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Research Article

# Flame Atomic Absorption (FAAS) and X-Ray Fluorescence (XRF) spectroscopicElemental Analysis of Commercial Fertilizers in Iraqi Market.

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**ABSTRACT**

**Qualitative and quantitative determination of elemental presence in six purchased fertilizers (Green Soul (red), Green Soul (green), Floral K, Alasala, POT GROND, and BIOZAR) with different trade marks from Baghdad-Iraq markets were determined. Flame Atomic Absorption (FAAS) and X-Ray Fluorescence (XRF) spectroscopies were applied to achieve this purpose.**

**Two different sample preparations were used; dry and wet methods; for FAAS determination of metals in fertilizers. Toxic elements like Cd, Pb, Co, Cu, Ni, Mn, and Fe were measured by FAAS. The results showed that Cd, Pb, and Co were in low contents. More than 40 elements were measured by XRF technique where Na, K, and Ca showed high present in fertilizer content.**

**The final conclusion of this work is the presence of these toxic metals in these materials that used in the life chain can affected plant, animal and human not in the present time of the use but also in the future because of their accumulation property.**

**Keywords:** elements, Atomic Absorption analysis, X-ray Fluorescence, fertilizers, Iraqi market, Floral K, Alasala, POT GROND, BIOZAR.

## INTRODUCTION

Plant growth can be affected with several environmental factors such as chemical components presented in soil or soil nutrients (fertilizers) especially the major ones (nitrogen, phosphor, potassium, …etc.). These nutrients may constitute as direct source of environmental heavy metals (lead, cadmium, mercury, arsenic, antimony, …etc.) and radioactive elements (potassium-40, uranium -234, …etc.) pollution that transferred during multistep production process. These toxic andharmful elements may drove to soil or water damage, accumulation in plant, animal, and human with no chance of metabolism process. The existed toxic elements with their accumulation character are considered as exporter of serious health problem[1-5].

In our previous published paper, 14 fertilizers from Iraqi markets with different sources and commercial trademarks were tested to determine major (sodium and potassium), minor (copper, nickel, and cobalt), and toxic (cadmium, chromium, lead, and zinc) elements by applying atomic absorption spectroscopic technique. The obtained results showed that sodium (1-185), potassium (4.5-142) ppm, copper (6.525-512) ppm, nickel (16.7-68.375) ppm, zinc (245-4700) ppm, lead (12.025-54.625) ppm, cadmium (30-3580) ppm, and chromium (25.325-125.75) ppm were obtained.[6]

In this study, the objective was qualitative and quantitative elemental presence determination in several purchased fertilizers from Iraqi markets by the use of atomic absorption (AAS) and x-rays fluorescence (XRF) spectroscopic techniques.

## EXPERIMENTAL SECTION

**Sample Materials:** Six brands of fertilizers (**Green Soul (red), Green Soul (green), Floral K, Alasala**, **POT GROND, and BIOZAR**)were purchased from Baghdad market, Iraq as shown in , Table -1-.

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

**Instruments:**

A Phoenix -986-Atomic 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 (Table-2-). X-Ray Fluorescence (XRF): X-Rays Fluorescence recorded using a Lab X (XRF), Shimadzu, Japan in Ministry of Science and Technology, Baghdad, Iraq . It is an controlled analytical instrument designed for the detection and the measurement of elements in samples (solids, powders, and liquids). The samples were weighed and ground in agate mortar and a binder (PVC dissolved in Toluene) was added to the samples,

**Procedures:**

**Elemental Composition of Selected fertilizers by AAS Method:**

For atomic absorption spectroscopic (AAS) technique, a 1000 mg/L 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.

**Method (A)**: Un-quantitated fertilizer was grinded to fine powder then 1 gm of the fertilizer was dissolved in 10 mL concentrated hydrochloric acid then evaporated nearly to dryness. The resulting residue was redissolved in 2N of the same acid, gently boiled, filtered in 100 mL of volumetric flask then completed to the mark with deionized water.[7]

**Method (B)**: 1 gm of fertilizer was charred on hot plate, ignited with muffle furnace for one hour at 500$^{o}$C with door propped open for air access in free. The residue was broken up then dissolved with 10 mL of concentrated hydrochloric acid. The resulting solution as boiled, evaporated to dryness, redissolved with 20 mL of 2N the same acid, and filtered into 100 mL volumetric flask. The filtrated solution was completed to mark with deionized water.[8]

**Elemental Composition of Selected fertilizers by XRF Method:**

The sample was carefully mixed and pressed in a hydraulic press into a 100mg /cm$^2$ pellet. The pellet was loaded in the sample chamber of the spectrometer and a voltage (45KV maximum), a current (0.5 mA maximum), method (Tq-3443), and target (Compton/ secondary Molybdenum) were applied to produce the X-rays to excite the sample for a preset time (5 minutes in this case). The spectrum from the sample was then analyzed to determine the concentration of the elements in the sample.

