Determination of total and soluble chromium(VI) in compost by ion chromatography-inductively coupled plasma mass spectrometry

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Ion chromatography coupled to inductively coupled plasma quadrupole mass spectrometry (IC-ICP-MS) was used for the specific determination of Cr(VI) in compost samples. Potential interferences from humic substances, carbon and chlorine species were avoided by chromatographic separation. Solution detection limits below $150\,ng\,L^{-1}$ were obtained for injection volumes of $100\,\mu L$. Total Cr(VI) was determined by the previous alkaline digestion of the sample, following the method EPA3060A. Recoveries of pre- and post-digestion spikes ($2.5\,\mu g$ and $50\,\mu g\,L^{-1}$ of Cr(VI) as potassium chromate, respectively) were better than 90%, indicating that the combined method can provide accurate results in spite of the high content of organic matter. Detection limits of $6\,ng\,g^{-1}$ were obtained for the total Cr(VI) determination, the repeatability was better than 2% (at $30\,\mu g\,L^{-1}$), and the reproducibility between extractions was around 6%. Soluble Cr(VI) was determined by the leaching of compost samples with water (liquid-to-solid ratio $10:1$). A total Cr(VI) content of $1.2\,\mu g\,g^{-1}$ was obtained for a compost from urban solid residues, whereas the soluble Cr(VI) in the pH range 4–10 was below the detection limit of the leaching method ($1\,ng\,g^{-1}$).

Keywords: Speciation; Chromium(VI); Ion chromatography; ICP-MS

1. Introduction

Compost is the product of the aerobic process during which micro-organisms decompose organic matter into a stable amendment for improving soil quality and fertility. A wide range of organic materials such as wastes from food and agriculture industries, manures, sewage sludges, or urban solid residues are used to produce composts.

The presence of heavy metals in composts can restrict its uses due to health or environmental risks. Basically, heavy metals can enter the environment and the food

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chain during agriculture uses, and workers of composting plants or applicators can be exposed to inhalation of compost dusts [1]. Due to these potential hazards, the maximum total concentrations for a range of heavy metals are one of the parameters used to establish compost quality standards in a number of countries [2]. One of the heavy metals which is subjected to these regulations is chromium. The maximum allowable concentrations of total chromium for compost in the strictest countries range from $50 \, mg \, kg^{-1}$ in the Netherlands to $100 \, mg \, kg^{-1}$ in Germany [2]. However, the total content information is of limited value, because the actual environmental impact of an element depends on the mobility, bioavailability, and toxicity of its different chemical forms [3]. For chromium, its most stable and common oxidation states, Cr(III) and Cr(VI), display quite different properties. Cr(VI) is considered the most toxic form; it has been classified by the International Agency for Research of Cancer as a Group 1 human carcinogen [4]. However, Cr(III) is essential for mammals, being involved in the metabolism of glucose [5], although it is considered a non-essential trace metal for micro-organisms and plants [6]. Cr(VI) compounds are usually highly soluble, mobile and bioavailable compared to Cr(III) compounds. In spite of these hazards, Cr(VI) is not regulated extensively in compost quality standards; only Italy and Greece include it in their regulations, with limits of 0.5 and $10 \, mg \, kg^{-1}$, respectively [2].

A number of methods have been developed for Cr(VI) determination in solid samples. These methods include an extraction step followed by the selective detection and quantification of Cr(VI). Several procedures have been proposed for extracting Cr(VI) from solids, although low recoveries, Cr(III)–Cr(VI) interconversion, and potential interferences have been reported in many cases [7]. Method EPA 3060A [8] can be considered one of most rigorous extraction methods, allowing the quantitative extraction of total Cr(VI) from soils [9] and preventing Cr(III)–Cr(VI) interconversion [10]. Under the strong alkaline conditions of this method, humic substances can be released, which can act as reductants and/or interfere in the subsequent Cr(VI) determination [7, 11]. Namely, the diphenylcarbazide method, which is the most common method for determining Cr(VI) in aqueous solutions [12, 13], suffers from the presence of humic substances, as well as other interfering compounds (molybdenum, mercury, iron, vanadium, hydrogen peroxide, sulfide, sulfite) [11]. The method involves the neutralization of the alkaline extracts prior to the reaction of the extracted Cr(VI) with diphenylcarbazide at pH 1–2. Huo et al. [14] have reported low Cr(VI) recoveries in soil extracts, due to the neutralization step. Several ion-chromatography methods have been proposed to separate Cr(VI) from other interferences, followed by its determination by post-column diphenylcarbazide derivatization and UV-visible molecular absorption [15, 16], conductivity [17] or inductively coupled plasma mass spectrometry (ICP-MS) detection [10].

