



Determination of chromium (VI) in primary and secondary fertilizer and their respective precursors



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HIGHLIGHTS

- Wet-chemical extraction method for Cr (VI) tested on recycling fertilizers.
- Low Cr (VI) amounts and fractions for most samples (below 2 mgkg⁻¹).
- Method suitable, but might be hampered by organic matter and Fe (II).

GRAPHICAL ABSTRACT



Reliable Analysis

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ABSTRACT

Hexavalent chromium species (Cr(VI)) are often carcinogenic, of high acute toxicity, highly mobile, and thus pose a severe risk to health and environment. Fertilizers usually contain significant amounts of chromium. Therefore, a reliable analysis of chromium and the fraction of Cr(VI) are crucial for safe use of fertilizers. This problem is expected to increase in the future, since more and more recycled fertilizers emerge due to increasing fertilizer demand and respective supply risks. However, existing analytical methods have been developed for conventional fertilizers and have to be tested whether they are suitable for the new materials. Thus, we performed a wet-chemical extraction for Cr(VI) on several matrices as well as respective quality control experiments including spiking with Cr(III) and Cr(VI) compounds. We found the Cr(VI) amounts to be below 2 mg/kg except for a thermally post-treated sewage sludge ash (SSA) that showed 12.3 mg/kg. The presence of organic matter e.g. in sludge or precipitated struvite caused a reduction of spiked Cr(VI) and thus no satisfying recovery for quality control. Cr(VI) reduction was also observed for SSA, presumably due to the presence of Fe(II) compounds. Even though the tested procedure can be hampered in some recycled fertilizer matrices, it might be adapted to be applicable also for these complex samples.

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1. Introduction

Environmental and health risks arising from chromium (Cr) are strongly related to its oxidation state. Whereas Cr(III) is considered to be a micronutrient and of low water solubility (Unceta et al., 2010), Cr(VI) species are often highly mobile, carcinogenic, and of

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high acute toxicity (Zhitkovich, 2011). Cr is ubiquitous due to its geogenic origin but also due to its widespread use in various industrial processes (Gómez and Callao, 2006). Especially effluents of the latter, as well as accidents, are a source of hexavalent Cr in the environment (Gao and Xia, 2011) and pose respective hazards. Furthermore, Cr species can be transformed into each other, including reduction and oxidation processes as well as conversion of insoluble into soluble compounds and vice versa (Farges, 2009; Zhitkovich, 2011). The Janus-faced properties of Cr - micro-nutrient on one hand and highly toxic species on the other hand - makes it a particular important issue for fertilizers. For instance, the German fertilizer ordinance states a labeling value for total Cr of 300 mg/kg and a limit value of 2 mg/kg of Cr(VI) (Düngemittelverordnung, 2012). The former value means that the respective mass fraction must be stated but the material is still allowed for fertilizer use. On the other hand, Cr(VI) above the limit value prohibits the respective use. Thus, a reliable analysis and speciation is necessary to determine Cr amounts in the environment and assess the respective risks. Even though a great deal of research was done so far on Cr determination and speciation, there are only few findings on Cr, especially its speciation, in fertilizers. Most of the research focuses on Cr speciation in water, wastewater, soil and sediments, and solid wastes (Gómez and Callao, 2006) as well as labor protection related matrices like soil, waste, air, corrosion protection layers, and waste electric and electronic equipment (Unceta et al., 2010). Another important topic is the Cr(VI) analysis in aqueous systems (Barrera-Díaz et al., 2012) and the remediation of contaminated sites. This includes various reduction applications (Barrera-Díaz et al., 2012), inactivation with lignocellulosic material (Miretzky and Cirelli, 2010), remediation from soils, mining and metallurgical waste (Dhal et al., 2013), and remediation with methane oxidizing bacteria (Al Hasin et al., 2010). Various extraction methods and analytical procedures have been developed to determine Cr (Gómez and Callao, 2006; Farges, 2009; Unceta et al., 2010). This includes the recently developed diffusion gradient thin film method (Zhang and Davison, 2015). However, this has been applied mostly to aqueous systems so far (Chen et al., 2014; Pan et al., 2015). The speciation of Cr can be influenced and hampered by the respective sample matrix, mainly oxidation and reduction processes and interaction of different Cr species. The major compounds that might affect the analysis are Fe(II) compounds, organic matter, sulfides, and MnO₂ (Miretzky and Cirelli, 2010; Unceta et al., 2010; Jardine et al., 2013). Regarding fertilizers, there are several procedures to analyze heavy metals, including Cr, but few are focused on speciation (Rezende and Coelho, 2014; Webb et al., 2014; Borges et al., 2015). In case of phosphate rock, the fossil precursor for mineral fertilizer, a Cr speciation technique was developed (El-Sheikh et al., 2013). In this process, Cr(III) is separated after nitric acid digestion with carbon nanotube solid phase extraction. Infrared spectroscopy and XANES were applied to determine Cr(III) and Cr(VI) in sewage sludge ashes (SSA) and thermochemically treated SSA intended for fertilizer use (Vogel et al., 2014, 2015).

