was developed as described in section 2.2.

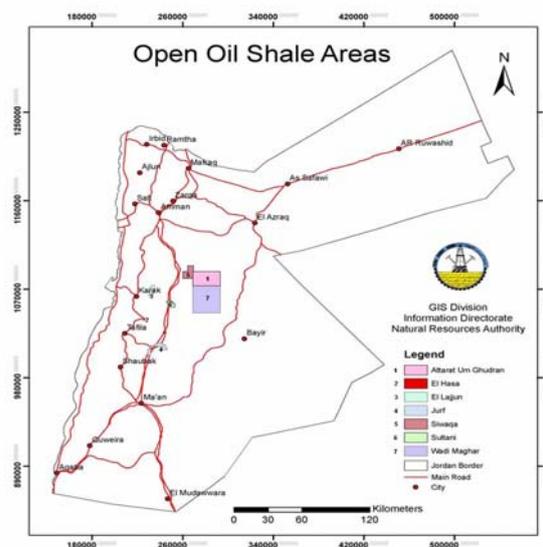


Fig 1. Map of oil shale deposits in Jordan and sampling site location, (Alali, 2003)

### 2.2. Homogeneity testing

The prepared sample material should be homogenous and has same distribution of analytes within the individual sample bottle and among all prepared sample bottles (units). Homogeneity was tested according to the British Standard Methods for sampling and chemical products number BS5309 part 1 (Walker and Brookman, 1998). The number of sub-samples to be tested for homogeneity were chosen according to the following formula ( $3x^3\sqrt{n}$  = number of tested units),  $n$  is number of prepared units. Each unit contains 100 g of the homogenous oil shale sample material. The homogeneity of the sample was tested using two-factor analysis of variance (ANOVA) without replication by comparing calculated F value ( $F_{\text{calc}}$ ) with critical F value ( $F_{\text{crit}}$ ) at 95% confidence level.

Three methods were used for homogeneity testing namely: sieve analysis, total (cross) alpha/beta activity, and Gamma spectrometry. The particle size distribution performed for 10 sub-samples by passing each sample through an automatic sieve machine shaker with four different sieves ( $<45$ , 53-45, 53-63, and 63-75 $\mu\text{m}$ ), each particle size portion was weighed and percentage was calculated. These results were double checked using laser grain size analyzer for selected samples, there was a significant conformity between sieve analysis and laser grain size analyzer results. Total (cross) alpha/beta activity measurements were carried out for 10 sub-samples using low background alpha/beta counting system model Tennelec LB 4100 (Canberra Proportional counter, USA). The sample from each unit (6-10)  $\text{mg}/\text{cm}^2$  was placed in 5-cm stainless steel discs and counted for alpha/beta activity. Gamma spectrometry activity and their daughters measurements were performed for 10 sub-samples using a special counting container. The gamma emitting daughter activity (Bk/kg) was monitored for 1 hour using gamma spectrometry at high resolution (1.85KeV at 1.33 MeV).

### 2.3. Chemical and Mineralogical Characterizations

The oil shale sample (SJL-1) chemical composition was analyzed using the following analytical techniques namely: X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), Inductively coupled plasma atomic emission spectroscopy (ICP-OES), neutron activation (NA), atomic absorption spectrometer (AAS), Gamma spectrometry, total organic carbon analyzer (TOC), Kjeldahli, and Fischer assay was used for determination of oil content and organic carbon. The mineralogical content was investigated mainly using X-ray diffraction (XRD) which indicated that the oil shale mainly composed of calcite and quartz.

### 2.4. Determination of the Water Content

Water content was determined by calculating the weight difference of an oil shale sample (1.5-3.0 g) before and after drying using two methods, an oven at 105°C for 24 hours and an Infrared (IR) apparatus model UHra-X210 (Gronert, Germany).

### 2.5. Determination of Total Organic Carbon (TOC)

About 5g of the homogenized oil shale sample was treated with excess HCl (12.5 %, v/v), until the disappearance of bubbles. The treated samples were filtered on a pre-weighed filter paper and washed with double deionized water to remove the excess amount of HCl. Then the filter paper was placed in an aluminum tray and dried in an oven for 24 hours at 108°C. After complete dryness, samples were reweighed, ground and five replicates of 5 to 10 mg aliquot of each sample was analyzed for their TOC content using DC-90 Total Organic Carbon Analyzer (Dohrmann, USA). The calibration curve was prepared using a mixture of oxalic acid with alumina ( $H_2C_2O_4/Al_2O_3$ ) in a ratio of (1:9) that ranged from 28 to 87 µg carbon.