Compost samples can contain up to 50–60%(w/w) of organic matter, with a high proportion of soluble humic substances (humic and fulvic acids), suitable for extraction in alkaline medium. Thus, the diphenylcarbazide method cannot be applied directly to the alkaline extract unless humic substances are removed [11]. Ion chromatography may be used for on-line separation of humic substances from Cr(VI); however, the use of acidic media should be avoided to prevent precipitation of humic acids. Thus, acidic mobile phases should not be used, and the post-column diphenylcarbazide derivatization, which is performed in $0.5 \, M \, H_2SO_4$, can lead to precipitation of humic acids.

The purpose of this article is to evaluate an analytical procedure for total Cr(VI) determination in composts. Whereas this determination has been extensively studied in

soils and sediments, procedures applied to compost samples have not been reported. The proposed procedure is based on the selective determination of Cr(VI), extracted following EPA Method 3060A, by ion chromatography with ICP-MS element specific detection (IC-ICP-MS). The detection by ICP-MS avoids Cr(VI) derivatization, essential for UV-visible determinations, and problems related to the precipitation of humic acids. The procedure is also applied to the determination of the soluble Cr(VI) in compost lixiviates at different pHs.

2. Experimental

2.1 *Instrumentation*

A Perkin-Elmer Sciex model ELAN 6000 ICP quadrupole mass spectrometer (Toronto, Canada) was used throughout. The sample introduction system consisted of a cross-flow nebulizer and a double-pass Scott-type spray chamber. The plasma operated at 1000 W and default flow rates of argon (outer: $15 \, L \, min^{-1}$, intermediate: $1.2 \, L \, min^{-1}$, nebulizer: $0.9 \, L \, min^{-1}$). Acquisition was performed in peak hopping mode, at one point per spectral peak; the data along the transient signals were acquired with just one sweep per point and dwell times of 500 ms. The following masses were monitored: ^{13}C, ^{35}Cl, ^{52}Cr, ^{53}Cr, and ^{133}Cs.

The high pressure liquid chromatograph system consisted of a Hewlett Packard HP1050 (Geneva, Switzerland). An AS7 column (25 cm length, i.d. 4 mm) with an AG7 guard column (5 cm length, i.d. 4 mm) (Dionex, Sunnyvale, CA) was used for anionic chromatography separations. The volume of the injection loop was 100 μL and the flow rate $1.00 \, mL \, min^{-1}$. An internal standard solution of $50 \, ng \, mL^{-1}$ Cs, prepared from CsCl (Merck, Darmstadt, Germany) in the mobile phase, was constantly pumped at $0.3 \, mL \, min^{-1}$ by a peristaltic pump and mixed with the outflow from the flow injection or the chromatographic system through a T-piece, and the final solution was delivered to the nebulizer of the spectrometer.

The treatment of the chromatograms was performed with the Turbochrom software (Perkin Elmer). Data processing was based on peak area.

2.2 *Reagents, standard solutions, and samples*

Standard stock solution ($1000 \, \mu g \, mL^{-1}$) of Cr(VI) was prepared from K_2CrO_4 (Merck, Darmstadt, Germany). Standard stock solution ($1000 \, \mu g \, mL^{-1}$) of Cr(III) was prepared from $Cr(NO_3)_3 \cdot 9H_2O$ (Merck, Darmstadt, Germany).

