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Elemental analysis of commercial fertilizers in Iraqi market

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ABSTRACT

Heavy metals in fertilizers are considered as a threat to life through taken up by plants and be present in edible tissue as a primary steps in whole pollution processes or toxicity. It is clear that the fertilizers vary in their metals content in the phosphate fertilizers. The aim of this study was to determine the concentration of (K, Na, and Zn) as common or major elements, (Ni and Co) as minor elements, and (Pb, Cd, Cr, and Cu) as environmental pollutants or toxic elements in 14 commercial phosphate fertilizers found in Iraqi market by atomic absorption spectroscopy. Our highest obtained results showed that cobalt, cadmium, chromium, lead, and nickel distributed in remarkable values in all collected samples

Keywords: phosphate, fertilizer, heavy metal, Iraqi market.

INTRODUCTION

Heavy metals are released into environment as a result of different industrial actions and they should be evaluated to prevent their harmful effects on human health and other life beings. The harmful health effects of heavy metals are associated with allergic , neurotoxicity, anemia, and cancer as a result of chromium, lead, and copper accumulation in human body respectively [1].

At trace levels, several determination methods had been applied to quantify heavy metal concentrations in different environmental samples such as flame atomic spectroscopic technique [2-7].

Phosphate is rock or ore containing phosphate ion [8-10]added to different products such as: drinks, cosmetic, creams, toothpaste, detergents, poultry feed, fertilizer …etc. Composition of phosphate fertilizer containing high concentration of radio- metal, rare earth, heavy polluting elements (Zn, Cr, Cd,..) depends on its origin [11].

Fertilizers as soil nutrients promote plant growth containing nitrogen, phosphorus and potassium as main effective chemical components for growth of plants and improving the quality of food. Heavy metal content considered as important factors for the quality of phosphate fertilizers with no standard permissible limit. The global range of different metals is given in Table -1-.

Table -1-: Several elements (ppm) in phosphate rock in different Arab countries

Country	Cr	Pb	Cd	Zn	Ni	Ref.
Algeria	-	-	134	-	-	12
Morocco	291 7	30	345	-	26	12
Syria	136	-	-	269	-	12
Tunis	161	-	-	515	-	12
Egypt	-	-	13.2	-	-	13
Saudi Arabia	176	-	-	88	-	14

Unsafe metals such as lead, cadmium and mercury…etc. existed in fertilizers [15] are known to be potentially toxic to humans contributing to different serious health problems [16].

The presence of heavy metal in fertilizer effects crops, plants, and food chain transferring and accumulation of these toxic metals beside type and chemistry of soil. The aim of this study was directed to determine major (sodium and potassium), minor (copper, nickel, and cobalt], and toxic (cadmium, chromium, lead, and zinc) elements in different commercial fertilizers in Iraqi markets by applying atomic absorption spectroscopic technique.

MATERIALS AND METHODS

Apparatus:
A Phoenix -986-Aatomic absorption spectrometer furnished with the Phoenix Deuterium ARC background correction, single element hollow cathode lamps and air-acetylene flame was used. All instrumental settings were those recommended by the manufacturer.

Chemicals:
All chemicals were of analytical reagent grade and were provided by Merck (Germany).

Reagents and solutions:
A 1000 mgL−1 stock solution of each metal ion salt was prepared in a 100 mL volumetric flask. Working solutions were prepared daily from the stock solutions by appropriate dilution with Deionized water. Stock solutions of diverse elements were prepared from high purity compounds without further purification.

Procedure: (According to Manual Part No. 0303-0152, Release D, 1996, Analytical Methods for Atomic Absorption Spectroscopy, The PerkinElmer Inc.):

The fertilizer sample (see Table -2-) (1gm) was boiled with concentrated HCl(10 ml) and evaporated almost to dryness. The precipitate was then redissolved in 2N HCl, filtered, and made to volume (100 mL) with deionized water.