The problems regarding Cr analysis in fertilizer materials are expected to increase in the future, since more and more matrices will get important, leading to analytical challenges. Conventional fertilizers face the problems of diminishing resources, energy consumption, supply risks, and contamination with hazardous substances (Scholz et al., 2013; Metson et al., 2015; Krüger, 2016). Thus, the importance of recycled fertilizers is expected to increase also. These recycled products include organic and inorganic materials from wastewater treatment (e.g. sludge, sewage sludge ashes, struvite, calcium phosphates, slags, lime). The existing regulations and standards do not cover these emerging materials (EC, 2003; Düngemittelverordnung, 2012). The respective ordinances are

about to be adapted to include organic fertilizers, for instance. However, it is not clear whether the existing analytical procedures are suitable for these materials and matrices. Thus we applied a standardized wet-chemical extraction for the determination of Cr(VI) in solid samples (DIN EN 15192 (2006)) for a broad variety of fertilizer related substances. Even though the method is well established, it was not yet applied to fertilizer and related materials. Those included organic fertilizer like sludge, recycled fertilizer products like struvite, recycled phosphates and converter lime, sewage sludge ashes as secondary raw materials for fertilizer production, conventional fertilizers and their respective precursors. For the first time, we determined total Cr and Cr(VI) in a broad spectrum of recycling fertilizer materials and performed intensive matrix effect studies. The major goal of the study was to determine whether the sample matrices influence or hamper extraction and analysis and if the procedure is applicable to recycled fertilizers in general.

2. Materials and methods

2.1. Sample acquisition

The tested samples are listed and described in Table 1. We obtained the sludge samples and SSA 1 from operators of three different wastewater treatment plants (WWTP) and SSA 2 from a sewage sludge mono-incineration facility. We received the struvite and recycled P samples courtesy of operators of phosphorus recovery facilities. We got TSP and K-Mg fertilizer from providers of conventional fertilizer and the P rock samples courtesy of Christian Kabbe from the Berlin Centre of Competence for Water. SSA 3 Na₂CO₃ was prepared as described recently (Vogel et al., 2014).

2.2. Sample preparation and Cr(VI) extraction procedure

The samples were air-dried, divided representatively by dividing cross and grinded with a tungsten carbide vibratory disc mill. For the determination of total Cr, the samples were dissolved by microwave-assisted digestion (according to a standard procedure (DIN ISO 11466, 1997-06)). We chose a mixture of perchloric,

Table 1
Primary and secondary raw materials for fertilizer production.

Sample	Description
Sludge 1a	dried sewage sludge from a municipal WWTP, independent samples
Sludge 1b	thickened sewage sludge from a municipal WWTP
Sludge 2	magnesium ammonium phosphate, crystallized from sludge liquor
Struvite 1	magnesium ammonium phosphate, precipitated from digested sludge
Struvite 2	calcium phosphate, crystallized from sewage, independent samples
Recycling P 1a	converter lime
Recycling P 1b	sewage sludge ash from fluidized bed incineration
Recycling P 2	sewage sludge ash from fluidized bed incineration, glowled at 1000 °C for 3 h
SSA 1	sewage sludge ash from grate firing incineration
SSA 1 glowled	sewage sludge ash from grate firing incineration, glowled at 1000 °C for 3 h
SSA 2	sewage sludge ash from grate firing incineration
SSA 2 glowled	sewage sludge ash from grate firing incineration, glowled at 1000 °C for 3 h
SSA 3 Na ₂ CO ₃	sewage sludge ash from fluidized bed incineration, treated with Na ₂ CO ₃ in a rotary furnace for 30 min at 950 °C
P rock magmatic	phosphate rock of magmatic origin
P rock sedimentary	phosphate rock of sedimentary origin
TSP	triple super phosphate, mineral fertilizer
K-Mg fertilizer	potassium chloride and magnesium salt mineral fertilizer

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