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

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## INTRODUCTION

Microwave-assisted extraction (MAE) is a process of using microwave energy to heat solvents in contact with a sample in order to partition analytes from the sample matrix into the solvent. The ability to rapidly heat the sample solvent mixture is inherent to MAE and the main advantage of this technique. Chromium occurs in the environment mainly in the trivalent and hexavalent oxidation states.

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. Hence, the main objective of this study is to develop a MAE of Cr(VI) from fertilizer products and investigate the effect of process variables (microwave power, irradiation time and extraction temperature). Thus, response surface methodology (RSM) using Box–Behnken design was employed in this study. The advantage of this methodology is the simultaneous investigation of individual and interactive effects of process factors on the response from a small number of experiments.

## MATERIALS AND METHODS

- Total Cr content was determined by ICP-OES technique (Varian 720-ES, Mulgrave, Australia) after microwave digestion in closed system (Mars 5 CEM, USA) using 9 ml $HNO_3$ (65% Suprapur®, Merck), 3 ml HCl (30% Suprapur®, Merck),
- Inter-elemental interferences correction was performed using scandium as the internal reference standard (1000 mg/L, SCP Science),
- Determination of Cr(VI) as $CrO_4^{2-}$ ion by IC technique with UV-VIS detection based on an ICS-3000 high performance ion chromatograph system (Dionex, USA).

**Table 1. Separation conditions**.

| | |
|---|---|
| **Guard column**<br>**Analytical column** | IonPac AG7 (4 x 50 mm)<br>IonPac AS7 (4 x 250 mm) |
| **Eluent** | 250 mmol/L $(NH_4)_2SO_4$ / 100 mmol/L $NH_3$aq |
| **Eluent flow rate** | 1.0 mL/min |
| **DPC as PCR flow rate** | 0.6 mL/min |
| **Injection volume** | 120 µL |
| **Detection** | UV/Vis<br>λ=540 nm |


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

| | Total content of Cr ± U, $mg \cdot kg^{-1}$ U* = 12 % | Microwave-assisted extraction (MAE) | | |
|---|---|---|---|---|
| | | Content of Cr(VI), $mg \cdot kg^{-1}$ | Percentage of Cr(VI) in total content, % | RSD, % |
| **Sample A** | 1533 ± 184 | 6.82 | 0.445 | 5.57 |
| **Sample B** | 1506 ± 181 | 6.91 | 0.459 | 12.6 |
| **Sample C** | 25.8 ± 3.1 | 0.18 | 0.702 | 3.28 |
| **Sample D** | 13.7 ± 1.6 | <LOD | - | - |
| **Sample E** | 10.9 ± 1.3 | <LOD | - | - |

*) *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.*

## RESULTS

Experimental factors including: extraction temperature (80–100 °C), microwave power (100–300 W), extraction time (5-60 min) were studied in fifteen trials. The combination of the three independent variables on the three levels was adopted according to Box-Behnken experimental design. The center point was repeated three times.

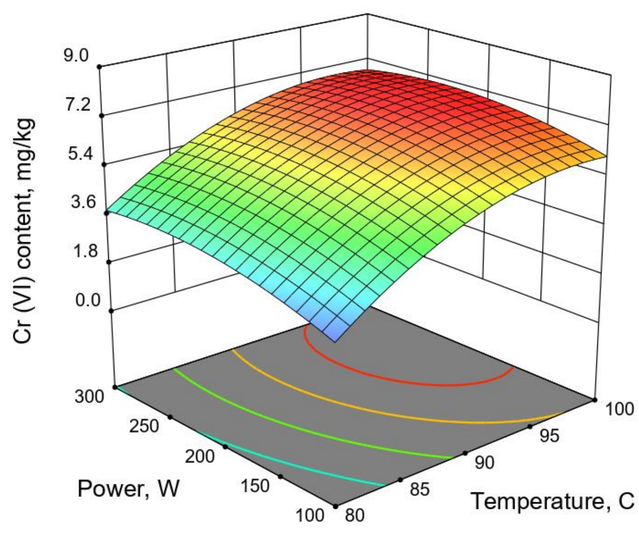


**Fig.1 Response surface plots for the effects of microwave power and extraction time on the Cr(VI) content**

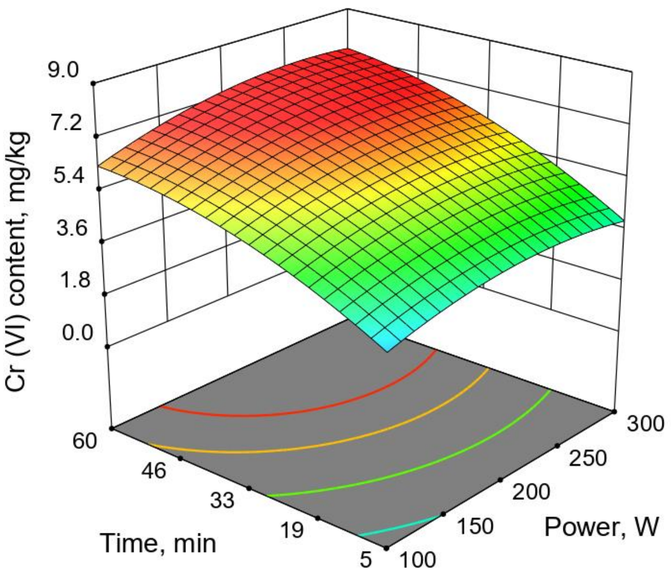


**Fig. 2 Response surface plots for the effects of microwave power and extraction temperature on the Cr(VI) content**

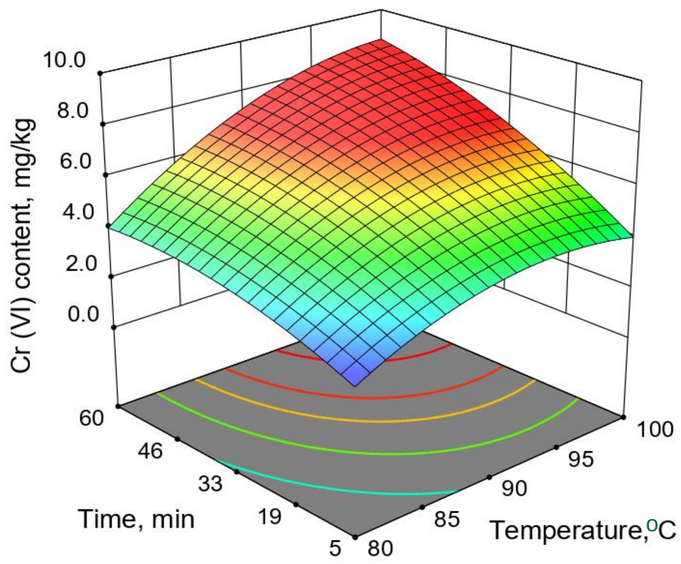


**Fig. 3 Response surface plots for the effects of extraction time and temperature on the Cr(VI) content**

The resulting models allowed for the construction of Response Surface as a function of process parameters, which enabled observations of changes in the dependent variables.

## CONCLUSION

- 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 is the reduction of the preparation time of samples,
- By using closed vessels the extraction can be performed at elevated temperatures accelerating the mass transfer of target compounds from the sample matrix,
- Application of Sc as an internal standard is an appropriate calibration method in the analysis of Cr in fertilizer products by ICP-OES.