Comparative Spectroscopic Study of Some Trace Elements in Sediment Samples from Suez Canal, Egypt

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Abstract: A comparative spectroscopic study of sixteen sediment samples from Suez Canal Egypt was investigation for the determination of some trace elements in these sediments. The sediment samples were collected from the canal at different depths. The investigated elements are Ca, Cd, Co, Cu, K, Fe, Mg, Mn, Na, Ni, Pb and Zn. The collected samples were acid digested and analyzed by five analytical techniques namely flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), flame photometry UV-VIS spectrophotometer and Laser fluoremetry.

Key words: Spectroscopic, trace elements, sediment samples, Suez Canal, Egypt.

INTRODUCTION

The environmental pollution is due to the rapid increase of the population and development of industry. The sources of pollution are the untreated domestic and industrial wastes, atmospheric and agricultural pollution (Merzwa *et al.* 1998 and Klemn and Bombach, 1995). Trace elements are good tracers to understand sources contributing to the pollution at a particular site. Wastes from different industries have fairly different compositions. For example, Pb is a good indicator of traffic – related sources or battery recycling plants, Cd is known to be rich in fly ash discharged to the marine environment, discharges from alloy producing ceramic plants, Cu is discharged particularly from metal plating and glass producing plants, Ni is discharged from the metal plating industry, Zn is enriched in discharges from various industries such as tanneries paint and metal plating. The sediments have the ability to reflect the water quality and can be for the assessment of marine pollution particularly for trace elements (Tuncer, 1995).

It is well known that the elements concentration in sediments reflect all types of inputs (Dickinson *et al.*, 1996 and Basaham and Al-lihaibi, 1993).

The present work was concentrated on the determination of some trace elements in sediment samples at different depths from Suez Canal Egypt .Different elemental concentrations in sediments can be used as an indicator of environmental pollution. This manifests the technical application of the present study.

Experiment
Sample Preparation:
Sediment samples were collected from Suez Canal, Egypt at different depths (20, 60, 70, 80, 100 and 120) from the bottom. A 5g from studied grind sample to 200 mesh size is taken in a Teflon beaker where a mixture of 5 ml conc. HNO_3 +5 ml of conc. H_2SO_4 + 15 ml HF were added. Then the Teflon beaker was covered, place the beaker on the steam bath and allow to heat overnight. The cover was removed and contains to heat the beaker on steam bath for about one hour or until acid fumes are no longer given off. The content of Teflon beaker was transfer to 100 ml Teflon beaker with the minimum amount of water. Then the beaker was placed on a hot plate and heat until fumes of SO2 start to evolve and was add 4 drops of 1:1 $HCLO_4$ /HNO_3 acid mixture. After cooling the solution was transfer to 250volumetric flask with distilled water (Shapiro and Brannock, 1962).

Preparation of Standard Solutions:
Stock solution containing 1000 µg ml for each of the studied elements was step wise diluted by bi-distilled water to prepare standard solution for the different element with different concentration except Ca, and Na which were prepared from calcium carbonate and sodium chloride .Standard solution were prepared fresh daily from this stock solution.

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Table 1: Operating Conditions for elements measured by FAAS.

Element	Wave length (nm)	Lamp Current (mA)	Burner Height (mm)	Fuel flow rate (L/min)	Band pass(nm)	Flame type
Cd	228.8	8	4.5	1.1	0.5	Air – Acetylene
Co	240.7	15	5.8	0.9	0.2	Air – Acetylene
Cu	324.2	5	7.0	0.9	0.5	Air – Acetylene
Fe	248.3	15	5.4	0.8	0.2	Air – Acetylene
K	766.5	8	3.8	1.2	0.5	Air – Acetylene
Mg	285.2	4	7.0	1.0	0.5	Air – Acetylene
Mn	279.5	12	7.0	1.0	0.2	Air – Acetylene
Ni	232.0	15	4.9	0.8	0.2	Air – Acetylene
Pb	217.0	10	4.5	1.0	0.5	Air – Acetylene
Zn	213.9	10	4.7	1.0	0.5	Air – Acetylene

Average values of three determinations listed in Table (2).

