

Application of microwave-assisted extraction (MAE) of Cr(VI) from the fertilizer products and determination by ion chromatography

U. Ryszko, B. Mazurek, J. Ostrowski, A. Drozd, A. Watros

Analitical Department, Łukasiewicz Research Network – New Chemical Syntheses Institute, 24-110 Puławy, Poland

Keywords: fertilizer, hexavalent chromium, microwave-assisted extraction, ion chromatography

Presenting author email: urszula.ryszko@ins.lukasiewicz.gov.pl

ABSTRACT

A microwave-assisted extraction method for the preparation of solid fertilizers samples to determine hexavalent chromium was developed. Optimal extraction conditions such as temperature, microwave power and extraction time were studied. Hexavalent chromium analysis were performed using ion chromatography technique with UV detection based on post-column derivatization with 1.5-diphenylcarbazide at 520 nm. The accuracy and the precision of the proposed procedure were evaluated by analysing the certified reference materials: SRM 2700 (NIST) with certified Cr(VI) content ($14.9 \pm 1.2 \text{ mg} \cdot \text{kg}^{-1}$) and CRM 041 with certified Cr(VI) content ($148 \pm 2 \text{ mg} \cdot \text{kg}^{-1}$). Satisfactory recovery values were obtained and the relative standard deviation (RSD) was below 6%. The total chromium content was determined using ICP-OES technique.

1. INTRODUCTION

Soil contamination with heavy metals is a serious problem for environmental protection and food production. The sources of soil contamination with chromium include various branches of industry, such as iron and steel production, leather tanning, petroleum refining, textile manufacturing and chemical production (Leśniewska and Godlewska-Żyłkiewicz, 2019). The use of mineral and organic fertilizers in agriculture has no significant impact on soil pollution due to relatively low content of heavy metals present in fertilizers. Therefore fertilizer products launched onto the EU market should meet strictly quality and safety requirements.

Chromium occurs in the environment mainly in the trivalent and hexavalent oxidation states. While Cr(III) is an essential trace element for the functioning of living organisms, Cr(VI) is considered to be toxic (Pyrzyńska, 2011), (Miyake *et al.*, 2017), and was classified by the International Agency for Research on Cancer as a Class I Carcinogen (IARC, 1990). Total chromium concentration in fertilizers products does not give enough information of the potential risk of this element to biota. The assessment of chromium's environmental impact and risk to human health should be based on the identification and quantification of its speciation forms. According to EU regulation 2019/1009 the maximum allowable concentration of Cr(VI) in fertilizer products such as mineral and organic fertilizers, liming materials, soil improvers, growing media and plant biostimulants is $2 \text{ mg} \cdot \text{kg}^{-1}$ of dry matter.

2. MATERIALS AND METHODS

For extraction of Cr(VI) content from fertilizer samples, a microwave-assisted extraction procedure was applied. This consisted of 1.25 g of fertilizer being weighed into a 50 mL digestion vessel and 25 mL extraction solution containing $0.5 \text{ mol} \cdot \text{L}^{-1}$ NaOH and $0.28 \text{ mol} \cdot \text{L}^{-1}$ Na_2CO_3 added. Then, 1 mL of $4 \text{ mol} \cdot \text{L}^{-1}$ MgCl_2 was added in order to prevent oxidation of Cr(III) during the extraction procedure, and 0.5 mL buffer solution of each $0.5 \text{ mol} \cdot \text{L}^{-1}$ K_2HPO_4 and KH_2PO_4 . All procedures were performed in triplicate, including the blank solution and SRMs. Capped digestion vessel was transferred to the Discover SP-D 80 microwave digestion system CEM (USA) equipped with infrared temperature control system. This device uses a non-contact, infrared sensor to measure the temperature the liquid inside the vessel. In this study the closed-vessel MAE equipment is selected because it allows performing the extraction at higher temperatures and provides the opportunity to reduce preparation time. After the extraction, the sample was cooled to room temperature, filled up to 50 mL with deionized water and finally filtered through a 0.45 mm membrane filter. Three microwave powers have been tested (100, 200 and 300 W). In order to investigate the optimum MAE time for fertilizers samples, the analysis of Cr(VI) was carried out with increasing extraction time for 5, 10, 15, 20, 30, 45 and 60 min, respectively. Extraction temperature was studied in a range of 90 to 95°C.

Total Cr content was determined by ICP-OES technique after microwave digestion in closed system Mars 5 CEM (USA), using a mixture of nitric and hydrochloric acids. The combination of HNO_3 with HCl in closed system increases the efficiency of digestion due to the high oxidizing power of the mixture and the higher pressure and temperature generated inside the digestion vessel. The accuracy of the method was confirmed through the analysis of the SRM 695 (NIST). Application of Sc as an internal reference standard was intended to compensate for the

strong matrix interference from Ca, Mg, Na, and K present in fertilizers at high concentrations which readily undergo the ionization effectiveness in ICP-OES plasma.



Figure 1. Microwave-assisted extraction.

For the selective determination of Cr(VI) as CrO_4^{2-} ion, an ion chromatography technique with UV-VIS detection based on an ICS-3000 high performance ion chromatograph system from Dionex (USA) was used. The system is equipped with an eluent reservoir, isocratic pump, valve, post-column reaction reagent feeder (PC-10), reaction loop (Dionex Reaction coil 375 μL), and a dual-beam UV/VIS detector (AD-25) with deuterium and tungsten lamp and readable values for $\lambda=540$ nm. After elution, the Cr(VI)-complex was formed using a post-column derivatization reaction with 1.5-diphenylcarbazide (DPC) through a reaction coil. Operating conditions are detailed in Table 1.