## RESULTS AND DISCUSSION

In sample treatment with AAS technique, dry and wet methods were used to overcome organic interfere or reaction with studied metal ions or used reagents. Oxidation or Dry method [9]produced oxides, sulphates, phosphates, chlorides, or silicates of the actual presented metals in materials under study by applying high temperature muffle furnace (450-500)$^{o}$C, low temperature (~ 120 $^{o}$C) with singlet state – oxygen, or microwave oven with open crucible and less required chemicals. Magnesium nitrate or oxide used as oxidizing reagent aided ashing step. The safety, expensive platinum crucible, volatilization loss, contamination, and some workup step difficulties are considered by analytical chemist in AAS-dry method of trace elements.[10]

Acid digestion is an easy open or closed system used for agricultural materials (food, plant parts)[9]. In this method, mineral (hydrochloric, sulphuric) or oxidizing acid (nitric acid alone or with others) plays an important role especially with matrix nature of the organic material under study. Closed digestion system is preferred for various biological or environmental sources because of its ability to improve oxidation efficiency with or without high applied pressure and reducing time, reagent quantities, contamination.

It is known that several heavy metals have important roles for human or animal (Table -3-) and its accumulations cause serious health problems. Lead accumulation associated with childhood development. Lead, gold, mercury may cause a very immunological issue by destroying immune system cell known as autoimmunity[11].

Potassium, Sodium, lead, copper, chromium, cadmium, or nickel content in fertilizer was reported in several scientific articles or international official documents[11-16]. Potassium and sodium accepted ranges are 10000 ppm and 4000 ppm respectively. Lead range in Africa, Peru, USA phosphate rock (7-43) ppm. Copper contain in phosphate rock in Africa, Peru, and USA phosphate rock (6-41) ppm or (<1.5-1.6) ppm in NPK Fertilizers.

Cadmium range was in phosphate rock (13.2-345) ppm or Africa, Peru, and USA phosphate rock (5-47) ppm, Middle East, Russia phosphate rock (0.1-60) ppm, (1.3-94) ppm in NPK Fertilizers. Chromium global range as reported was (1-233) ppm, (18-331) ppm in Africa, Peru, USA phosphate rock. The level of nickel limited by the Canadian Standards for fertilizers is 180 ppm and the allowable level by the WHO was 10 ppm.

In 2014, AAS was used to qualified and quantified major (sodium and potassium), minor (copper, nickel, and cobalt), and toxic (cadmium, chromium, lead, and zinc) elements in various fertilizersamples from Baghdad markets with different sources and commercial trademarks. The published results confirmed the presence of copper, nickel, zinc, lead, cadmium, and chromium[6].

In our present study, elemental analysis for different commercial fertilizers used in Iraq was carried out (Tables -2-, -4-, and -5-, Figure-1-) to determine the concentration of elements using Atomic Absorption (five samples) and X-Rays Fluorescence (six samples) spectrometers. The analytical results are summarized in Table -4- for AAS and in Table -5- for XRF results.

