Article

CHROMIUM SPECIATION IN ORGANIC FERTILIZERS BY SPECTROPHOTOMETRY

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Received: 03/07/2024; accepted: 06/19/2024; published online: 07/25/2024

In the present study a spectrophotometric method for Cr(VI) determination in organic fertilizers, especially those from tanning industry residues, is proposed. Conditions for chromium extraction, extract clean-up and analytical characteristics of the method were established. The method is based on the complexation of Cr(VI) with 1,5-diphenylcarbazide (DPC) in acid medium (pH 2.0). A mixture of NaOH and Na_2CO_3 solution at 0.125 and 0.07 mol L^{-1} (pH 12), respectively, and heating at 90 °C for 60 min were the best conditions for chromium extraction. Florisil and activated charcoal were tested for clean-up of the extract, with activated charcoal being effective. Under the established conditions, the calibration linear range is up to 2500 μg L^{-1} Cr(VI), the results obtained are in agreement with the value of a certified reference material (CRM041), precision is better than 5% for five consecutive determinations of a solution at 1000 μg L^{-1} of Cr(VI) and the limit of quantification is 1.62 μg g^{-1}. In can be concluded that the method is robust, accurate and precise, and can be easily applied for the determination of Cr(VI) in routine analysis, since it complies with legislation of most countries regarding the maximum allowed concentration of 2 μg g^{-1} of Cr(VI).

Keywords: chromium speciation; organic fertilizers; UV-Vis spectrophotometry.

INTRODUCTION

Chromium is naturally present in rocks, volcanic emissions, soils, plants and animals, and can be in different oxidation states, ranging from –2 to +6. However, in the environment, the most stable oxidation states are +3 and +6, which differ significantly in geochemical, toxicological and biological properties. In humans and animals, Cr(III) is an essential nutrient that plays roles in the metabolism of glucose, fat and proteins, enhancing the action of insulin.[1-3]

Cr(III) has low mobility in the environment and at low concentrations is essential for the functioning of some living organisms, while Cr(VI) has greater mobility. In addition, Cr(VI) is very toxic to humans due to its high oxidizing potential, damaging the DNA inside cells. Cr(VI) is found in several forms, such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions.[4] The CrO_4^{2-} ion is present in solution with pH higher than 6, while $Cr_2O_7^{2-}$ is present at pH lower than 6. At higher pH Cr(III) will form sparingly soluble compounds which presence, concentration and forms in a given compartment of the environment depend on different chemical and physical processes, such as hydrolysis, complexation, redox reactions and adsorption.[5] Chromium is used for a variety of purposes, but around 80% is used by the metallurgical industry, followed by the chemical (8%) and refractory industries (11%). Accordingly, chromium is used in the manufacture of ferrous (stainless steel) and non-ferrous metal alloys. Its main use is in civil construction structures, electroplating, leather tanning, wood preservative and catalyst in the synthesis of organic compounds.[6]

As a consequence of chromium applications, the element is dispersed in the environment, which may negatively affect animals and plants, depending on the chemical form and concentration, as already mentioned.[7]

It is also noteworthy that chromium may be present in soil correctives and in organic fertilizers from industrial waste, including tanneries. The use of this waste has been growing owing to the significant number of industries in this field, and as an alternative for the profitable use of the waste from this sector. Studies prove that the use of waste from tanneries as fertilizers and acidity correctors for the soil is effective due to its considerable amount of nitrogen - around 14% - in its organic form. In addition, these residues have a content of organic matter itself. Therefore, it is a residual material that has a high value for agriculture.[8] Another important aspect of this fertilizer is the slow and controlled release of nutrients to the plants, unlike other fertilizers, such as urea.

Similarly, organic fertilizers from other raw material sources are also increasingly produced and applied to the cultivation of different crops. These, in addition to organic matter, both from vegetable and animal source, can be supplemented with various added nutrients, usually organominerals. As is known, these nutrients are responsible for increasing agricultural production, most of which come from naturally occurring raw materials,[9] but may contain several metals in a large range of concentrations.

In view of the characteristics of chromium, it is particularly important to monitor and quantify chromium species contained in different kinds of samples,[10,11] especially in organic fertilizers, mainly from the tanning segment. These fertilizers can contain high levels of the element, which can lead to contamination of the soil, water and plants.[12] This is also necessary and indispensable due to the fact that legislation in several countries, such as Brazil,[13] and those of the European Union (EU),[14] limits the maximum concentration of Cr(VI) to 2 mg kg^{-1} (2 μg g^{-1}). With regard to total Cr, maximum amount of 200 and 300 mg kg^{-1} is established in Brazil[13] and Germany[15] regulations, respectively, while values for the presence of Cr(III) are not estimated. Therefore, in view of the characteristics of the Cr species, the most important aspect is to find out if Cr(VI) is present and what is its concentration in organic fertilizers.