A $0.25 \, mol \, L^{-1}$ $(NH_4)_2SO_4$ and $0.1 \, mol \, L^{-1}$ NH_3 at pH 8.5 was used as eluent for anionic chromatography. Solutions were prepared from concentrated sulfuric acid (Scharlau for trace analysis, Barcelona) and ammonia (Merck Suprapure, Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q system (Millipore, Molsheim, France). The compost used in this work was obtained from a Spanish composting plant. The starting material is the organic fraction recovered from solid residues.

2.3 *Procedures*

2.3.1 Extraction of Cr(VI) from compost by EPA3060A [8].   Approximately 2.5 g of dry compost was placed into a 250 mL beaker; 50 mL of the extraction solution ($0.5\,mol\,L^{-1}$ NaOH and $0.28\,mol\,L^{-1}$ Na_2CO_3), 0.5 mL of $1.0\,mol\,L^{-1}$ K_2HPO_4/KH_2PO_4 buffer (pH 7), and 60 mg of $Mg(NO_3)_2$ were added to the solid sample. Magnesium is added to suppress the oxidation of Cr(III). Magnesium nitrate was used, instead of the chloride prescribed by the method, to avoid matrix effects and polyatomic interferences in ICP-MS [10]. The solid was separated by vacuum filtration through a 0.45-µm pore size filtration membrane, and the filtrate and rinses were adjusted to 100 mL with ultrapure water and kept at 4°C until analysis.

2.3.2 Leaching of compost.   A fixed amount of dry compost (40 g) together with 400 mL of the leaching solution (ultrapure water with added nitric acid of potassium hydroxide depending on the final pH) was placed into a polyethylene bottle and agitated in a rotary tumbler at a speed of 28 ± 2 rpm at room temperature for 48 h. Leachates were subsequently clarified by centrifugation at 4000 rpm for 10 min. The pH and the oxidation reduction potential of the supernatant solution were measured and the solid separated from the remaining liquid by vacuum filtration through a 0.45 µm pore size filtration membrane. Three leaching pHs were tested: 4.7, 7.3, and 10.3. Leachates were kept at 4°C until analysis.

3. Results and discussion

3.1 *Chromatographic separation*

Separation of Cr(VI) was performed by using an anion-exchange column. $(NH_4)_2SO_4$/NH_3 at pH 8.5 is recommended by the manufacturer. By using $0.25\,mol\,L^{-1}$ $(NH_4)_2SO_4$/$0.1\,mol\,L^{-1}$ NH_3 (pH 8.5) at a flow rate of $1.00\,mL\,min^{-1}$, Cr(VI) eluted as chromate in 320 s; whereas if the mobile phase was diluted 10-fold, elution time increased up to 600 s, with a significant broadening of the peak. Figure 1 shows the chromatograms of the chromium species and potential interferences. It can be seen that Cr(III) is also retained in the anion-exchange column, with a retention time of 130 s (dead time: 90 s), although the peak showed a significant broadening. Tirez *et al.* also reported retention of Cr(III) in this type of columns [10]. As will be discussed below, Cr(III) was not studied any further, because Cr(III) is extracted as complexes with humic substances, which are partially retained by the column.

