Determination of Heavy Metals in Fertilizer Samples by X-ray Fluorescence Techniques

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Abstract

The concentrations of heavy metals in the fertilizer samples collected from Iraq have been determined by X-ray fluorescence (XRF). The agricultural practices have led to the depletion of the natural elements in soils. Therefore, phosphate fertilizers are used in huge amounts everywhere and are essential for agricultural crops, to increase the heavy metals in soil. The average concentration of Fe, K, Zn, Mg, Cu, Mn, Cr, and Ni were found to 5.27, 23.02, 0.36, 2.49, 0.171, 0.261, 0.052 and 0.021 %, respectively. The average heavy metal of Fe, K, Zn, Mg, Cu, Mn, Cr, and Ni were within the limits of those used worldwide. The obtained data could be useful as baseline data for heavy metals in fertilizers. The organic fertilizers are the main chemicals used by the agricultural sector. On the other hand, the results demonstrate the widely supported use of organic fertilizers in agriculture.

Key words: XRF, heavy metal, fertilizers.

الخلاصة

تم حساب تركيز العناصر الثقيلة في نماذج الاسمدة التي جمعت من العراق باستخدام تقنية الاشعة السينية. ان التطبيقات الزراعية تعمل على زيادة العناصر الاساسية الطبيعية في التربة. لذلك فان استخدام الاسمدة بكميات كبيرة في انتاج المحاصيل الزراعيه يساعد على زيادة العناصر الثقيلة في التربة. ووجد ان معدل تركيز العناصر الثقيلة (Fe, K, Zn, Mg, Cu, Mn, Cr, Ni) كالتالي (5.27, 23.02, 0.36, 2.49, 0.171, 0.261, 0.052, 0.021) % , على التوالي. كانت نتائج تركيز العناصر الثقيلة في الاسمدة ضمن الحدود المسموح بها. هذه الدراسة مهمة ومفيدة وتعتبر كقاعدة بيانات لحساب تركيز العناصر الثقيلة في الاسمدة. وكذلك عززت هذه الدراسة استخدم الاسمدة الكيميائية في الزراعة.

الكلمات المفتاحية: تقنية الاشعة السينيه, العناصر الثقيلة, الاسمدة.

1. Introduction

Phosphate rocks constitute the bulk of the raw materials for the manufacture of phosphate fertilizers and some phosphorus based chemicals. Phosphate fertilizers are well known that contain a variety of stable and radioactive elements and heavy metals that could be of environmental concern to the public (UNSCEAR, 2000; Guimond & Hardin, 1989; Al-Nafiey *et al.*, 2014). The hazard of the used phosphate fertilizers could arise from the use of rock material in industrial plants especially in the fertilizers, due to the release of dust and polluted waters into the environment; the accumulation of these effluents in vitally important media such as soil, water and food are undesirable (Ogunleye, 2002). The chemical industries and fertilizers application are the most important sources of heavy metals in soils and water (Suciu et al., 2008; Chopin & Alloway, 2007). The human activity leads to increase levels of heavy metal contamination in the environment, so that the agricultural practices have led to the depletion of the heavy metal elements in soils (Ahmed & El-Arabi, 2005). Therefore, phosphate fertilizers are being used to overcome this depletion and enrich the respective soils (Aswood *et al.*, 2014). Heavy metals are considered to be one of the most important sources of pollution in the environment, since they have a significant effect on its ecological quality (Türkdoğan *et al.*, 2003). The presence of heavy metals in soil can affect the quality of food, surface water, groundwater and plant growth (Vries *et al.*, 2007). A huge variety of unsafe metals may exist in fertilizers which may include: cadmium, arsenic, zinc, nickel and lead, (Chen *et al.*, 2007). Several studies have shown that heavy metals in phosphatic fertilizers can accumulate in soil and become readily available to plants and vegetables (Resende & Nascentes, 2016). Chauhan and Chauhan assessed the concentration of major elements (Al, Si, P, S, Cl, and K) in fertilizer samples that were measured by XRF analysis (Chauhan & Chauhan, 2013). According to the Environmental Protection Agency, of the USA, these metals are known to be potentially toxic to humans contributing to cancer, developmental effects, reproductive problems, birth defects and kidney damage. Th children are particularly susceptible to the toxic effects of fertilizers because they spend more time on the ground and tend to put their hands in their mouths without washing them (García-Rico *et al.*, 2007).