Table 2: Concentration in (µg/g) of elements measred by FAAS

Depth	Sample No.	Cd	Co	Cu	Fe	K	Mg	Mn	Ni	Pb	Zn
20	1	1.15	14.65	10.7	7466.35	10.036	1612.95	504.3	321.5	2.4	783.2
	2	1.2	33.2	12	8523.65	10.864	1497.35	741.6	380	2.65	750
60	3	1.5	21.1	18.3	8668.3	9.683	1656.55	768.55	434.45	3.8	810.318
70	4	1.1	32.7	19.8	8616	10.174	2500	851.85	490	3.9	890
	5	1	32.6	20.25	8785.05	10.547	1504.55	945.05	634	4.45	949.6
	6	0.75	39.55	20.65	8613.5	9.6	942.55	1236.5	590	5.5	960
80	7	1.5	30.25	21.1	8525.9	11.572	1719.8	1194.75	530	5.7	905
	8	1.2	27.8	24.65	8611.55	10.864	1656.1	658.85	480	6.05	866
	9	1.75	31.45	33.5	8608	10.817	1534.25	828.05	420	6.8	885
100	10	1.5	24	39.05	8682.45	11.386	1690.5	1011.85	425	7.2	890
	11	0.8	33.3	39.1	8646.15	10.688	1549.5	938.95	470	7.6	895
	12	1.3	34	40.0	8588.15	9.877	1501.35	852.6	475	9.8	902.7
	13	1.35	30.95	41.9	8598.8	11.523	1480.45	736.9	499	11.0	926
	14	0.9	34.2	48.85	9039.8	13.169	1816	952.95	510	11.05	952
	15	1.25	36.05	51	8692.75	11.336	1535.05	1057.3	520	11.2	987.45
120	16	0.85	33.75	56	8722.35	11.288	1508.55	1200	550.35	11.45	1172.2

Table 3: Operating Conditions for elements measured by GFAAS.

Optimal Conditions

Element	Wave length nn	Slit width nn	V	Chemical modifier	Temperature Dry	Ash	Atomization	Clean
Cd	228.8	0.7	220	0.015mg pd+0.01 mg Mg(NO$_3$)$_2$	120ºC	850ºC	1650ºC	2400ºC
Pb	283.3	0.7	220	0.01 mg Mg (NO$_3$)$_2$	120ºC	700ºC	1800ºC	2500ºC

Analytical Procedures:

Collected samples were analyzed by four techniques:

Atomic Absorption Process:

Flame AAS analysis of samples were performed using a Thermo Elemental Atomic Absorption Spectrophotometer. Ten elements namely Cd, Co, Cu, Fe, K, Mg, Mn, Ni, Pb, and Zn were determined using air-acetylene flame, except Al element was determined using nitrous oxide –acetylene flame (Doner and Ege, 2005). Both the sample solution and standard solution were niebulized at some optimal condition illustrated in Table (1). The PH value for the standards, samples and blank were adjusted to the some values. The absorbance of standard solution were determined and plotted against the concentration to obtained calibration curves. The concentration of trace elements in sediments was determined by using the calibration curves.

Graphite Furnace Atomic Absorption Spectrometry:

Perkin Elmer HGA 600 with autos ampler 60 was used to determine Cd and Pb. For analysis a known volume of sample (20 µl) was dispensed into the furnace. The sample is then subjected to a multistep temperature program. Table (3) illustrates the operating conditions consideration in that work under the manufacture guide of the AAS 3100 (Atgin *et al.*, 2000). The obtained results are shown in Table (4).

Table 4: Concentration in (µg/g) of Cd and Pb measured by GFAAS.