 Chromium detection by ICP-MS is associated with polyatomic interferences generated by the presence of carbon or chlorine, which can produce positive bias on the two most abundant chromium isotopes (^{52}Cr and ^{53}Cr). The most significant interferences are $^{40}Ar^{12}C$ and $^{35}Cl^{16}OH$ on ^{52}Cr, and $^{35}Cl^{17}O$ and $^{40}Ar^{13}C$ on ^{53}Cr [18]. Anion-exchange chromatography allows elution of carbon- and chlorine-containing species (e.g. carbonate or chloride) at different times to chromate [10]. As can be seen in figure 1, Cr(VI) is clearly separated from carbonate and chloride, which are eluted before Cr(VI), thus rendering unnecessary the use of reaction cells [19], high-resolution
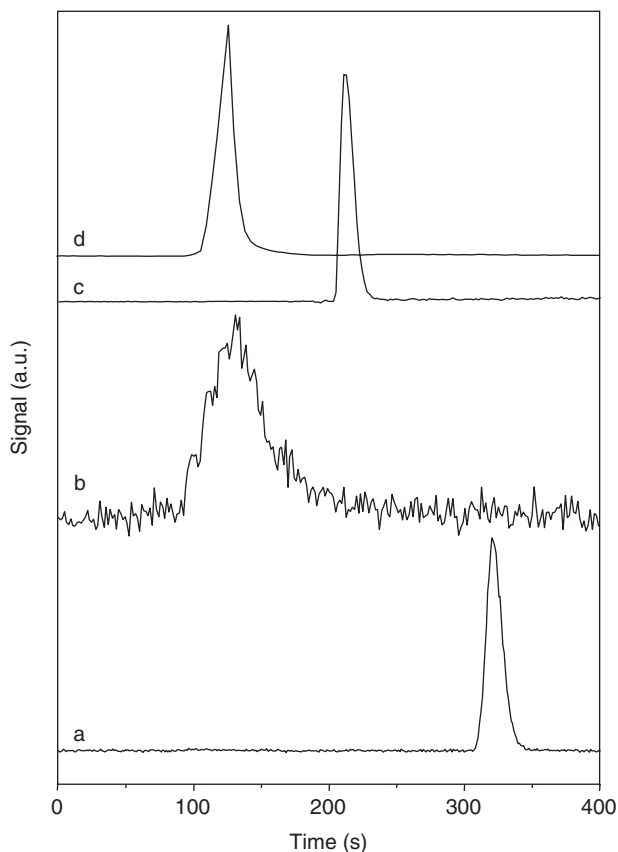
Figure 1.   IC-ICP-MS chromatograms of Cr(VI) (a), Cr(III) (b), chloride (c), and carbonate (d). Isotopes monitored: ^{53}Cr (a and b), ^{35}Cl (c), and ^{13}C (d).

mass spectrometers [20], or mathematical correction procedures [18], to avoid or correct these spectral interferences.

For correction of non-spectroscopic matrix effects and instrumental drift, the eluent was merged at the exit of the column with a solution of $50 \, ng \, mL^{-1}$ caesium at a flow rate of $0.30 \, mL \, min^{-1}$ provided by a peristaltic pump. Thus, the nebulizer of the ICP-MS was fed at the standard flow rate of the instrument, $1.2–1.3 \, mL \, min^{-1}$. The ratio of the measurement at every mass to the ^{133}Cs signal was obtained at each data point along the chromatogram, before integration of the peaks.

Using a 100-μL injection volume, the detection limits for Cr(VI), calculated as three times the standard deviation of the baseline divided by the sensitivity expressed as peak height, were 520 and $140 \, ng \, L^{-1}$ using ^{52}Cr and ^{53}Cr, respectively. Better detection limits were obtained for ^{53}Cr, in spite of its lower abundance, because of the higher baseline signal obtained for ^{52}Cr due to polyatomic contributions ($^{36}Ar^{16}O$ from the plasma and $^{40}Ar^{12}C$ from CO_2 absorbed in the basic mobile phase). Table 1 lists the mass detection limits for the EPA3060A and the leaching methods used in the work. The relative standard deviations of three replicate injections were 2.0 and 1.5% for ^{52}Cr and ^{53}Cr, respectively.

Table 1. Figures of merit of Cr(VI) determination by IC-ICP-MS.

Detection limits[a]	^{52}Cr	^{53}Cr
Concentration (ng L^{-1})	520	140
EPA3060A method (ng g^{-1})	21	6
Leaching method (ng g^{-1})	5	1

[a]3σ criterion.

3.2 Determination of total Cr(VI) in compost. The pH and the oxidation reduction potential of the compost were determined following the EPA Method 9045C [21]. The pH of the compost solution was 8.10 ± 0.3, and its potential 368 ± 5 mV (*vs.* Ag|AgCl|KCl(sat) reference electrode). When these data were plotted in the potential/pH diagram provided by the EPA Method 3060A for soils and sediments [8], no conclusive information about the reducing/oxidizing nature of the sample could be obtained, because the potential/pH data point corresponds to the frontier area in the diagram. Thus, no *a priori* information could be obtained about the major oxidation state of chromium in the sample.