Table -2-: Description of collected phosphate fertilizers (in Iraqi local markets)

Sample Identity	Origin or commercial name
A1	Dutch
A2	Dutch1
A3	Washphspit
A4	washphspit1
A5	Cyprus
A6	Cyrpus1
A7	Kilen Feed
A8	Kilen Feed1
A9	phosphate compound
A10	phosphate compound1
A11	Jordan granular
A12	Jordan granular1
A13	Jordan
A14	Jordan1

RESULTS AND DISCUSSION

Elements were classified in to major (calcium, phosphorus, sodium and chloride), trace (iron, copper, cobalt, potassium, magnesium, iodine, zinc, manganese, molybdenum, fluoride, chromium, selenium, and sulfur), and ultra-trace (boron, silicon, arsenic, and nickel) categories. The major elements are required in amounts more than 100 mg/100mL and the minor are required in amounts less than this quantity [17]. Other elements such as cadmium, lead, tin, lithium, and vanadium cannot be considered as important for plants.

The presence of any element in plants depends on several factors [18,19] such as element chemical form, element concentration in water, type of plant, and soil chemistry (composition, pH,…) that may affected element transfer to plant tissue. The major sources of heavy metals in plants are soil as results of industrial processes and uptake of different types of fertilizers, while the minor sources are effects of climate changes on earth surface. Several elements can be harmful to plants and humans even at low concentrations [20].

Elemental analysis for 14 commercial phosphate fertilizers (Table -2-) used in Iraq was carried out to determine the concentration of heavy metals using Atomic Absorption Spectrometer. The analytical results are summarized in Table-3-.

Potassium has an important function in growth regulation (beside nitrogen and phosphorus) [21] with other various processes in plants such as protein synthesis, photosynthesis, maintaining cation-anion balancing by some increase in cellular sodium levels…etc. [22].

Potassium and sodium are important in the maintenance of osmotic balance between cells [17] and they cannot be considered as hazard metals where their ranges may be more than **10000 ppm** and **4000 ppm** for K and Na respectively as accepted ranges. In the present study, potassium **(4.5-142) ppm** and sodium **(1-185) ppm** were found less than accepted ranges. The increasing level order of sodium in the collected samples was: **A3=A4 <A2<A9=A10 <A12<A13 <A11<A14 <A8<A7 <A1<A6<A5** while for potassium was **A3<A9< A8=A13=A14 <A4<A7<A6<A10 <A5<A12<A11<A1<A2**.

Zinc occurs in plant and all living cells as a constituent of many enzymes that involved in macronutrient metabolism and cell replication [23]. In long term, toxicity disease in humans including gastrointestinal irritation, vomiting, and a reduction in high density lipoprotein cholesterol may be concluded as a results of zinc high concentration [24]. The obtained concentration of zinc ranged from **245 ppm** to **4700 ppm** while the zinc phosphate rock concentration in different Arab countries ranged **(6-515) ppm**[25] or **(88-515) ppm** (Table -1-).

Polluted environmental and industrial lead detected in environmental and biological systems such as water pipes, insecticides, petroleum refining. It can be accumulated in plant leaves that put human beings in a dangerous situation when these parts swallowed and its uptake by plant may be decreased when it immobilized with increasing pH of soil [26]. Lead range in Africa, Peru, USA phosphate rock **(7-43) ppm**[27] or **(<9-12) ppm** in NPK Fertilizers [28] was less than its concentrations range **(12.025 - 54.625) ppm**in all our samples (Table -3-) gave a future image of accumulation in plants, water, and soil with continuous usages.

The presence of cadmium is of greatest considerations in health, industry, and science as a result of its toxicity, and ability to accumulate or bioaccumulate [29,30] in plants and animals with no biochemical or nutritional function [15]. In addition, cadmium and certain cadmium compounds are listed by US Department of Health and Human Services as carcinogenic and known human carcinogens (USPHS) [31] .