### 2.6. Elemental Analysis (ELEM)

Elemental analysis of hydrogen, nitrogen, carbon and sulfur in oil shale material was carried out according to the standard operating procedure of EURO EA Elemental Analyzer (HEKAtech GmbH, Germany). A 12 mg of oil shale sample was mixed with ( $V_2O_5$ ) as catalysts for measuring sulfur using sulphanylamine and BBOT (2-4 mg) as reference standards.

### 2.7. XRF Analysis

The homogenous oil shale sample was analyzed for oxides content using Energy Dispersive XRF Spectrometer (EDXRF). The sample placed into a polyethylene cup together with SGR-1 reference standard material. Additionally, the quantitative oxides analysis using Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF) was performed through preparing XRF disk by mixing 0.3g of oil shale sample with ( $2.7g + 3x LOI$ ) of  $Li_2B_4O_7$  and 0.3g of absorbing X-ray reagent ( $La_2O_3$ ), the mixing ratio of sample to ( $Li_2B_4O_7$  and  $La_2O_3$ ) was 1:10. The oxides concentrations were determined as percentages.

### 2.8. Sample Preparation for Elements Analysis

The elements were determined by ICP-MS, ICP-OES, NA and AAS after digestion using two methods, an open acid digestion in a mixture of (HF-HNO<sub>3</sub>-HClO<sub>4</sub>) and a

microwave digestion in a mixture of (HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and HF). The detailed digestion procedures are described in the following sections.

#### 2.8.1. Open Acid Digestion

A 0.2 g of oil shale sample was placed into a polytetrafluoroethylene (PTFE) bottle. A mixture of (HF-HNO<sub>3</sub>-HClO<sub>4</sub>) was added in the ratio (v/v) of 7ml HF (47%), 7ml HNO<sub>3</sub> (69%) and 2ml HClO<sub>4</sub> (70%) and allowed to heat at 120°C for 3 hour using heating blocks. Then switched to 160°C for 24 hours and evaporated to dryness, to the residue a 10 ml of 1M HNO<sub>3</sub> was added and resulting solution was transferred to 20ml polyethylene volumetric flask and complete to mark with deionized water. Finally, the solution filtered through a 0.45 µm syringe filter and the sample was ready for measurement. All glassware were cleaned, dried and rinse with 5% HNO<sub>3</sub> before use.

#### 2.8.2. Microwave Digestion

A 0.2 g of oil shale sample was digested in a cleaned PFA Teflon vessels with a mixture of 8ml HNO<sub>3</sub> (69%), 2ml H<sub>2</sub>O<sub>2</sub> (30%), and 4ml HF (47%) using a microwave digestion system model star\*-system (MHS-product, Germany). The vessels left opened for 12 hours to get rid of gasses, and then vessels were capped and placed inside the rotor bodies, sealed, tightened and digested in the microwave digestion system. Then the solution poured into PFA beaker and heated at 110°C until dryness to get rid of HF. Then 20ml of 10% HNO<sub>3</sub> was added to each sample and transferred into 20ml polyethylene volumetric flask. Each digestion series included a sample reference and sample blank which was cleaned Teflon vessel containing the same type and amount of the reagents only.

### 2.9. Quality Control

The results of the analytical methods (ICP/OES, ICP/MS, ICP-OES, XRF, NA, AAS and Elemental analysis) were validated by analyzing the following certified reference materials: SGR-1, BBOT, Sulfanilamide, OREAS24P, OREAS45P and Basalt Rock SRM-688, following the same analytical procedures used for the oil shale samples analyses. The accuracy of the method was evaluated by comparing the mean measured values with the certified values.

## 3. Results and Discussion

### 3.1. Homogeneity test results

The between-bottle homogeneity of the oil shale samples was verified using three types of analysis namely: sieving analysis, Gamma spectrometry, and total alpha/beta spectrometry. Ten sub-samples were selected randomly from the total number of prepared samples according to the British Standard methods for sampling and chemical products number BS5309 part 1 (Walker and Brookman, 1998). The homogeneity of the samples was tested using two-factor analysis of variance (ANOVA) without replication by comparing calculated F value ( $F_{calc}$ ) with critical F value ( $F_{crit}$ ) at 95% confidence level. Additionally, single factor analysis of variance (ANOVA) was applied to verify between-bottle and within-bottle

homogeneity (between groups and within group homogeneity).