**Table 1**
**Description of the studied fertilizers from Baghdad- Iraq market.**

| Sample identity | Sample name and its description |
|---|---|
| 1 | Green Soul (red)<br>Unknown production source with Arabic words |
| 2 | Green Soul (green)<br>Unknown production source with Arabic words |
| 3 | Floral K<br>MIGIORA LA QUALITÁ; Polveresolubile<br>(CIFO S.P.A., Italy); PR01114<br>N: total 12%, nitrate 10%, ammonium 2%<br>$P_2O_5$ soluble: 5%; $K_2O$ soluble: 35%; B soluble: 0.1%; Cu soluble: 0.1%; Cu-EDTA: 0.1%<br>Mn soluble: 0.1%; Mn –EDTA: 0.1%; Zn soluble: 0.1%; Zn-EDTA: 0.1% |
| 4 | Alasala<br>Peat moss, Unknown production source with Arabic words |
| 5 | POT GROND; FLORENTUS; Netherland<br>www.veenbaas.nl<br>Major constituents: 25%; Major organic 20%; Electrical conductivity: 40µs/m; pH 5-6.5; NPK 14-16-18 1.2 kg/$m^3$ |
| 6 | BIOZAR<br>NANO BIOLOGICAL FERTILIZER FOR HOME FLOWER<br>KHOMEIN-IRAN; www.agrinano.ir |

**Table 2**
**Standard atomic absorption parameters of the measured elements.**

| Metal | Wavelength, nm | Slit width, nm | Atomization temperature, °C |
|---|---|---|---|
| Iron | 248.3 | 0.2 | 1700 |
| Cobalt | 240.7 | 0.2 | 1300 |
| Copper | 324.7 | 0.4 | 2000 |
| Manganese | 279.5 | 0.2 | 1700 |
| Cadmium | 228.8 | 0.4 | 1000 |
| Nickel | 232.0 | 0.2 | 1300 |
| Lead | 283.7 | 0.4 | 1500 |

**Hollow- cathode lamp current: 2.0 mA; Flame: Air-Acetylene**

**Table 3**
**Health roles of some elements to human or animals.**

| Element | Health role |
|---|---|
| Iron | Essential for plant growth, human life by bounded in haemoglobin, Fe-dependent tissue enzymes, ferritin, and hemosiderin. It is not toxic in usual amount except Fee repletion can be considered as hazardous. |
| Cobalt | Required as trace element for several biological action in human body. |
| Manganese | Necessary for plant, animal, and human as enzyme cofactor. |
| Nickel | Essential for animal nutrition and its toxicity and responsibility for many health problems and diseases. |

**Table 4**
**Elemental analysis (in ppm) of five purchased fertilizers from Iraqi market by AAS.**

| Metal | 1<br>Method (A)<br>[Method(B)] | 2<br>Method (A)<br>[Method(B)] | 3<br>Method (A)<br>[Method(B)] | 4<br>Method (A)<br>[Method(B)] | 5<br>Method (A)<br>[Method(B)] |
|---|---|---|---|---|---|
| Iron (Fe) | 711.6<br>[963] | 667.1<br>[686.9] | 99<br>[24.6] | 440<br>[714.7] | 997.6<br>[954.7] |
| Manganese (Mn) | 64.6<br>[67.6] | 10.3<br>[6.8] | 599.7<br>[802.9] | 23.6<br>[21.8] | 35.3<br>[25.4] |
| Nickel (Ni) | 7.9<br>[3.9] | 7.4<br>[3.4] | 15.8<br>[5.4] | 9.7<br>[6.1] | 10.18<br>[4.5] |
| Copper (Cu) | 15.5<br>[24.9] | 2.0<br>[1.1] | 1302<br>[1302] | 2.1<br>[1.9] | 5.6<br>[7.9] |
| Lead (Pb) | <0.2<br>[<0.2] | <0.2<br>[<0.2] | 118.1<br>[<0.2] | <0.2<br>[<0.2] | <0.2<br>[8.8] |
| Cobalt (Co) | <0.1<br>[1.4] | <0.1<br>[1.4] | 7.7<br>[3.1] | <0.1<br>[1.6] | <0.1<br>[2.4] |
| Cadmium (Cd) | <0.01<br>[<0.01] | <0.01<br>[<0.01] | <0.01<br>[<0.01] | <0.01<br>[<0.01] | <0.01<br>[<0.01] |

Table -4- showed that maximum content in all samples with both preparation methods was iron except sample (3). With wet method, Mn, Ni, Cu, Pb, and Co maximum quantities were presented in sample (3) but not for Fe in sample (5). Mn, Cu, and Co maximum contents with dry method were in sample (3) but not iron (sample (1)) or lead (sample (5)). **Nickel** ranged was **(7.4-15.8) ppm –method A and (3.4-6.1) ppm – method B** and the presence of nickel **(15.8 ppm) in sample 3** was more than the acceptable limit set by WHO. **Copper** content in **sample (3)** with both AAS sample preparation methods **(1302) ppm** was more than NPK fertilizers and in Africa, Peru, USA phosphate rocks. In sample (3)-method A**. Lead** in **sample (3)** was out of highest acceptable limits in Africa, Peru, and USA phosphate rockwhen it was measured with method A**.** These

notes are important to be considered because of their toxicity and accumulation effects on human and animal health with time.
XRF technique was used to determine the elemental composition of nine fertilizers purchased from Zaria-Nigeria. The obtained results showed that (Cr, Ni, Si, V, Zn) as toxic elements were within the agricultural soils ranges except Cr in one sample[17].