Cadmium range in the present study **(30-3580) ppm** were higher than phosphate rock (Table -1-) **(13.2-345) ppm** or Africa, Peru, USA phosphate rock **(5-47) ppm**, Middle East, Russia phosphate rock **(0.1-60) ppm**[27], **(1.3-94) ppm** in NPK Fertilizers [28].

Chromium is known as an essential element and toxic towards all life chain members depending on its oxidation state in spite of chromium (III) role in consuming fat, protein, or sugar [17,32-35].It was found that the average content of chromium in our commercial phosphate fertilizers was found to be ranged between **(25.325-125.75) ppm** while the global range as reported **(1-233) ppm**[25], **(18-331) ppm** in Africa, Peru, USA phosphate rock [27], or **(136-2917)ppm** as tabulated in Table -1-.

Nickel is moderately soluble in soil water and increases at low pH [36]. Its toxicity is low and known as no known biochemical function in humans. It was reported that the level of nickel limited by the Canadian Standards for fertilizers is **180 ppm**[37a] and the allowable level by the WHO were **10 ppm**[37b].

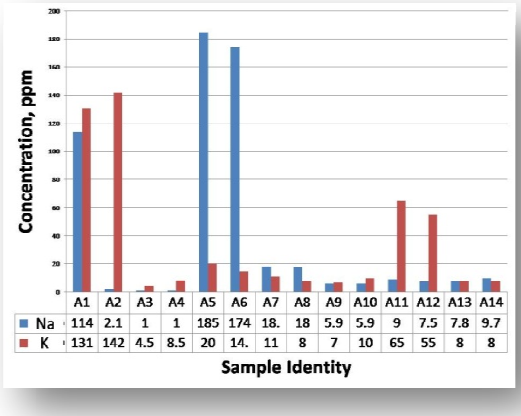
Nickel content in this study ranged **(16.7-68.375) ppm** is unaccepted where it is higher than fertilizer rock content **(1-61) ppm**[27], or the above mentioned official reports [37].

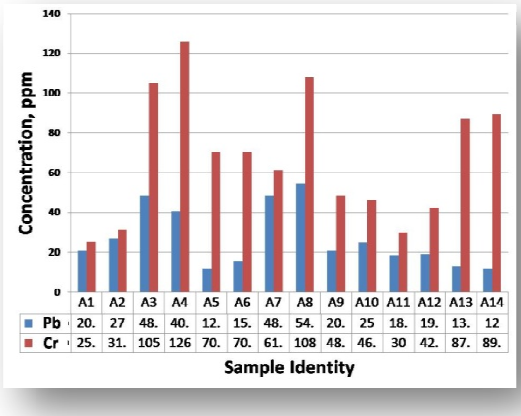
Copper is essential micro-nutrient necessary in several biological systems by being constituent of enzymes and playing a role in iron absorption [17,38]. Plant copper uptake affected by phosphate fertilizer level [39] and chemical form of nitrogen fertilizer [11]. The copper concentration in the present study ranged **(6.525-512) ppm** greater than found inAfrica, Peru, USA phosphate rock **(6-41) ppm**[27] or **(<1.5-1.6) ppm** in NPK Fertilizers [28].

Table -3-: Concentration (ppm) of Some toxic, major, and minor elements [Mean±SD] in commercial phosphate fertilizers