Depth	Sample	Concentration	
		Cd	Pb
20	1	1.33	2.9
	2	1.49	3.19
60	3	1.9	3.5
70	4	1.5	4.7
	5	1.2	4.12
	6	0.93	11.9
80	7	1.86	5.3
	8	-	5.6
	9	2.17	6.3
100	10	2.011	6.7
	11	0.9	7
	12	1.6	9.1
	13	1.67	10.19
	14	1.1	11.20
	15	1.6	10.3
120	16	1.05	10.53

Table 5: Concentration in (µg/g) of K and Na measured by flame photometry

Depth	Sample	Concentration	
		K	Na
20	1	10.62	11000
	2	11.5	21250
60	3	10.25	27250
70	4	10.5	20250
	5	12.75	21750
	6	11	22750
80	7	12.25	23250
	8	11.5	20250
	9	11.5	21250
100	10	12	23500
	11	12	21750
	12	10.5	24750
	13	12.25	22750
	14	14	24500
	15	12	24100
120	16	12	25000

Flame Photometer:

Sherwood model 410 flame photometry was used to determine K and Na. Both the sample and standard solutions were buffered with excess sodium (1000µg /ml) because of its enhancement effect on the potassium emission (Cooper, 1962). The results are listed in Table (5).

The Spectrophotometer:

A Shimdazu double monochromatic recording spectrophotometer model UV 360 was used to determine Cu, Fe and Mg to determine the concentration of Fe by this method (Cooper, 1962), 10 ml of sulphosilicate acid was added to 5 ml sample then few drops of ammonia solution till be yellow. After that 2 ml of ammonia solution was added. The solution was completed with distilled water in 100 ml measuring flask and the absorbance at wavelength 425 nm was measured. Fig. (1) shows the absorption spectra of sulphosite acid and its iron complex, whereas Fig. (2) shows the calibration curve obtainer by spectrophotometer.

In case of determination the Ca concentration the PH of the sample solution was adjusted at 6-8. Then 10 mg of ascorbic acid and 10 mg of polaxomncyanide were added. After 2-3 min 5 M of mureoxide solution (0.02%) and 2.5 ml of 1M NaCO were added and the volume was completed to 50 ml in measuring flask by distilled water.

Mueoxid indicator (ammonium purpurated II) form 1:1 complex with calcium in alkaline solution. The color changes from violet to pink when the reagent complexes calcium. Optimum PH value for the reaction is 12.5.Magnesium in fine fold quantity relative to calcium does not interfere. For mureoxide dye only is at 552 nm while the calcium mureoxide complex is at 512 nm (Cooper, 1962). The absorbance at 512 nm against a proper blank solution was measured. Fig. (3) illustrates the obtained absorption spectra.
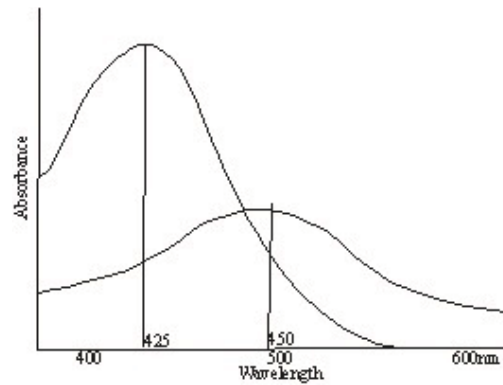
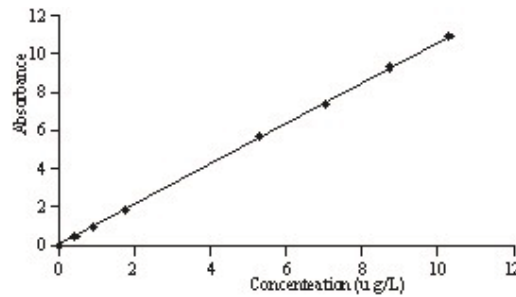**Fig. 1:** Absorption spectrum of Sulphosalicytic acid (1) and Iron complex (2).

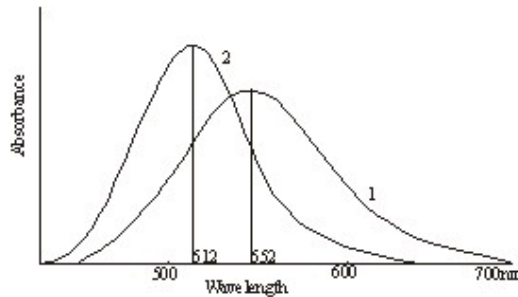**Fig. 2:** Calibration Curve for Fe using Uv-Vis spectrometer.