EPA Method 3060A was applied to compost samples to extract total Cr(VI) followed by its specific determination by the IC-HPLC-ICP-MS method described above. Compost samples were spiked with 2.5 µg of Cr(VI) as CrO_4^{2-}, and extraction recoveries in the range of 85–92% were obtained (averaged recovery: $90 \pm 3\%$). This result means that, in spite of the organic content of the compost (38% w/w), the sample is not reductive enough, being capable of supporting Cr(VI). The extracts were spiked with 50 ng mL^{-1} Cr(VI) to check for matrix interferences or Cr(VI) reduction during the measurement process. Since averaged recoveries of $96 \pm 6\%$ were obtained, no significant reduction of Cr(VI) was produced, and quantification could be performed by external calibration.

Figure 2 shows the chromatograms of the alkaline extracts of compost for ^{52}Cr and ^{53}Cr. The chromatograms were also mathematically corrected point by point for polyatomic interferences, following a method developed by Laborda *et al.* [18]. A contribution from ^{35}Cl^{17}O can be clearly identified for ^{53}Cr, as well as the ArC contributions both on ^{52}Cr and ^{53}Cr. After correction, other chromium species could be observed at low retention times, probably Cr(III) complexes with organic matter. The quantification of the Cr(VI) peak provided similar results with both chromium isotopes, as can be seen in table 2. The reproducibility obtained for three independent analysis was 4.5 and 6.0% for ^{52}Cr and ^{53}Cr, respectively. A total Cr(VI) content of 1.2 µg g^{-1} was obtained, which accounts for 6% of the total chromium in the compost studied (total Cr: 19 ± 1 µg g^{-1}) [22].

3.3 *Determination of soluble Cr(VI) in compost leachates*

Water extractions have been used to quantify and define operationally soluble forms of Cr(VI) in soils [9]. Recently, the European Standard EN12506 for characterization of wastes has included the determination of Cr(VI) in water leachates [23]. These leaching processes imply that the Cr(VI)/Cr(III) present in the solid sample may be reduced/oxidized due to the matrix components, altering the original distribution of both
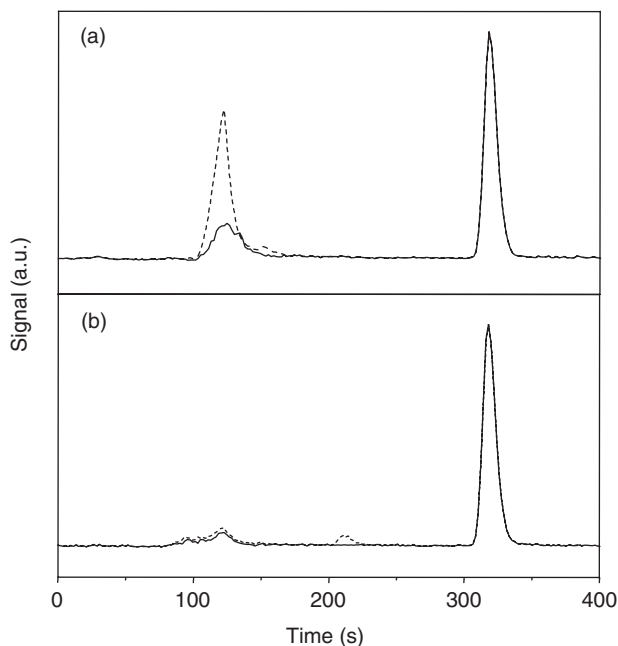
Figure 2.   IC-ICP-MS chromatograms of EPA 3060A extracts from compost samples. (a) [52]Cr, (b) [53]Cr. Dashed line: uncorrected chromatograms; continuous line: corrected chromatograms.

Table 2.   Cr(VI) concentration in compost determined by IC-ICP-MS.

Cr(VI) content ($\mu g\,g^{-1}$)	[52]Cr	[53]Cr
Total Cr(VI)	1.24 ± 0.05	1.21 ± 0.07
Soluble Cr(VI)[a]	<0.005	<0.001

oxidation states [10]. Thus, these procedures are not suitable for total Cr(VI) determinations, although the Cr(VI) extracted provides information about the mobile Cr(VI) fraction, which can be leached to ground waters or absorbed by plants and micro-organisms.