Table -5- and Figure -1- show the XRF elemental analysis of the six fertilizers purchased from Baghdad-Iraq market. The maximum content of metals in tested samples were sodium (samples (1) and (2)), potassium (sample (3)), calcium (samples (4) and (5)), and zinc (sample (6)). Also, sample (3) was with the maximum content of Na, P, S, K, Cu, Hg, Tl, and Th while sample (6) was with Mg, V, Cr, Mn, Fe, Co, Ni, Zn, Cd, Sb, and W.

**Table 5**
**Elemental analysis (in ppm) of five purchased fertilizers from Iraqi market by XRF.**

| | 1 | 2 | 3 | 4 | 5 | 6* |
|---|---|---|---|---|---|---|
| Na | <1000 | <1000 | <2100 | <820 | <690 | - |
| Mg | <100 | <100 | <310 | <120 | <100 | 3160 |
| Al | <20 | <20 | <92 | 173.2 | 142.1 | <280 |
| Si | 88.9 | 30.8 | 2889 | 2247 | 2358 | 195 |
| P | 9.4 | 6.8 | 3750 | 76.8 | 298.7 | >1580 |
| S | 316.5 | 143 | 3874 | 338.8 | 1361 | - |
| Cl | 116.8 | 44.1 | 2103 | 103.4 | 210 | - |
| K | 494 | 359.9 | >315200 | 502 | 1485 | - |
| Ca | 506.3 | 299.8 | <290 | 9278 | 13230 | - |
| Ti | <5 | <5 | <2.7 | 79.9 | 85.6 | <34 |
| V | 10.9 | 9.2 | <3.3 | 12.5 | 11 | 98.2 |
| Cr | 14.3 | 10.1 | 35 | 17.3 | 20 | 764 |
| Mn | 84.4 | 33.6 | 1343 | 131.7 | 90.7 | 80070 |
| Fe | 916.7 | 521.2 | 84.2 | 1732 | 2040 | 98320 |
| Co | 4 | <3 | <5.5 | 6.9 | 6.8 | 418 |
| Ni | 3 | 2.3 | 11.3 | 5.7 | 3.2 | 1448 |
| Cu | 15.9 | 1.1 | >2431 | 4.1 | 16.9 | 266 |
| Zn | 38.8 | 1.9 | 2263 | 26.5 | 28.6 | 676600 |
| Ga | <1 | <1 | <2.1 | 0.9 | 0.9 | 25.7 |
| Ge | <1 | <1 | <1.5 | <0.5 | <0.5 | - |
| As | <1 | <1 | <1.1 | <0.5 | 2.3 | - |
| Se | <1 | <1 | <1 | 0.6 | 0.9 | - |
| Br | <1 | <1 | 7.1 | 1.2 | 37.2 | - |
| Rb | <3 | <3 | 36.6 | 3.5 | 4.6 | - |
| Sr | <5 | <5 | <0.9 | 31.8 | 36.7 | - |
| Y | <7 | <7 | <1.3 | <7 | 7.1 | - |
| Mo | <10 | <10 | <31 | <23 | <20 | 13780 |
| Ag | <5 | <5 | <5 | <5.1 | <5.2 | 44 |
| Cd | <5 | <6 | <5.1 | <5.1 | <6.2 | 75 |
| Sn | <6 | 18.6 | <8.8 | <5.4 | <9.7 | <47 |
| Sb | 7.8 | 35.3 | <6.8 | <8.2 | <8.8 | <37 |
| Te | 11.9 | 66.3 | <9.1 | <7.8 | 31.9 | - |
| I | 32.9 | 163 | 22.4 | 28.7 | <23 | - |
| Ba | 592 | <2 | <32 | <37 | 40.4 | - |
| W | <2 | <2 | <24 | 2 | <1.7 | <270 |
| Hg | <2 | <2 | <2.4 | 1.8 | 1.7 | - |
| Tl | <2 | <2 | <2.4 | 0.7 | 1.1 | - |
| Pb | <2 | <2 | <2.6 | 4.2 | 12.5 | <20 |
| Bi | <2 | <2 | <2.2 | 1.4 | 0.7 | - |
| Th | <2 | <2 | <2.1 | 2 | 1.6 | - |
| U | <3 | <3 | <2.5 | 2.3 | 3 | - |