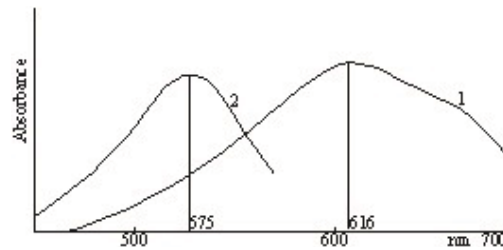**Fig. 3:** Absorption spectrum of Mureoxide (1) and its Calcium complex (2).

Fig. 4: Absorption spectrum of Eriochrome black T (1) and its Magnesium complex (2).

For Mg determination, PH value of sample solution was adjusted at (8-9). Then 20 mg of ascorbic acid and 20 mg of potassium cyanide was added. After that 5 ml of buffer solution PH 9.6 an 5 ml of eriochrome black T (0.02%in methane) was added. The absorbance at 520 nm was measured. Fig. (4) shows the absorption spectrum of Eriochrome black T and its Mg complex (Cooper, 1962).

Inaly in case of determining U, adding 1.5 ml of Arsenazo III (Marcezenko, 1986) dye (0.25 %), 0.6ml of disteled water and 0.2 ml of Ammonia solution to the sample solutions. All solutions were shaken weel for 3 minetes. Then, adding 4 ml of concentrated nitric acid, after cooling the sample solutions then completed to 10 ml

Table 6: Concentration in (µg/g) of Ca, Fe, Mg and U measured by UV-VIS Spectrophotometry at different depths

Depth	Sample	Concentration			
		Ca	Fe	Mg	U
20	1	1120	5864.25	403.6	UDL
	2	1890	6702	807.2	UDL
60	3	1400	8656.75	2522.5	UDL
70	4	700	7539.75	2018	198
	5	700	9215.25	1816.2	UDL
	6	1400	6981.25	2018	500
80	7	1470	8656.75	908.1	282
	8	1890	7539.75	1311.7	UDL
	9	1400	8098.25	2018	UDL
100	10	1400	8656.75	-	UDL
	11	1260	7260.5	1210.8	285
	12	770	8098.25	1614.4	UDL
	13	630	8936	3834.2	UDL
	14	770	19547.5	1816.2	UDL
	15	800	9215.25	1917.1	UDL
120	16	1050	8377.5	2018	UDL

Table 7: Concentration of U in (µg/l) measured by Laser Fluoremetry

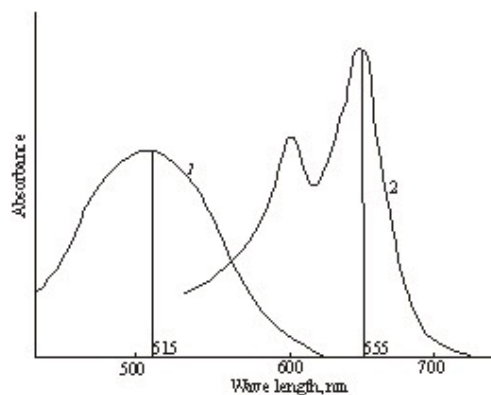| Depth	20		60	70			80			100						120
Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Concentration (µg/g)	UDL	UDL	501	200	UDL	UDL	285	UDL	UDL	UDL	286.22	UDL	UDL	UDL	UDL	UDL

Fig. 5: Shows the absorption spectrum of Arsennzo III(1) and its Uranium complex(2).
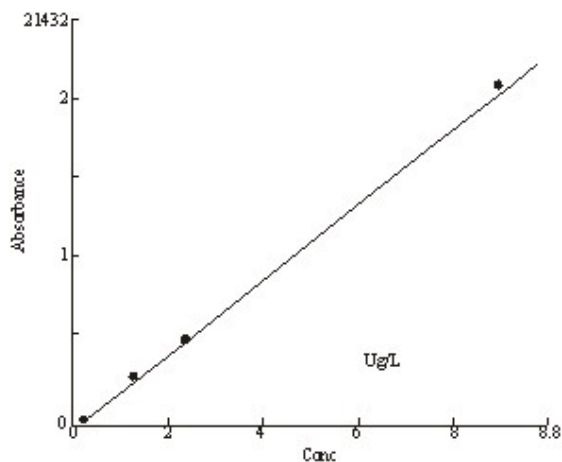