A leaching procedure based on those used for characterization of waste materials was applied for extracting soluble Cr(VI) from compost [24]. Leaching tests were performed in batch mode, at a liquid : solid ratio of 10 : 1, and at three controlled pHs: natural pH (ultrapure water as leaching solution, final pH 7.3), and pHs 4.7 and 10.3 (pH adjusted with nitric acid and potassium hydroxide, respectively). These three conditions cover the most typical environmental situations.

The IC-ICP-MS method described above was applied to the compost leachates at the different pHs. Figure 3 shows the chromatograms of the compost leachates at pH 7.3 for [52]Cr and [53]Cr; similar chromatograms were obtained at the other pHs. As for total Cr(VI), the polyatomic interferences from carbon and chlorine were mathematically corrected to obtain 'clean' chromatograms. Cr(VI) was not detected in the compost leachates at the three pHs studied. Leachates were spiked with $50\,ng\,mL^{-1}$ Cr(VI) to
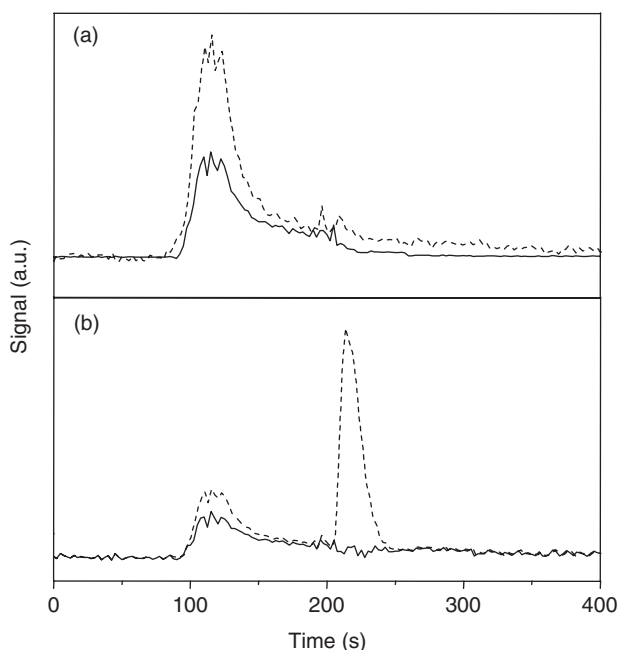
Figure 3. IC-ICP-MS chromatograms of compost leachates (pH 7.3). (a) ^{52}Cr, (b) ^{53}Cr. Dashed line: uncorrected chromatograms; continuous line: corrected chromatograms.

check for matrix interferences, and recoveries in the range of 93–102% were obtained. The corrected chromatograms show the elution of other chromium species at retention times of 100–150 s. However, the elution of these chromium species was not quantitative because the column recoveries were always below 40%. The column recovery was calculated as the ratio of the total corrected peak area of the chromatogram divided by the corrected area of the flow injection peak obtained in the absence of column. These results suggest that Cr(III), probably forming complexes with organic matter, is partially retained in the column, thus preventing its determination.

4. Conclusions

The results from this study show that the alkaline digestion of compost following the Method EPA3060A, and the specific determination of the Cr(VI) extracted by anionic-exchange chromatography and ICP-MS detection, allows the determination of the total Cr(VI) content in this type of materials, which contain high levels of organic matter. When the IC-ICP-MS method is applied to water leachates at different pHs, information on the soluble Cr(VI) and the potential mobility of this species in the environment can be obtained. According to these procedures, the concentration of total Cr(VI) in the compost studied is $1.2 \pm 0.1\,\mu g\,g^{-1}$, whereas the Cr(VI) mobilized in the pH range 4–10 was below $1\,ng\,g^{-1}$. Thus, in spite of its high content in organic reductants, compost is able to support hexavalent chromium, although chromium is not mobilized in this oxidation state.

Acknowledgements

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