Sample Identity	Major elements			Toxic elements				Minor elements	
	Na, ppm	**K, ppm**	**Zn**	**Pb, ppm**	**Cd, ppm**	**Cr, ppm**	**Cu, ppm**	**Ni, ppm**	**Co, ppm**
A1	113.75±2.165064	131	275±43.3	20.825±1.449784	198.275±8.520673	25.325±5.419121	67.25±1.089725	17.675±0.491808	12.975±0.62998
A2	2.1	142	315±8.66	27.025±3.741908	222±4.242641	31.425±3.932795	66	18.3±0.514782	12.65±0.086603
A3	1	4.5	250	48.475±2.962579	1700±12.247	105.15±8.486607	17.875±0.414578	46.625±0.216506	11.55±0.287228
A4	1	8.5	275±4.33	40.775±2.366828	1500	125.75±9.038114	15.9±0.173205	32.375±0.491808	11.45±0.320156
A5	185±0.433013	20	2800	12.125±2.328492	30±4.242641	70.5	512	55.725±0.476314	43.625±0.216506
A6	174.1±0.070711	14.7	2750±50	15.875±1.948557	54±7.348469	70.5	496.5±13.5	55.225±0.928372	57.525±0.258602
A7	18.125±0.216506	11	545±55.9	48.45±2.191461	3850±111.8	61.5±7.491662	23.875±0.544862	67.75±0.433013	17.475±0.641775
A8	18	8	450	54.625±0.909327	3800	108.075±4.900701	24±0.353553	68.375±0.216506	17.45±0.259808
A9	5.925±0.129904	7	300	20.9±2.830194	1375±43.3	48.5±6.344289	12.525±0.043301	26.3	10..125±0.330404
A10	5.925±0.129904	10	305±8.66	25±1.414214	1550±50	46.5±5.678908	13.05±0.357071	36.5±0.173205	10.575±0.585235
A11	9	65	4075±82.92	18.75±3.902243	451.75±4.602988	30±8.83544	7.3	16.7	5.7±0.2
A12	7.5	55	4700±100	19.25±1.734215	496.5±4.974937	42.65±11.12958	6.525±0.043301	17.4±0.34641	10.075±0.236291
A13	7.85±0.217945	8	245±15	13.25±1.887459	856±16.15549	87.25±2.839454	14.075±0.129904	25	13.1±0.765942
A14	9.775±0.129904	8	247.4±16.39	12.025±2.996143	1000	89.575±11.95478	14.35±0.4272	28.675±0.506828	6±0.326599
Max.	**185**	**142**	**4700**	**54.625**	**3850**	**125.75**	**512**	**68.375**	**57.525**

Figure -1- shows comparison between the obtained results (ppm) of [sodium and potassium], [lead and chromium], and [copper and nickel] in different commercial phosphate fertilizers obtained from Iraqi market. Our highest obtained results showed that cobalt, cadmium, chromium, lead, and nickel distributed in remarkable values in all collected samples





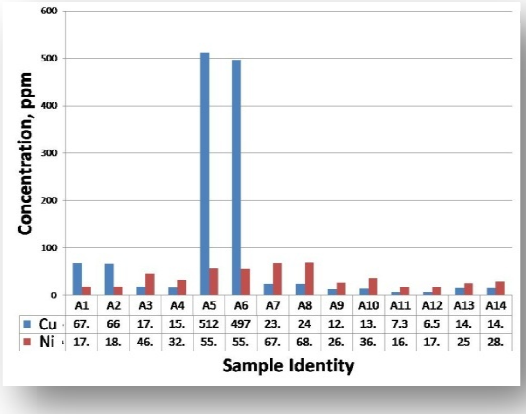


Figure -1-: Concentration (ppm) of Sodium, Potassium, Lead, Chromium, Copper, and Nickel in different commercial phosphate fertilizers

CONCLUSION

Nonessential metals, such as lead, nickel, and cadmium are toxic even in trace amounts where the intake of cadmium above safe limit causes serious health problem to human such as liver disease and nerve or brain damage. The essential metals can also produce toxic effects at higher concentrations by tending to bio-accumulate, cause toxicity to plants, and contaminate the food chain.

Heavy metals present in the fertilizer contaminate soil and the irrigated water then transferred into the plants and accumulate there so to other life chain. Lead and cadmium have been included in the regulations of the European Union for hazardous metals while chromium and nickel were in the US Food and Drug Administration (USFDA) list.

For the above reasons, elementary analysis had been done to determine several major, minor, and toxic elements in randomly selected commercial fertilizers from Iraqi market and showed important considered notes about their concentrations.

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