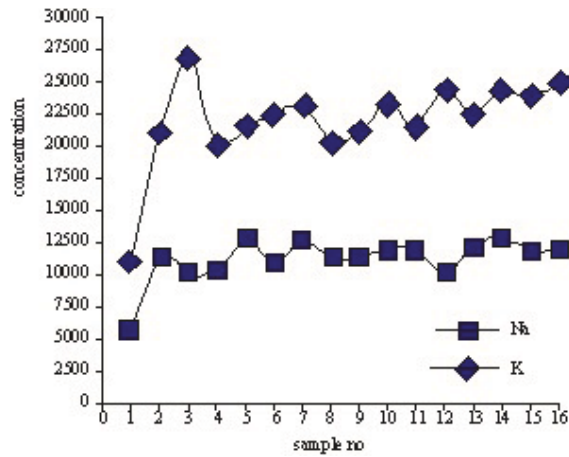**Fig. 6:** Analytical Calibration Curve for U by Laser Floremetry.

Fig. 7: Variation of concentration of K and Na Elements with sample Nº.
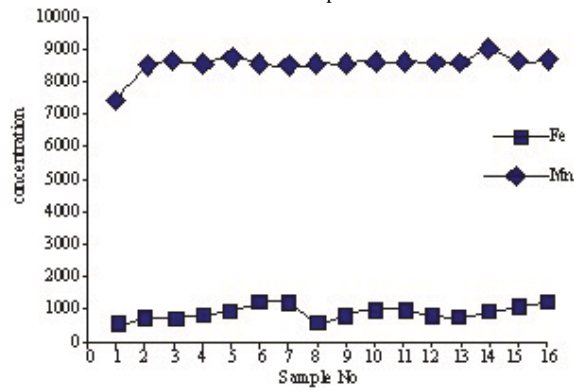

Fig. 8: Variation of Concentration of Fe and Mn Elements with Sample Nº
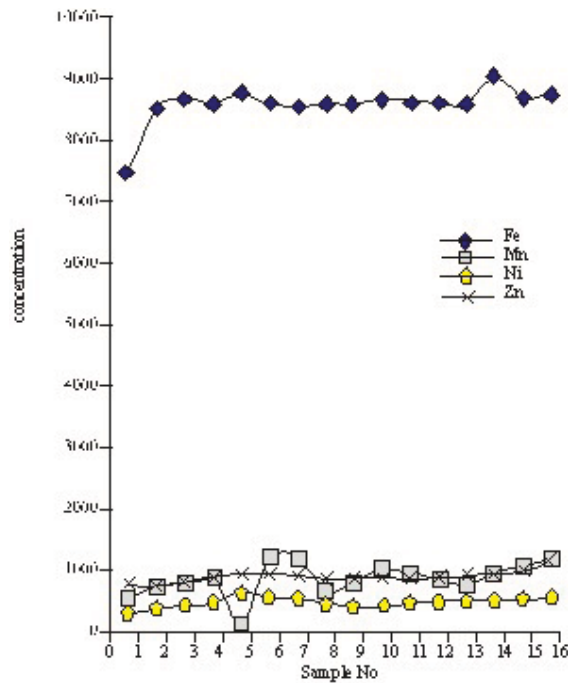

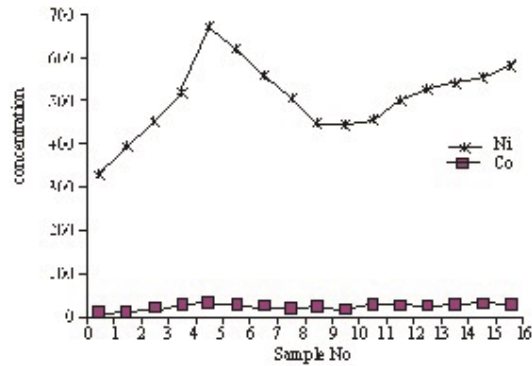**Fig. 9:** Variation of Concentration of Fe, Mn, Ni and Zn Elements with Sample Nº

