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A Study of the Distribution of Iron Element in the Sands of the Syrian Coast

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Abstract: **Sequential extraction is a useful method of identifying how toxic trace metals bind to sand particles and the strength of these bonds. Sequential extraction uses a series of extractions on the same sample, by using extraction liquids expected to promote decreasing mobility of metal fractions in the sand. The selected sequence process named BCR (Community Burean of Reference), is consisting of four-steps, but with improvements in the fourth step (so it has become two parts ;the first is: by using the Aqua regia and the second is : by using Hydrofluoric acid).Seven different samples of sand from coastal areas in Syria have been studied. Fe has been analyzied and their concentrations have been determined by using Atomic Absorption Spectrometry (AAS), the results have shown that the increasing percentage concentration for Fe in the residual fraction, are: for Fe in Jiblah between 0.001% - 0.97% In Tartous between 0.001%-1.2%.In Banias between0.16%-4.11%. In Al- Baseet between 0.1%-3019%. In Shkifat between 0.009%-1.69%. In Ras Ibn Hani between 0.005%-1.24% In Alkhuder Shrine between 0.005%-1.48%.**

Keywords: **Heavy metals, Sequential extraction, sand, Syria.**

I. INTRODUCTION

The sequential extraction method is used to determine the actual (real) concentration of some toxic trace elements in order to identify the toxicity of metals to soil organisms, as the total content of minerals in the soil does not provide sufficient information to illustrate this toxicity. The solubility of metals makes them move to living organisms through the food chain reaching humans [1].

The process of fragmentation of the extraction stages indicates the difference in the distribution of minerals in each phase and is considered a "real" indicator of the difference in minerals by the strength of its bond with the soil grains [2].

The highly soluble parts can move highly to the plant, consequently they will be more toxic to plants, animals and humans. Therefore, the extraction of minerals from soil is the most important indicator for describing the characteristics of the metal rather than the determination of its total content, which is achieved by sequential extraction [3]. The multi-stage sequential extraction procedures aim to break down trace minerals in soil, clay, sand and sediments according to the chemical nature of each. However, while this process takes "long" time, it provides important information on the original state of soil or sand, bioavailability, chemical availability, and the kinetics of trace minerals within it. [4]

The methods of this theory have varied in the successive chemical extraction on the same sample and have evolved over time to differ from each other by the number of stages of each method. This is a set of phases of separation in which the researcher must adhere when performing chemical separation processes: [5]

1- The interchangeable parts stage.

2 - separation of the returnable part or associated with iron oxides and manganese.

3 - Separation of the oxidative part or associated with organic and sulfuric substances

4 - phase of the remaining part or associated with silicate

Metal ions are trapped in these phases by several mechanisms: ion exchange, adsorption, sedimentation or co-precipitation [6].

The mineral content of each extract is determined by using available analytical techniques, including the AAS and the ICP and other technologies.

These four approaches were identified [7]:

- Tessier(1979)
- Sposito(1928)
- BCR(1999)
- Silver(2006)

Each method is characterized by stages of the process of separation in particular, and differed from other methods of chemical reagents used, which are shown in the following tables:

Table 1: tessier 1979 [8]

Stage	Solvent	Conditions
Exchangeable	8 ml 1M $MgCl_2$ (pH= 7)	1 h, room temperature
Carbonates	8 ml 1M NaOAc (pH= 5)	5 h, room temperature
Fe and Mn oxides	20 ml 0.04M NH_2OH/HCl in 25% (v/v) HOAc	6 h, 96°C
Organic matter	3 ml 0.02M HNO_3 + 5 ml 30% H_2O_2 (pH= 2)	3 h, 85°C
Residual	HNO_3-HCl digestion	

Table 2: sposito 1982 [7]

Stage	Solvent	Conditions
Exchangeable	10 ml 0.5M KNO_3	16 h, 25°C
Organic matter	10 ml 0.5M NaOH	16 h, 25°C
Fe and Mn oxides	10 ml 0.05M Na_2EDTA	6 h, 25°C
Residual	10 ml 4M HNO_3	16 h, 25°C

Table 3: BCR 1999 [9]