There are many methods to perform simultaneous multi-elemental determinations have led to an extensive application in research laboratories of accurate and sensitive atomic analytical techniques for the investigation of different types of materials, such as neutron activation analysis, atomic absorption spectroscopy, XRF and particle-induced X-ray emission (Stihi *et al.*, 2000; El-Taher & Althoyaib, 2012; Chauhan *et al.*, 2013). The analysis of environmental samples by XRF has the advantage of being a rapid and inexpensive method with a simple sample preparation. Qualitative and quantitative analyses are performed without acid digestion processes and a great number of elements can be determined simultaneously in a short time. The main goal of the present research which has used XRF technique is to assess the heavy metals concentration in fertilizer samples that were collected from farms and various companies dealing with agrochemicals in Iraq.

2. Material and methods

2.1. Collect Samples

The fertilizers are used in agriculture for crops improvement. The major types of fertilizers are urea, potassium sulphate and nitrogen (N), phosphorus (P) and potassium (K), ammonium phosphate, ammonium sulphate, phosphate rock, super phosphates, compound as well as organic fertilizers such as animal droppings (FAO, 2004). Thirty fertilizer samples, that are considered representative, are used in farming whereby these samples were obtained from farms and various companies dealing with agrochemicals. A 50 g was taken from each fertilizer and kept in containers. The samples then were labeled as type, time and date for each sample.

2.2. Sample preparation

Samples generally need little preparation although materials should be presented to the spectrometer in a homogenous and reproducible form. Metals may be ground to give a flat surface, while powders are reduced to a controlled particle size and pressed into pellets for convenience of handling. The fertilizer samples were crushed to fine powder of a mean particle diameter of 100 μm. Thereafter, the powder was heated at 100 ^{o}C in the oven for 24 h to remove moisture. Eight grams of samples are put in suitable sample cups as showed in Figure1.