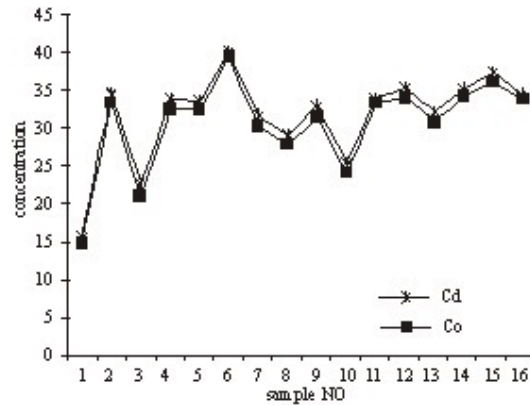**Fig. 10:** Variation of Concentration of Co and Ni Elements with Sample N$^{\underline{o}}$

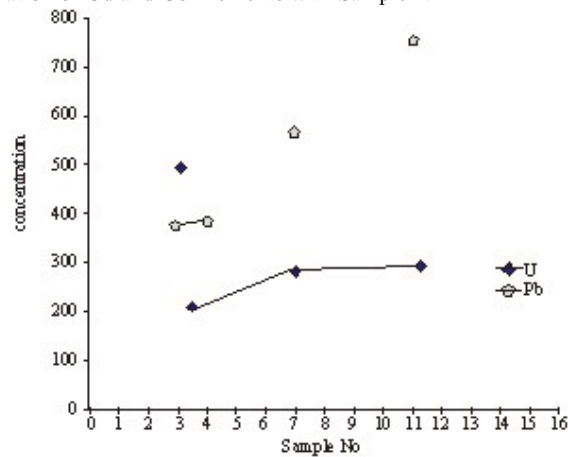**Fig. 11:** Variation of Concentration of Cd and Co Elements with Sample N$^{\underline{o}}$

Fig. 12: Relation between U, Pb Elements.

using volumetric flask Fig. (5) shows the absorption spectrum of Arsennzo III (1) and its Uranium complex (2). The obtaind results for these determined elements were listed in Table (6).

Laser Fluoremeter:

In this investigation a Scintrex UA-3 uranium analyzer was used. The analytical procedure for this method is as follows:

5ml of sample solution is dried and redissolved in 4 ml conc., nitric acid. Then in 7 ml, coveted 10 µL sample was taken and added to 0.8 ml of Fluran solution. Fig (6) shows the obtained standard curve while Table (7) shows the result of Uranium concentration by laser fluoremetry.

Table 8: Comparison of element concentration in determined by μ g/g by various techniques.