Table 1. Separation conditions.

Guard column	IonPac AG7 (4 x 50 mm)
Analytical column	IonPac AS7 (4 x 250 mm)
Eluent	250 mmol/L $(\text{NH}_4)_2\text{SO}_4$ / 100 mmol/L NH_3aq
Eluent flow rate	1.0 mL/min
DPC as PCR flow rate	0.6 mL/min
Injection volume	120 μL
Detection	UV/Vis $\lambda=540$ nm

3. RESULTS AND DISCUSSION

Table 2 shows the total chromium content of the tested fertilizers samples as well as the Cr(VI) content determined by IC technique. The amount of total chromium ranged from (10.9 ± 1.3) $\text{mg}\cdot\text{kg}^{-1}$ to (1651 ± 198) $\text{mg}\cdot\text{kg}^{-1}$, and Cr(VI) content from 0.18 $\text{mg}\cdot\text{kg}^{-1}$ to 6.17 $\text{mg}\cdot\text{kg}^{-1}$. In the three samples, the amounts of Cr(VI) were above the maximum allowable concentration 2 $\text{mg}\cdot\text{kg}^{-1}$, indicating that these materials cannot be used as fertilizers in agriculture. As listed in Table 3, the accuracy of developed method was verified by two certified reference materials.

Table 2. Concentration of Cr(VI) in analyzed samples.

	Total content of Cr $\pm$ U ($\text{mg}\cdot\text{kg}^{-1}$)	Microwave-assisted extraction (MAE)		
		Content of Cr(VI), ($\text{mg}\cdot\text{kg}^{-1}$)	Percentage of Cr(VI) in total content (%)	RSD (%)
Sample A	1533 ± 184	5.08	0.331	5.64
Sample B	1506 ± 181	6.17	0.410	3.59
Sample C	1600 ± 192	3.20	0.200	3.48
Sample D	1651 ± 198	1.31	0.069	5.32
Sample E	25.8 ± 3.1	0.18	0.702	3.28
Sample F	13.7 ± 1.6	<LOD	-	-
Sample G	10.9 ± 1.3	<LOD	-	-

Table 3. Results of Cr(VI) in certified reference materials.

	Found (mg·kg ⁻¹)	Certified value (mg·kg ⁻¹)	Recovery (%)
SRM 2700	13.2	14.9 ± 1.2	88.6
CRM 041	142	148 ± 2	95.9

The determination of trace amounts of chromium by ICP-OES is related to the occurrence of spectral and non-spectral interferences resulting from the great diversity of the chemical matrix of mineral fertilizers. Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra. When spectral overlaps operative and uncorrected, these interferences will produce false-positive determinations and be reported as analyte concentrations. Spectral overlaps may be avoided by using an alternate wavelength or by using an appropriate calibration technique, such as the internal standard method, which consists in adding the same amount of solution of the selected substance to standard, blank and analysed sample solutions. The effectiveness of the interference correction method using scandium as an internal standard was determined by the chromium recovery from certified reference materials SRM 695 and SRM 2700 (NIST).

Table 4. The influence of the calibration method on the result of chromium analysis by ICP-OES technique.

Total content of Cr $\lambda = 267.716$ nm	Calibration method	
	Without correction	Internal standard correction – Sc $\lambda = 255.235$ nm
	mg·kg ⁻¹ ± U U*) = 12%	
Sample A	1430 ± 172	1533 ± 184
Sample B	1407 ± 169	1506 ± 181
Sample C	1280 ± 166	1600 ± 192
Sample D	1314 ± 171	1651 ± 198
SRM 695	Certified value: 244 ± 6 (mg·kg ⁻¹)	
	202 (recovery 82.7%)	236 (recovery 96.5%)
SRM 2700	Certified value: 1055 ± 180 (mg·kg ⁻¹)	
	846 (recovery 80.2%)	854 (recovery 81.0%)

*) the given extended uncertainty (U) is based on standard uncertainty multiplied by extension factor k=2 providing confidence level of 95%. Sampling uncertainty was not taken into account in calculations.

4. CONCLUSION

In the present study microwave-assisted extraction has been successfully used in the preparation of fertilizer samples for the determination of Cr(VI) by ion chromatography. The main advantage of MAE in the preparation of samples to determine Cr(VI) in fertilizer products, is the reduction of the preparation time. The results showed that the present method has a good sensitivity and precision in the Cr(VI) analysis. Further optimization of MAE operating conditions parameters is underway performed. Application of Sc as an internal standard is an appropriate calibration method in the analysis of Cr in fertilizer products by ICP-OES.

REFERENCES

1. Leśniewska, B., and Godlewska-Żyłkiewicz, B. Speciation of chromium in alkaline soil extracts by an ion-pair reversed phase HPLC-ICP MS method. *Molecules*, **24**(6), 1172 (2019).
2. Pyrzynska, K. Redox speciation of chromium using sorption-based systems. *Trends Analyt Chem*, **32**, 100-112 (2012).
3. Miyake, Y., Tokumura, M., Iwazaki, Y., Wang, Q., Amagai, T., Horii, Y., and Oguchi, M. Determination of hexavalent chromium concentration in industrial waste incinerator stack gas by using a modified ion chromatography with post-column derivatization method. *J. Chromatogr. A*, **1502**, 24-29 (2017).
4. IARC. Evaluation of Carcinogenic Risk to Humans: Chromium and Chromium Compounds: Biological Data Relevant to the Evaluation of Carcinogenic Risk to Humans. IARC Monographs. International Agency for Research on Cancer Lyon, France, Volume 49, 49–214 (1990).