***other elements: Nb (53 ppm) and Zr (210ppm)**

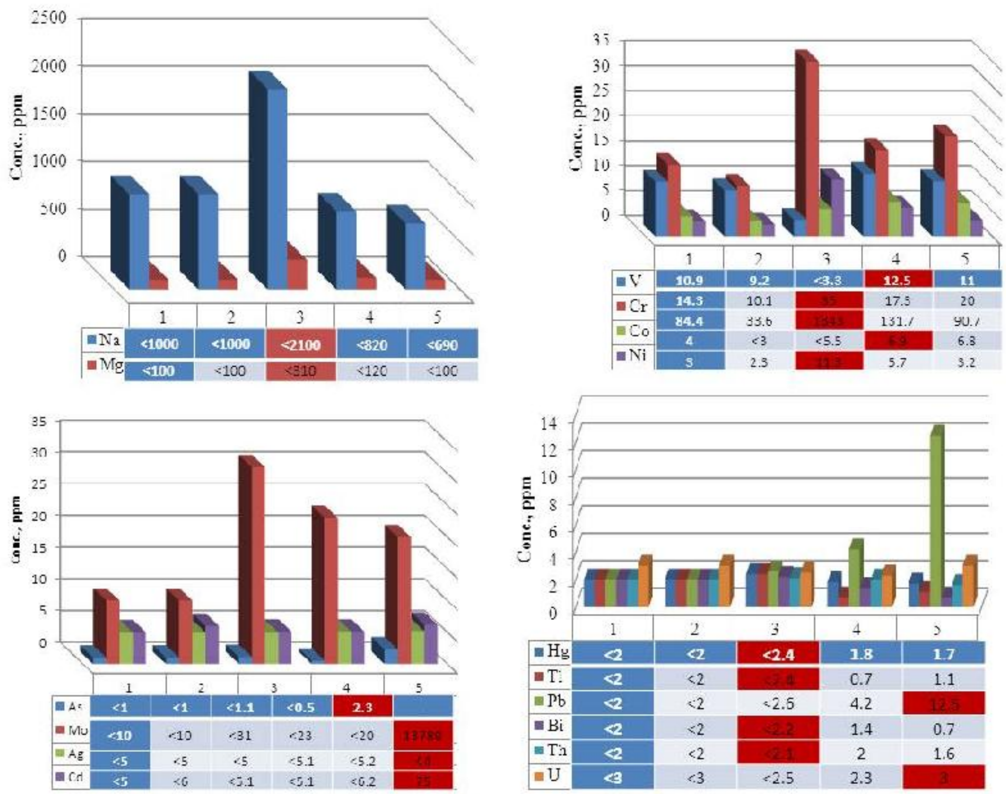


**Figure 1**

**Several measured elements in the five purchased fertilizers in Baghdad- Iraq market by XRF technique.**

According to EPA document, 2009, **thallium** and its compound are known as toxic especially $Tl^+$ compound with its high solubility in water and adsorption through the skin beside suspected carcinogen for human and other health problems in kidney, intestines, liver, and hair loss[18]. In this study, its range was **(0.7-<2.4) ppm**. **Thorium** is famous element as radioactive actinide metal and its aerosol exposure can cause lung, pancreas, and blood cancer diseases [19]. This radioactive metal range in all tested fertilizer by XRF was **(1.6-<2.4) ppm** while the famous radioactive metal (**uranium**) was **(2.3-<3.0) ppm** (Table -5-). **Mercury** as a toxic adsorbed and inhaled element ranged **(1.7-<2.4) ppm** (Table -5-)[20]. **Arsenic** and its compounds are classified as toxic, dangerous for environment, and Group 1 carcinogen agents [21]. It was found in samples (1-5) with concentration range **(<0.5-2.3) ppm** (Table -5-).

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