3.1.1. Sieving analysis

The particle size distribution analysis of the oil shale samples showed that 82% of the total particles size were less than 45µm, 4% ranged between 45-53µm, 6% in the range of 53-63µm and 4% in the range of 63-75 µm, Table 1. The statistical results of ten sub-samples using Two-factor analysis of variance (ANOVA) without replication showed that the sample was homogenous, where calculated F value ( $F_{calc}=0.693$ ) was less than critical F value ( $F_{crit}=2.250$ ) at 95% confidence level, Table 1.

The analysis of variance (ANOVA) had been used often worldwide to check whether the variance among sample batches is significant at 95% confidence level (Biagini, et al. 1995; Walker and Brookman, 1998; Van der Veen et al. 2001; Zischka et al. 2002).

Table 1. Sieving analysis for 10 sub-samples of SJL-1.

Sample ID	% Size (µm)			
	<45	45-53	53-63	63-75
S1	81.98	6.18	6.60	3.05
S2	80.40	5.16	5.00	3.88
S3	82.77	2.19	5.11	2.82
S4	82.28	4.74	5.78	4.30
S5	80.84	4.8	6.16	4.76
S6	81.55	4.46	6.69	3.71
S7	82.76	2.96	6.68	4.24
S8	82.46	4.40	7.06	4.63
S9	82.20	2.70	6.47	4.85
S10	82.15	2.55	6.52	5.09

Two-Factor Analysis Without Replication (ANOVA)				
SUMMARY	Count	Sum	Average	Variance
Row 1	4	97.81	24.45	1473.36
Row 2	4	94.44	23.61	1433.70
Row 3	4	92.89	23.22	1577.53
Row 4	4	97.10	24.27	1496.75
Row 5	4	96.56	24.14	1429.26
Row 6	4	96.41	24.10	1468.36
Row 7	4	96.64	24.16	1528.59
Row 8	4	98.55	24.64	1487.42
Row 9	4	96.22	24.05	1504.98
Row 10	4	96.31	24.08	1501.55

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F <sub>crit</sub>
Rows	5.818	9	0.646	0.693	0.709	2.250

$F_{calc}(0.693) < F_{crit}(2.250)$ , so the sample is homogenous

3.1.2. Gamma Spectrometry

The single factor analysis of variance (ANOVA) was applied to calculate the F value according to equation (1). Also, P-value of ANOVA analysis which presents the probability of exceeding the observed value was used for the same purpose as F value. Both tests verified the sample homogeneity between groups and within group equally.

$$F' = \frac{MS_{bs}}{MS_{ws}} \tag{1}$$

Where:

MS<sub>bs</sub>: is the normalized variance between samples.

MS<sub>ws</sub>: is the normalized variance within the sample.

The gamma spectrometric analysis performed on ten randomly selected oil shale sub-samples showed Uranium (<sup>238</sup>U) average radio activity of 366.89 (Bq/kg). The data were analyzed statically using single factor analysis of variance (ANOVA) and showed that the oil shale sample was homogenous, where  $F_{calc}$  (0.893) was less than  $F_{crit}$  (2.393), Table 2. Additionally, P-value confirmed the sample homogeneity. Therefore, the candidate SRM oil shale material was verified for its homogeneity between groups and within group, Table 2.

Table 2. Gamma activity (Bq/kg) for <sup>238</sup>U in ten sub-samples of SJL-1.

Sample ID	Trial 1	Trial 2	Trial 3
S1	333.88	326.79	373.23
S2	395.08	363.64	406.58
S3	330.03	335.51	385.87
S4	356.16	355.70	378.28
S5	317.87	365.19	341.10
S6	346.05	322.94	392.81
S7	385.01	335.79	359.24
S8	386.09	390.67	370.78
S9	365.26	339.03	370.46
S10	358.37	318.65	420.93

ANOVA: Single Factor				
SUMMARY				
Groups	Count	Sum	Average	Variance
Column1	3	1033.90	344.63	625.89
Column2	3	1165.30	388.43	494.10
Column3	3	1051.41	350.47	947.38
Column4	3	1090.14	363.38	166.56
Column5	3	1024.16	341.39	559.86
Column6	3	1061.80	353.93	1267.06
Column7	3	1080.04	360.01	606.10
Column8	3	1147.54	382.51	108.50
Column9	3	1074.75	358.25	283.82
Column10	3	1097.95	365.98	2658.77