Concentration

| Sample No.	AAS					GFAAS		Flame photometry	Laser florometry	UV-VIS Spectrophotometry			
	Cd	Fe	K	Mg	Pb	Cd	Pb	K	U	Ca	Fe	Mg	U
1	1.15	1466.35	10.036	1612.95	2.4	1.33	2.9	10.62	UDL	1120	5864.25	403.6	UDL
2	1.2	8523.65	10.864	1497.35	2.65	1.49	3.19	11.5	UDL	1890	6702	807.2	UDL
3	1.5	8668.3	9.683	1656.55	3.8	1.9	3.5	10.25	501	1400	8656.75	2522.2	525
4	1.1	8616	10.174	2500	3.9	1.5	4.7	10.5	200	700	7539.758	2018	198
5	1	8785.05	10.547	1504.55	4.45	1.2	4.12	12.75	UDL	700	9215.25	1816.2	UDL
6	0.75	8613.5	9.6	942.55	5.5	0.93	11.9	11	UDL	1400	6981.25	2018	UDL
7	1.5	8525.9	11.572	1719.8	5.7	1.86	5.3	12.25	285	1470	8656.75	908.1	290
8	1.2	8611.55	10.864	1656.1	6.05	-	5.6	11.5	UDL	1890	7539.75	1311.7	UDL
9	1.75	8608	10.817	1534.25	6.8	2.17	6.8	11.5	UDL	1400	8098.25	2018	UDL
10	1.5	8682.45	11.336	1690.5	7.2	2.011	6.7	12	UDL	1400	8656.75	-	UDL
11	0.8	8646.15	10.688	1549.5	7.6	0.9	7	12	286.22	1260	7260.5	1210.8	285
12	1.3	8588.15	9.877	1501.35	9.8	1.6	9.1	10.5	UDL	770	8098.25	1614.4	UDL
13	1.35	8598.8	11.523	1480.45	11	1.67	10.19	12.25	UDL	630	8936	3834.2	UDL
14	0.9	9039.8	13.169	1816	11.05	1.1	11.20	14	UDL	770	19547.5	1816.2	UDL
15	1.25	8692.75	11.336	1535.05	11.2	1.6	10.3	12	UDL	800	9215.25	1917.1	UDL
16	0.85	8722.35	11.288	1508	11.45	1.05	10.33	12	UDL	1050	8377.5	2018	UDL
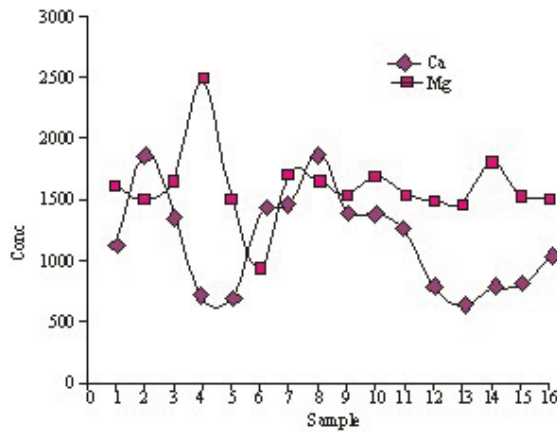
Fig. 13: Variation of Concentration of Ca and Mg Elements with Sample.

Variation between measured elements: Sodium and potassium are plays a major roles in animals and plants, potassium is found inside the cells in contrast to sodium which is found outside, also it was precipitated on sediments. The two elements are correlated to each other. Fig. (7) shows the relation between them. Both the iron –most abundant element-and manganese- second abundant element-are found as trace elements in soils. Large quantities of Mn are to be found nodules on the sea bed. The relation between them is in Fig. (8). Fig. (9) shows the relation between Zn, Ni, Mn and Fe, it is observed the Zn and Ni are absorbed on Mn oxide and Fe oxide at oxidizing conditions (PH<4) So, Zn and Ni are moderately mobile.

Cobalt nearly always occurs together with nickel, the average ratio Co-Ni is around 1:4. Fig. (10) shown the nearly increasing concentration with each other. Fig. (11) shows that cobalt and cadmium are adsorbed on Fe oxides (Siegel, 1992). This mean that the two elements are slightly mobile at oxidizing condition (P H 5-8) . The distribution of pb and U were depicted in Fig. (12) which illustrated that the concentration of U increases with the increase of depth and Pb is most probably radiogenic element due to the decay of U. (Banat and Howari, 2003). The relation between Ca and Mg are depicted in Fig. (13). It can be seen that as Mg increases, Ca decreases, this means that the two elements are correlated to each other i.e., as Ca found Mg exist.

Conclusion:

The target of the present work is to compare the concentration results from various techniques (5 techniques) with each other and with depth. The detection limit achieved for the determined element by FAAS were very satisfactory, the values lie between 0.0046 μg ml for Mg to 0.14083 for Ni. Also the precision lie between 0.0197%

to 5.65% for Cd and Pb (Dias, 2005 and Acar, 2005). The concentrations obtained for Cd, Fe, K, Mg, Pb and U by two different techniques are in good agreement with each other, which indicate the validity of these methods. The concentrations of Co, Cu, Mn, Ni, Pb , Zn and U increase with increasing depth duo to their adsorption on clay minerals (Banat and Howari, 2003). The achieved element concentration results indicate that there are many toxic elements such as Cd, Co, Ni, Zn and U in Suez Canal sediments due to the waste of ships and sample type. Table (8) shows the concentration of some element with various techniques. Determination of Cd, Co, Cu, Fe, K, Mg, Mn, Ni, Pb, and Zn by flame atomic absorption seems to be easier recommended and more rapid .However laser fluoremetry is the best technique for determination U (Merzwa *et al.,* 1998).

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