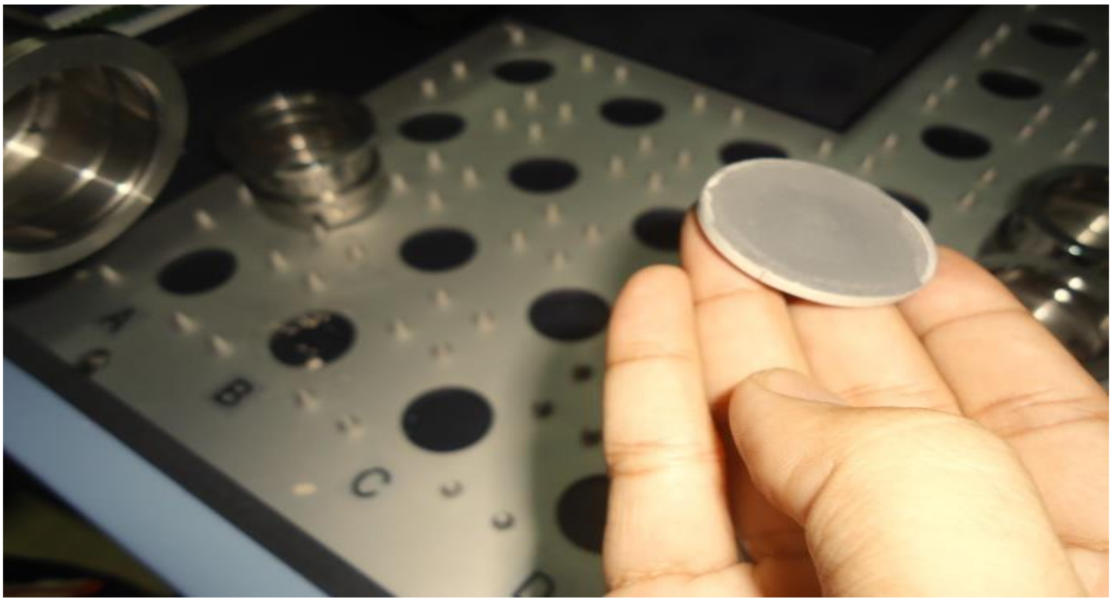


Figure 1. The samples put in cups

2.3. X-ray fluorescence (XRF) techniques

A Bruker AXS, S8 Tiger A15X10-A3E1A1-E2EA1, X-ray fluorescence - Serial-No 206156, 220V. 3-50/60 Hz, kVA, D- 76181 Karlsruhe, Germany were used in this research to determine Fe, K, Cu, Mg, Zn, Mn, Cr and Ni in the fertilizer samples. The advantages of using this technique were the optimal measurement conditions programmable for each element, very high sensitivity and low detection limits. The conversion of measured X-ray intensities into element concentration is based on calibration of the spectrometer by measuring the peak intensities for a series of reference can or standards of known composition. Figure 2, shows the XRF used in this research.

Figure 2. Photo of X-ray fluorescence

3. Results and discussion

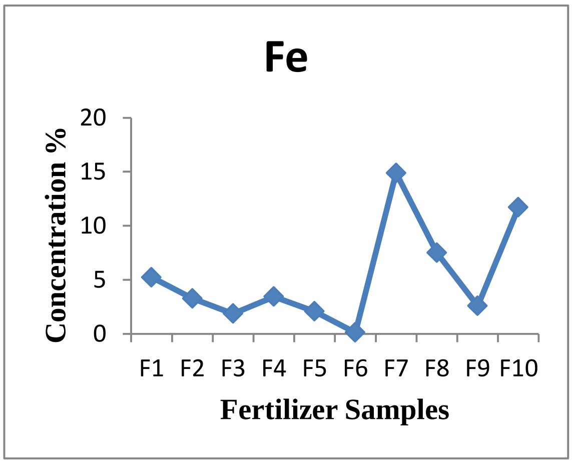
The eight major elemental concentrations found in fertilizer samples were: Fe, K, Zn, Mg, Cu, Mn, Cr, and Ni as shown in Table 1. The highest concentration of Fe (14.89%) was found in phosphorus and lowest concentration (0.12%) was found in muriate potash while, the lowest concentration of K (0.05%) was observed in phosphorus and the highest concentration (45.29%) was observed in muriate potash as shown in Figure 3. The concentration of Zn was ranged from (1.814%) in rock phosphate to (0.018%) in muriate potash. Similarly, the concentration of Mg was ranged from (0.23%) in phosphorus to (6.19%) in sheep waste as shown in Figure 4. The highest concentration of Cu and Mn (1.02%) and (0.614%) were found in rock phosphate and single supper phosphate respectively, where the lowest concentrations were found in muriate potash as shown in Figure 5. The concentration of Cr was found in chicken waste, phosphorus, single supper phosphate, triple supper phosphate and rock phosphate and the highest concentration (0.290%) was found in rock phosphate whilst, the concentration of Ni was found in phosphorus, triple supper phosphate and rock phosphate and the highest concentration was (0.192%) in rock phosphate as shown in Figure 6. The concentration of Ni, Cr and Cu were relatively higher in the rock phosphate, triple supper phosphate, single superphosphate and phosphorus samples as compared to their concentrations in organic fertilizer and urea samples.The data indicate that the mean concentration of heavy metals varied considerably with metal and the type of fertilizers. In comparison as shown in Table 2, the concentration of Cr, Cu, Zn, Ni, and Mn in fertilizer samples contained less than the standards concentration in world (Herrick & Friedland, 1990). On the other hand, the obtained values for Cr, Cu, Zn, Ni, and Mn were lower to those reported in cancer region in Turkey (Türkdoğan et al., 2002).

4. Conclusions

The XRF was undertaken to determine the concentration of heavy metals in fertilizer samples, which was collected from Iraq. The average heavy metal contents of the fertilizers are within the limits of those used worldwide. The use of these fertilizers is not expected to cause detrimental effects with regard to heavy metals pollution. However, a slight annual increase could be expected. This increase is coupled with other possible inputs of heavy metals to agricultural soils. The obtained data could be useful as the baseline data for heavy metals in fertilizers. The organic fertilizers are the main chemicals used by the agricultural sector. On the other hand, the results demonstrate the widely supported use of organic fertilizers in agriculture.