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F <sub>crit</sub>
Between Groups	6203.142	9	689.238	0.893	0.548	2.393
Within Group	15436.070	20	771.803			
Total	21639.210	29				

$F_{calc}(0.893) < F_{crit}(2.393)$ , So the sample is homogenous

3.1.3. Total Alpha/Beta Activity

The total alpha/beta activity spectrometric analysis performed on ten randomly selected oil shale sub-samples indicated a total average activity of 2.2 (Bq/kg). Their single factor analysis of variance (ANOVA) showed that the oil shale sample was homogenous, where  $F_{calc}$  (1.349) was less than  $F_{crit}$  (2.393), additionally P-values confirmed this results, Table 3. Therefore, the candidate SRM oil shale material was verified for its homogeneity between groups and within group.

The analysis of soil and oil shale samples using either gamma spectrometry or total alpha beta activity is affected often by different factors such as sample geometry, stability, homogeneity, and the complexity of the obtained spectrums. Therefore, it was necessary to use the same homogeneity testing method protocol for the spiked reference materials and the candidate SRM (Biagini et al. 1995).

Table 3. Total alpha/beta activity (Bq/kg) for 10 sub-samples of SJL-1.

Sample ID	Trial1	Trial2	Trial3
S1	2.36	2.10	2.34
S2	2.26	2.18	2.26
S3	2.69	2.09	2.28
S4	2.34	2.10	2.23
S5	2.56	2.36	2.40
S6	1.74	2.03	2.29
S7	2.12	2.24	2.03
S8	2.38	2.09	2.28
S9	2.36	2.14	2.02
S10	2.02	2.31	2.17

Single Factor Analysis (ANOVA)

SUMMARY				
Groups	Count	Sum	Average	Variance
Column1	3	6.80	2.267	0.021
Column2	3	6.70	2.233	0.002
Column3	3	7.06	2.353	0.094
Column4	3	6.67	2.223	0.014
Column5	3	7.32	2.440	0.011
Column6	3	6.06	2.020	0.076
Column7	3	6.39	2.130	0.011
Column8	3	6.75	2.250	0.022
Column9	3	6.52	2.173	0.030
Column10	3	6.50	2.167	0.020

ANOVA

Source of Variation	ss	df	MS	F	P-value	Fcrit
Between Groups	0.367	9	0.041	1.349	0.274	2.393
Within Group	0.604	20	0.030			
Total	0.971	29				

$F_{calc}(1.349) < F_{crit}(2.393)$ , So the sample is homogenous

### 3.2. Results of Interlaboratory Study

Twelve laboratories from Jordan, Canada, Germany and Saudi Arabia participated in the preliminary interlaboratories study. The different analytical methods used by the participating laboratories for the different analytes were summarized in Table 4. Calibration was performed by a calibration graph or standard addition methods. Each participating laboratory received two sample bottles containing 100 g of candidate oil shale SRM and was asked to conduct a minimum of five independent replicates on the available analytical methods (Quevauviller, 2001; Zischka, 2002).

The results collected from the participation laboratories were analyzed statistically after outlying the extreme values applying Q-test. The satisfying result for each laboratory was evaluated using z scores method ( $|z| \leq 2$ ). Based on statistical analyses which are described in the following sections, the oil shale candidate SRM constitutes were classified into three groups: 16 certified 8 averages and 37 either range or information. Two examples of interlaboratory study results for Fe<sub>2</sub>O<sub>3</sub> and Zn are presented with lab codes and methods, Figure 2-a and 2-b.

Table 4. Summary of analytical methods used for certification of SJL-1 analytes.

