



## 7<sup>th</sup> BRAZILIAN MEETING ON CHEMICAL SPECIATION

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### Chemical speciation of hexavalent chromium in organic fertilizer by LC-ICP-MS and spectrophotometry

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Normative Instruction n. 7 of 04/12/2016 of the Ministry of Agriculture, Livestock and Food Supply (MAPA) defines the maximum values of contaminants allowed in organic fertilizers and soil conditioners, including chromium(VI), with a maximum allowed value of 2 mg kg<sup>-1</sup>[1]. The suggested method for this determination is the alkaline extraction by the USEPA 30602 method and the spectrophotometric determination by the 7196A method, with the reaction of Cr(VI) with 1,5-diphenylcarbazide[2]. However, in the case of organic fertilizers, which are quite heterogeneous, in many cases, the basic extraction has the inconvenience of also extracting humic acids present in the sample, resulting in a dark-colored extract, which makes spectrophotometric quantification impossible. Furthermore, humic acids reduce the chromium present in the solution. To overcome this drawback, an extraction method based on ISO 17075-2:2017 is proposed, consisting of extracting the analyte in the fertilizer sample in a pH 8 phosphate buffer. The detection can be done by spectrophotometry and also by Liquid Chromatography - Inductively Coupled Plasma Mass Spectrometry (LC-ICP-MS). In the spectrophotometric procedure, the pH of the extracted sample is adjusted to 2, the complexing agent 1,5-diphenylcarbazide is added, and the Cr(VI) concentration is determined at 540 nm. In the chromatographic method, the extract is diluted in a mobile phase composed of 25 mmol ammonium sulfate and 1 mmol sodium hydroxide, pH 8.0 and determined by LC-ICP-MS. Analytical parameters were calculated. For the spectrophotometric method, a detection limit of 0.12 mg kg<sup>-1</sup> and a quantification limit of 0.40 mg kg<sup>-1</sup> were obtained. For the chromatographic method, a detection limit of 0.016 mg kg<sup>-1</sup> and a quantification limit of 0.054 mg kg<sup>-1</sup> were obtained. Veracity was assessed by analyzing CRM 2701 Hexavalent Chromium in contaminated soil, and recoveries were 90-103% for both methods. These methods are suitable for the determination of Cr(VI) in organic fertilizers, meeting the requirements of IN 7 of MAPA. The proposed procedure employed extraction at pH 8 at room temperature and proved to be a simple, viable and sensitive way to determine this analyte.

1 <http://www.agricultura.gov.br/assuntos/insumos-agropecuarios/insumos-agricolas/fertilizantes/legislacao/in-sda-27-de-05-06-2006-alterada-pela-in-sda-07-de-12-4-16-republicada-em-2-5-16.pdf> (acesso em 20/08/2023).

2 [2] United States Environmental Protection Agency, Method 3060A, in: Alkaline Digestion for Hexavalent Chromium. Office of Solid Waste and Emergency Response, Washington, DC, 1996.

3 ISO 17075-2:2017 | IULTCS/IUC 18-2 Leather — Chemical determination of chromium(VI) content in leather. <https://www.iso.org/standard/67097.html>

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