Stage	Solvent	Conditions
Exchangeable	40 ml 0.11M CH_3COOH	16 h, room temperature
Reducible (Fe and Mn oxides)	40 ml 0.5M NH_2OH-HCl (pH= 1.5)	16 h, room temperature
Oxidisable (Organic matter)	10 ml 8.8M H_2O_2	16 h, room temperature
Residual	HNO_3-HCl digestion	

Table 4: Silveira 2006 [7]

Stage	Solvent	Conditions
Soluble-exchangeable	15 ml 0.1M $CaCl_2$	2 h, room temperature
Surface adsorbed	30 ml 1M NaOAC (Ph= 5)	5 h, room temperature
Organic matter	5 ml NaOCl (pH =8.5)	30 min, 90–95°C

Mn oxides	30 ml 0.05M NH2OH-HCl (pH= 2)	30 min, room temperature
Poor crystalline Fe oxides	30 ml 0.2M oxalic acid + 0.2M NH4 oxalate (pH 3)	2 h, dark
Crystalline Fe oxides	40 ml 6M HCl	24 h, room temperature
Residual	HNO3-HCl digestion	

II. EXPERIMENTAL

2.1. Equipment and materials used:

Chlorinated water (37% highly pure), Acetic acid (99.5%), nitrogen acid (65% highly pure), Hydroxylamine hydrochloric acid, Oxygen water (33%), Fluorine acid (48%), Distilled water, standard iron solution (1000 ppm Merck), standard manganese solution (1000 ppm Merck), standard nickel solution (Merck1000 ppm), atomic absorption device (AAS), Fluorescent X- ray measurement device (XRF).

2.2. Sampling:

The sand samples were collected from seven sites spread along the Syrian coast: Tartous Beach, Banias Beach, Jiblah Beach, Alkhuder shrine Beach, Jibla Beach - Shkifat, Al-Baseet Beach, Ras Ibn Hani Beach.

Samples were sampled by a cylinder made of Poly Vinyl Chloride (P.V.C). They are placed in polythene bags, transported to the laboratory and kept in the freezer at -20 ° C until they are extracted.

2.3. Analysis of XRF using a copper elevator and the Kα spectral line for samples of the sands of the Syrian coastal strip as shown in the following table:

Table 5: The results of the analysis of sand samples using X-ray fluorine:

	Tartous	Jiblah	Alkhuder shrine	Al-Baseet	Shkifat	Ras Ibn Hani	Banias
	Average	Average	Average	Average	Average	Average	Average
K ppm	9187	12377	11980	5104	8317	8105	6895
Ca %	35.8	51.9	51.3	6.63	29.9	16.3	25.2
Ti ppm	1976	870	245	4009	1016	1140	1.50
Mn ppm	522	560	328	1128	569	697	1042
Fe%	1.39	1.08	2.09	4.77	2.79	1.50	6.32
Ni ppm	25.4	25.7	27.8	427	289	31.4	127
Cu ppm	<16	<16	99.0	37.5	<16	18.2	21.3
Zn ppm	28.0	31.4	288	69.4	36.0	40.3	71.3
Br ppm	7.41	14.6	34.1	1.70	19.7	4.26	11.7
Rb ppm	2.35	4.60	2.85	9.57	6.80	18.5	3.40
Sr ppm	2391	2434	2845	190	987	498	1153
Y ppm	11.6	15.4	5.62	9.15	10.8	8.35	14.6
Pb ppm	<35	<35	<35	<35	<35	<35	<35

2.4. The process steps for analyzing by Atomic Absorption Spectrometry Device:

Washing phase: 10 g of the sample of sand is washed with normal water and then with 1: 1 expanded nitrogen acid, then washed with distilled water until the acid is vanished.

The washed sample is taken and placed in a 500 ml Erlenmeyer and the process stages shown in the following table begin:

Table 6: Stages of processing sand samples:

Stage	Solvent	Conditions
exchangeable	100ml,0.11M CH3COOH	18h,100°,PH=2
Fe and Mn oxide	100ml,0.5 MNH2OH-HCL	18h,100°,PH=2
Organic matter	100ml,8.8H2O2	18h,100°,PH=2
Residual	90mlHCL+30mlHNO3	20h,100°,PH=2
Silicat	50mlHF	24h,100°,PH=2

The filtration is separated by a 6000-rpm process.