Analyte	Method
Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , MgO, Fe <sub>2</sub> O <sub>3</sub>	WDXRF, EDXRF, ICP/MS, ICP/OES, AAS
P <sub>2</sub> O <sub>5</sub> , K <sub>2</sub> O	WDXRF, EDXRF, ICP/MS, ICP/OES
Na <sub>2</sub> O, CaO	WDXRF, EDXRF, ICP/MS, ICP/OES, AAS, NA
MnO	WDXRF, ICP/MS, ICP/OES
SiO <sub>2</sub>	WDXRF, XRF
S	ELEM, EDXRF, ICP/MS, ICP/OES
C, H, C <sub>org</sub>	ELEM
N	ELEM, Kjeldahl
U	ICP/MS, EDXRF, NA, Gamma
Zn, Cr	WDXRF, EDXRF, ICP/MS, ICP/OES, AAS, NA
Ni	WDXRF, ICP/MS, ICP/OES, AAS, NA
V	WDXRF, EDXRF, ICP/MS, AAS
Sr	WDXRF, EDXRF, ICP/MS, ICP/OES-MIC
Cu	WDXRF, EDXRF, ICP/MS, ICP/OES-MIC, AAS
Mo	ICP/MS, ICP/OES, AAS, NA
Ba, Co	ICP/MS, ICP/OES, NA
Cd	EDXRF, ICP/MS, ICP/OES
As, Rb	EDXRF, ICP/MS, ICP/OES, NA
Li	ICP/MS
Sb, Ca, Ta, Th	ICP/MS, NA
Se, Hf, La, Ag, W, Sc	EDXRF, NA
Y	EDXRF, ICP/MS
Zr	WDXRF, EDXRF, ICP/MS
Ru	WDXRF, EDXRF
LOI, Ash	Gravimetry
H <sub>2</sub> O	Gravimetry, IR

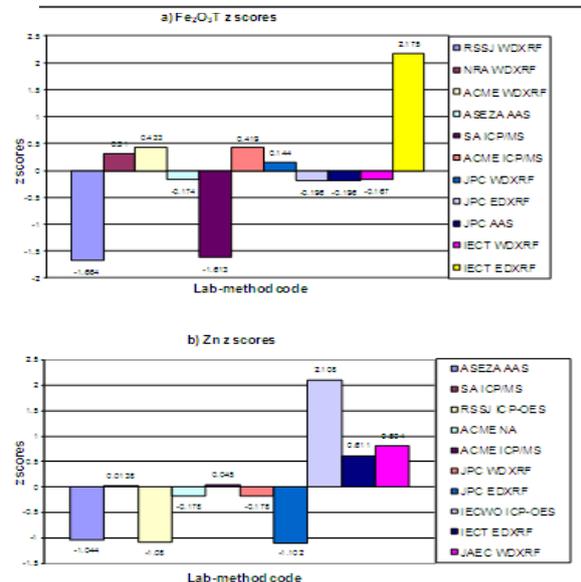


Fig 2. Z scores from interlaboratory study results a) Fe<sub>2</sub>O<sub>3</sub> b) Zn including lab codes and methods.

### 3.3. Certification Measurements

Certified values of the analytes in candidate SRMs were determined using different statistical approaches that frequently used for preparation and certification of SRMs (Abbey, et al., 1979; Kane, et al. 1990; Quevauviller, 2001; Zischka, 2002; Al-Masri). Q-test was applied to check whether a certain suspected data joined belongs to the set of data or not, then average value should lie within  $\pm 2S$  (standard deviation) to be accepted. The criteria used in the present work for determining the certified concentrations was developed according to the following procedure:

1. Estimation of the following parameters at 95% confidence level: arithmetic mean, standard deviation, median, coefficient of skewness, coefficient of kurtosis and relative standard deviation (RSD).
2. If RSD, skewness and kurtosis coefficients deviate from the normal distribution significantly at 95% confidence level. Then extreme values are rejected one at a time until the coefficients (skewness and kurtosis) and ( RSD) indicate a normal distribution.
3. If RSD<15% stop rejection as attainable conformity between individual data and overall means is achieved, then go to step 6.
4. Use (two – sided T-test) to determine whether additional rejection is needed. If ( $T > T_c$ ) reject until no T-test rejection is needed, If ( $T < T_c$ ) proceed to step 6.
5. Check new RSD after each rejection and compare it as in step 3.
6. After getting acceptable RSD as in step 3, use ANOVA single factor analysis to check for the analyte results obtained from different methods. If ( $F_{calc} < F_{crit}$ ) at 95% confidence level and P-value are insignificant. Then agreement between at least three independent methods of analysis was verified according to the requirement for certifying a constituent concentration (Biagini et al. 1995; Walker and Brookmeen, 1998; Vander Veen et al. 2001).

After performing the last rejection according to the previous criteria, the oil shale candidate SRM analyte concentrations were classified into three groups: certified, average and range.