Table 1: Major elemental concentration in different fertilizer samples using XRF spectrometry.

Elemental	**Concentration (%)**							
Fertilizer Samples	Fe	K	Zn	Mg	Cu	Mn	Cr	Ni
NPK (F1)	5.23	23.84	0.018	0.98	0.005	0.048	-	-
Chicken (F2)	3.28	20.16	0.032	1.26	0.023	0.120	0.005	-
Cow (F3)	1.87	18.87	0.745	4.56	0.097	0.619	-	-
Sheep (F4)	3.44	35.46	0.600	6.19	0.188	0.210	-	-
Urea (F5)	2.07	33.41	0.068	0.95	0.015	0.077	-	-
Muriate Potash (F6)	0.12	45.29	-	0.54	-	-	-	-
Phosphorus (F7)	14.89	0.05	0.107	0.23	0.023	0.283	0.102	0.008
Single Superphosphate (F8)	7.51	30.24	0.126	2.35	0.101	0.614	0.053	-
Triple Supper Phosphate (F9)	2.58	20.58	0.054	3.81	0.240	0.460	0.059	0.011
Rock Phosphate (F10)	11.7	2.24	1.814	4.01	1.02	0.176	0.290	0.192
Average	**5. 27**	**23.02**	**0.36**	**2.49**	**0.171**	**0.261**	**0.052**	**0.021**