2.5. Results of iron element analysis in sand samples sampled from different locations using AAS:

Table 7: Results of iron determination

Fe%	Alkhuder shrine	Ibn Hani	Shkifat	Albaseet	Tartous	Banias	Jiblah
Exchangeable	0.005853	0.005833	0.009986	0.16425	0.001233	0.1633	0.001
Fe and Mn Oxides	0.57895	0.2432	0.99888	1.39462	0.14872	1.9939	0.1023
Oxidisable							
Residual	1.488079	1.24764	1.69705	3.19705	1.22819	4.11822	0.97266

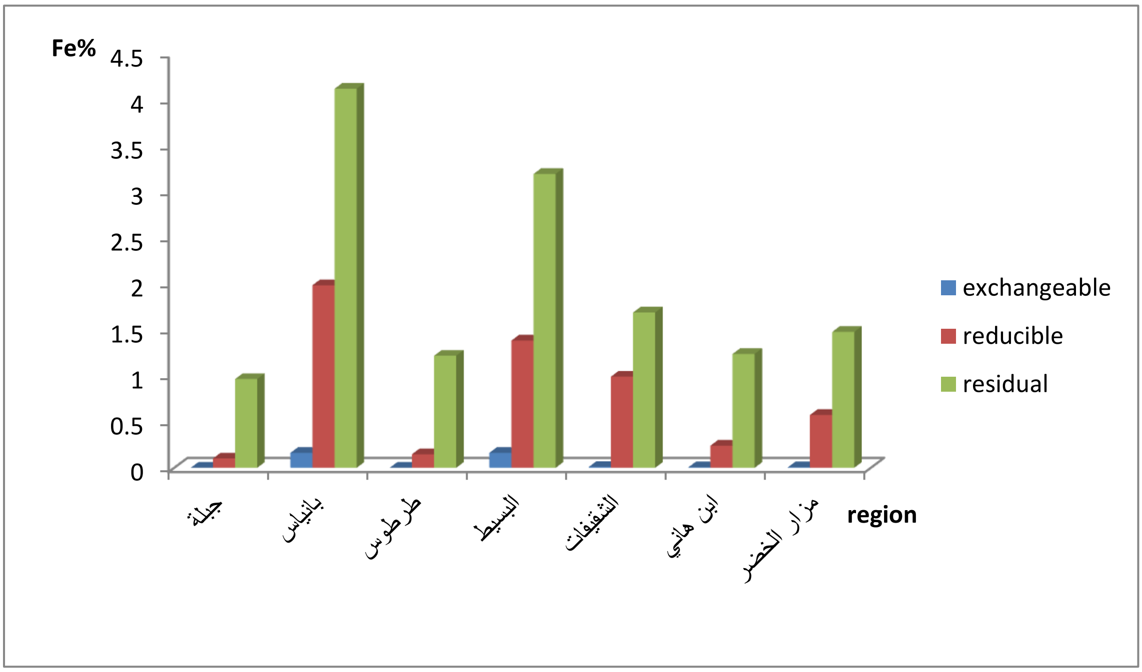

Fig 1: shows the distribution of iron in the coastal strip by the stage difference

The figure shows the difference in the distribution of the iron element in the Syrian coastline, where the minimum concentration of iron in the phase of interchangeable parts and the highest concentration in the phase of the parts in all regions. It also clarifies the concentration of iron in Bania > Albaseet > ALshkifat > Alkhuder shrine> Ras Ibn Hani> Tartous> Jiblah.

III. CONCLUSIONS

1 - We conclude that the total concentrations of the elements obtained in successive sequential extraction stages are approximately equal to the concentrations resulting from the XRF analysis, so there is a convergence of the two methods of sand analysis.

2 - We conclude that the higher concentrations of the elements appear late in the remaining parts stage because sand does not dissolve into the silice only after the addition of fluorine HF.

3 - We conclude that the concentrations of iron in the areas of AlBaseet and Banias is the highest due to the nature of the rock there. There are the rocks of mica, which contains within the composition of the proportion of iron.

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