1. Certified value is reported, if:
  - At least five laboratory averages remain after last rejection.
  - At least three different methods of analysis used after last rejection without significant difference by using ANOVA single factor analysis as in step 6 ( $F_{calc} < F_{crit}$ ) at 95% confidence level.
  - RSD < 15% after last rejection.
2. Average value is reported if at least five laboratory averages remain after last rejection, but either or both of the other conditions for certification are fail.
3. Range value is only reported for the surviving laboratory average if there are fewer than five laboratory averages remain after the last rejection.

### 3.4 Certificate

The results of the certificated values of SJL-1 were calculated using equation (2) according to the same procedure used often for certification worldwide (Griepink and Muntau, 1987; Al-Masri, et al., 2004; Kane and Potts,

2007), and they were presented as means at  $\pm 95\%$  confidence level.

$$\bar{x} \pm T_c (\pm S, P\%, n) \tag{2}$$

Where

$\bar{x}$  : The mean of the measurements.

$P\%$  : Confidence level.

$T_c$  : The scattering of the individual results, which is given in the following equation:

$$T_c = \frac{t}{\sqrt{n}}$$

Where

$t$  : The student factor for the ten replicates at 95% certified level.

$S$ : Standard deviation.

$n$  = Number of individual results.

The final concentration of analytes in the oil shale sample (SLJ-1) expressed as certified and average values with their uncertainty are shown in Table 4. However, range values were mentioned only without the statistical uncertainty.

**Table 5.** Certificate for El-Lajjun Oil Shale (SJL-1).

Certified values		
Oxide	wt%	± uncertainty
Al <sub>2</sub> O <sub>3</sub>	2.513	0.130
P <sub>2</sub> O <sub>5</sub>	2.899	0.092
CaO	25.512	1.434
TiO <sub>2</sub>	0.134	0.014
MgO	0.686	0.060
K <sub>2</sub> O	0.360	0.020
Fe <sub>2</sub> O <sub>3</sub> total	0.967	0.088
Na <sub>2</sub> O	0.178	0.015
MnO	0.0037	0.0005
Element	ppm	± uncertainty
S	3.638	0.450
Element	ppm	± uncertainty
U	27.26	3.68
V	265.28	10.89
Cr	396.40	28.28
Zn	755.42	61.95
Ni	193.61	19.66
Cu	97.09	6.98
Sr	800.52	65.08
Average values		
Constituent	wt%	± uncertainty
LOI	37.01	1.02
SiO <sub>2</sub>	26.163	0.83
Element	ppm	± uncertainty
Cd	69.33	24.65
Mo	197.06	50.61
Co	2.62	0.70
Pb	22.26	12.40
Ba	56.33	13.78
As	14.40	6.78
Range values		
Element	ppm	
H		2.235
N		0.435
C <sub>total</sub>		21.591
C <sub>org</sub>		16.153
Rb		11.314
Sb		2.900
La		10.430
Ce		12.330

Ag	3.550
Li	8.362
W	0.785
Th	1.429
Sc	3.265
Se	41.835
Y	22.733
Hf	0.716
Ru	48.000
Zr	26.177
Ta	0.300
Rh	<1- 65
Cl	<1- 814
Nb	2.370
Be	<1
Sm	1.170
Nd	8.670
Bi	0.100
Yb	1.200
Tb	0.500
Cs	1.000
Ir	5.000
Sn	0.870-100
Au	0.00087-5
Br	4.730
Eu	0.300
<b>Constituents</b>	<b>Wt%</b>
Gas loss	4.720
Total oil	13.790
Calorific value	8508.7 J/g

#### 4. Availability

The SJL-1 standard reference material is available from Prince Faisal Center for Dead Sea Environmental and Energy Research at Mutah University, Karak, Jordan. Email: [Batarseh@mutah.edu.jo](mailto:Batarseh@mutah.edu.jo), Fax: 00962 32397169. A full report and certificate of analysis is delivered upon the request of the reference material, containing detailed information on the preparation of the material, homogeneity, technical and statistical evaluation results and analytical methods used and individual results for each analyte.

The final product of the certified standard reference material packed as 100 g in polyethylene bottles and supplied with a certificate of analysis. This oil shale material (SJL-1) can be used as standard reference material (SRM) for quality assurance, laboratory methods validation and instruments calibration for the analysis of the oil shale ores on national and international research and industrial studies.