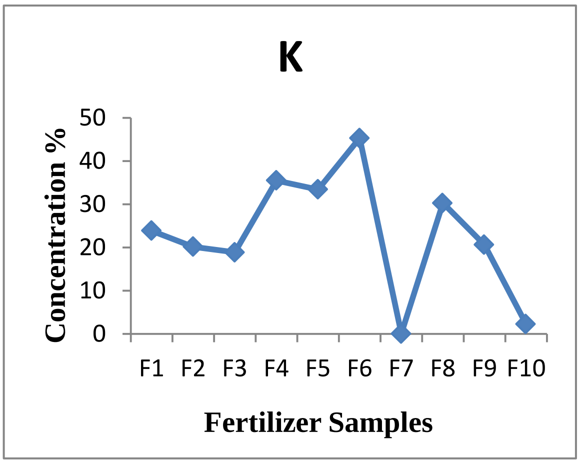


Figure 3: - Concentration of Fe and K metals with fertiliser samples

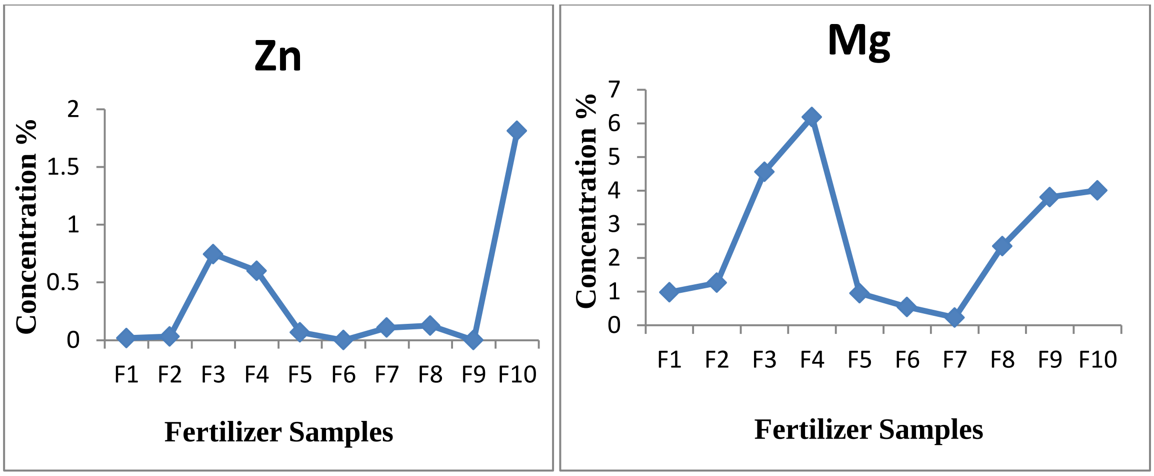


Figure 4: - Concentration of Zn and Mg metals with fertiliser samples

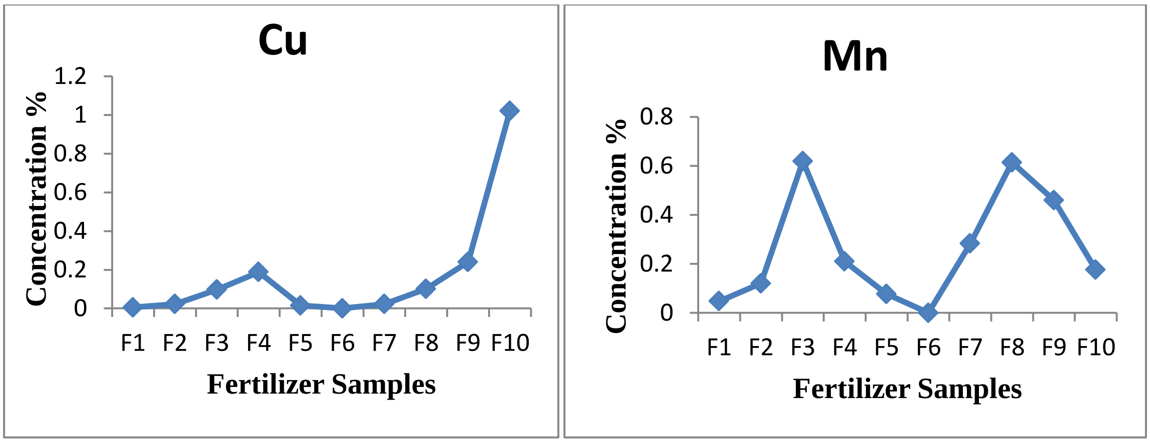


Figure 5: - Concentration of Cu and Mn metals with fertiliser samples.

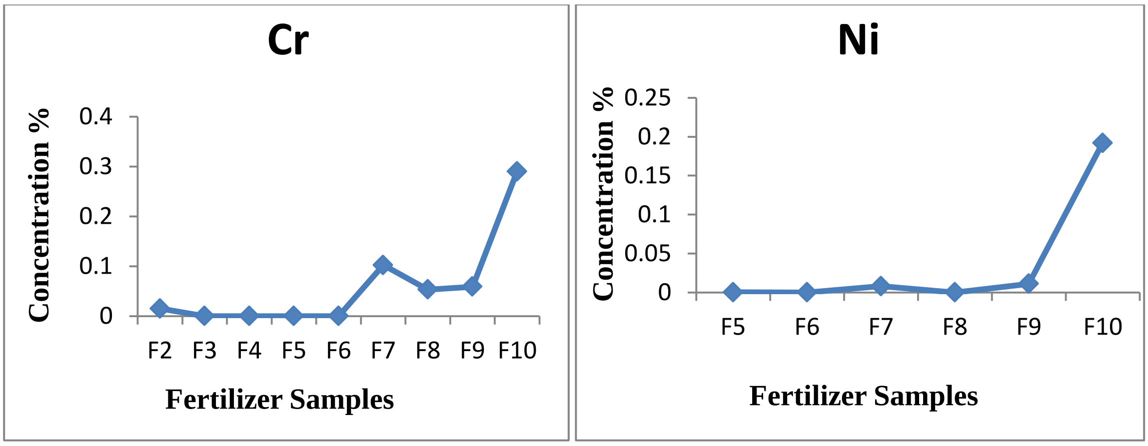


Figure 6: - Concentration of Cr and Ni metals with fertiliser samples.

Table 2: A comparison of the concentrations of heavy metals in fertilizer samples with the standards values and other Cancer region

Metal	Cr	Cu	Zn	Ni	Mn	References
standards	10-80	5-5.6	60-780	10-50	100-400	Herrick,1990
cancer region	-	20± 6	12.1±6	22±12	171±91	Türkdoğan,2003
present study	0.005-0.290	1.02-0.005	1.814-0.018	0.192-0.008	0.619-0.048	

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