#### Acknowledgements

The authors would like to acknowledge the University of Jordan for the financial support of this work. The authors are also extending their thankful to all national and

international contributing laboratories for their invaluable help and support for conducting the different analyses of the oil shale sample SJL-1.

#### Dedication

The authors are dedicating this work for the spirit of deceased Prof. Najwa Zaharan, who was served as vice president of Egyptian Atomic Energy Agency and the coordinator of this project within the Arab collaborative projects initiated by Arab Atomic Energy Agency (AAEA), 2007-2009.

#### References

- [1] Alali, J., 2006. International Conference on Oils Shale: "Recent Trends in Oil Shale", Jordan Oil Shale, Availability, Distribution, and Investment Opportunity. 7-9 November 2006, Amman, Jordan.
- [2] Abbey, S., Meeds, R., Belanger., 1979. Reference samples of rocks, the search for best values, *Geostandards Newslett*, 3: 121- 133.
- [3] Al-Masri, M. Aba, A. Al-Hamwi, A. and Shakhshiro, A., 2004. Preparation of in house reference soil sample containing high levels of naturally occurring radioactive materials from the oil industry, *Appl Radiat Isotopes*, 61:1397-1402 .
- [4] Biagini, R. Dersch, R. De Felice, P. Jerome, S.M. Perkin, E. Pona, C. De Sanoit, J. Woods, M.J., 1995. Homogeneity testing of spiked reference materials, *Sci.Total Environ*, 173/174: 267-274.
- [5] Gladney, E.S. and Roelandts, I., 1988. Compilation of elemental concentration data for USGS BHVO-1, MAG-1, QLO-1, RGM-1, SCo-1, SDC-1, SGR-1 and STM-1, *Geostandards Newslett*, 12: 253-362.
- [6] Heidelberg, S.B., 1988. Standard reference materials for the determination of polycyclic aromatic hydrocarbons, *Fres. J Anal. Chem*, 332(6): 573-582.
- [7] Kane, J.S, Arbogast, B. and Leventhal, J., 1990. Characterization of Devonian Ohio shale SDO-1 as a USGS geochemical reference sample, *Geostandards Newslett*, 14:169-196.
- [8] Petrov, L.L, Korotaeva, I.Ya, Kornakov, V.V. Yu.H, Persikova, Malykh, L.A, Prokopchuk, S.I. and Susloparova, V.E., 1999. Development of multi element reference samples of the composition of rocks in the black-shale formation with certification of some noble metals, *Platinum of Russia, Collection Transact*, 4: 263-280.
- [9] Petrov, L., Kornakov, Y., Korotaeva, I, Anchutina, E., Persikova, L., Susloparova, V., Fedorova, I, Shibanov, V., 2004. Multi-Element Reference Samples of Black Shale. *Geostandards and Geoanalytical Research* 28(1), 89-102.
- [10] Quevauviller, Ph., 2001. Certified reference materials for the quality control of inorganic analyses of manufacturing products (glass, polymers, paint coatings). *Trends in Analytical Chemistry* 20(8), 446-456.
- [11] Smirnova, E. V, Fedorova, I. N, Sandimirova, G. P, Petrov, L. L ,Balbekina, N. G. and Lozhkin, V. I., 2003. Determination of rare earth elements in black shales by inductively coupled plasma mass spectrometry, *Spectrochim. Acta B*, 58 (2): 329-340.

- [12] Schmid, S and Andersson, J.T., 1997. Critical Examination of the Quantification of Aromatic Compounds in Three Standard Reference Materials, *Anal. Chem.*, 69(17): 3476-3481.
- [13] Vander Veen, A.M.H., Linsinger, T., Pauwels, J., 2001. Uncertainty calculations in the certification of reference materials (2-Homogeneity study), *Accred. Qual. Assur.*, 6: 26.
- [14] Walker, R.F., Brookman, B., 1998, Guidelines for the in-house production of reference LGC/VAN/1998/040.
- [15] Wise, S.A., 2002. Standard Reference Material (SRM) for the determination of polycyclic aromatic compounds—twenty years of progress, *Polycycl. Aromat. Comp.*, 22(3): 197-230.
- [16] Zischka, M., Schramel, P., Muntau, H., Rehnert, A., Gomez, M., Stojanik, B., Wannemaker, G., Dams, R., Quevauviller, P., and Maier, E., 2002. A new certified reference material for the quality control of palladium, platinum and rhodium in road dust, BCR-723. *Trends in Analytical Chemistry* 21(12), 851-868.