Hexavalent chromium determination can be done by spectrophotometry at 540 nm (visible region, Vis), based on the complexation of Cr(VI) with diphenylcarbazide (DPC).[11,16] This reaction is very specific for Cr(VI), while Cr(III) does not form a complex, thus allowing the direct determination of Cr(VI) in solution. On the other hand, chromatographic methods based mainly on ion exchange (IC) are the most used for chromium speciation analysis, mostly Cr(VI).[16] In this case, Vis-spectrophotometry, with post column derivatization with

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Associate Editor handled this article: Eduardo M. Richter

DPC, and inductively coupled plasma mass spectrometry (ICP-MS) are among the most used techniques for detection and quantification of the analyte; being reference methods for Cr speciation analysis.[17] In the case of ICP-MS, the determination can be made via external calibration or by isotopic dilution (ID). ID-ICP-MS is indicated by United States Environmental Protection Agency (USEPA)[18] and was evaluated by Huo and Kingston,[19] and Zuliani *et al.*,[20] for Cr speciation analysis in environmental solid samples. Determination by ID-ICP-MS, mainly by species-specific isotopic dilution (SSID), leads to more accurate results, since possible interconversions of Cr species can be monitored and considered during the analysis. In this method, sample is spiked with a ^{53}Cr(VI) (enriched in ^{53}Cr) and a ^{iso}Cr(III) (enriched in ^{50}Cr). The large quantity of ^{iso}Cr(III) in an easily oxidizable form competes with sample Cr(III) in the oxidization, reducing the method-induced oxidation of Cr(III) in the sample. This method also corrects for the reduction of Cr(VI).[19,21]

Maintaining chromium species is one of the greatest difficulties during the analytical process, especially the Cr(VI) species, which is not much stable, especially in acidic solutions and in the presence of reducing species, such as organic matter and Fe(II). In this context, despite different proposals for extraction solutions for chromium species from solid samples, the most recommended is the extraction of Cr(VI) by using aqueous solutions with a pH around 12.[10,19] For this, solutions of NaOH, Na_2CO_3 or a mixture of NaOH and Na_2CO_3 are the most used.[22] However, extraction of chromium for chemical speciation analysis is performed with other extractors, such as water, sodium phosphate and sulfuric acid solutions.[23] Regarding the determination of Cr(VI) in different types of fertilizers, both conventional or obtained from different residues, most analytical methods are based on the extraction of Cr(VI) by an alkaline medium and determination by Vis, ICP-MS, IC-ICP-MS and other analytical techniques. However, it is not uncommon to report difficulties in the analyte extraction and chromium species determination, where interconversion of chromium species can occur.[24,25]

Owing to the difficulties of chromium speciation analysis, the aim of the present work is to quantify the Cr(VI) species quickly, effectively and at low cost using Vis-spectrophotometry with DPC, in order to meet the maximum limit established for organic fertilizers. Evaluations related to the conditions of Cr(VI) extraction and extract clean-up, the most critical steps in the method, were studied. The accuracy of the method was evaluated through the analysis of certified reference material (CRM) and applied for the determination of Cr(VI) in organic fertilizer of different origins.

EXPERIMENTAL

Equipment

Weighing of the samples was done by using an analytical balance (Shimadzu model AY220, Barueri, Brazil). Heating of the solutions for the chromium extraction procedure was carried out on a heating plate (Marconi, model 239, Piracicaba, Brazil). For absorbance measurements of the absorbance of the Cr-DPC complex, monitored at 540 nm, an Ocean Optics spectrophotometer was used (model USB 2000, Orlando, USA).

Total chromium was determined by inductively coupled plasma optical emission spectrometry (ICP OES) using a Spectro Cirus CCD spectrometer (Spectro, Kleve, Germany).

Reagents and solutions

All solutions were prepared with ultrapure water (18.2 MΩ cm), obtained by a Milli-Q (Merck Darmstadt, Germany) purification system. Reference solutions and reagents were of high analytical grade or better. The calibration curve was prepared by appropriate dilution of a stock solution of 100 mg L^{-1} of Cr that was prepared from potassium chromate (K_2CrO_4, Merck, Darmstadt, Germany). Solutions of sodium hydroxide (NaOH, Neon, São Paulo, Brazil), sodium carbonate (Na_2CO_3, Neon, São Paulo, Brazil) and a mixture of NaOH and Na_2CO_3 were tested for chromium extraction. A solution of 1,5-diphenylcarbazide (Vetec Química Fina, Rio de Janeiro, Brazil) at 0.2 mmol L^{-1} was prepared by solubilizing DPC in 30 mL of acetone and completed to 100 mL with high-purity water.

A buffer solution at pH 2.0 was prepared by mixing 3.8 mL of a 0.2 mol L^{-1} solution of potassium chloride (KCl, Merck, Darmstadt, Germany) and 0.9 mL of a 0.2 mol L^{-1} hydrochloric acid (HCl, Merck, Darmstadt, Germany), and completed to 15 mL with purified water. This solution and a solution of sulfuric acid (H_2SO_4, Merck, Darmstadt, Germany) in water, in a 1:3 ratio, was used to adjust the pH of the solution where the complexation of DPC with Cr(VI) occurs. All solutions were prepared and kept in 15 or 50 mL polypropylene flasks (Sarstedt, Nümbrecht, Germany).

Florisil (Merck, Darmstadt, Germany), with a particle size of 150 to 250 μm, and activated charcoal (Sigma-Aldrich, Brazil), with a particle size less than 100 μm, were evaluated for clean-up of the extracts. Filters with a porosity of 0.22 μm (Sartorius, Goettingen, Germany), adaptable to a syringe, were used to filter the solutions before analysis.

Samples and certified reference material

Samples of organic fertilizers from leather waste were provided by the Federal Laboratory for Agricultural Defence (LFDA, MAPA), in powder form and with a particle diameter less than 100 μm (identified as sample A). No additional treatment was performed, except drying at 105 ± 2 °C, either for total chromium determination or for chromium speciation analysis. Other samples of organic fertilizer were acquired from local market and identified as samples B, C and D. These samples are not from tanning residues. The samples were also dried at 105 ± 2 °C until constant weight and a portion was ground in a ball mill (Retsch model PM200, Haan, Germany) until achieving particle size lower than 100 μm.

To evaluate the accuracy of the proposed method for chromium speciation analysis, the certified reference material (CRM) "Chromium VI Sandy clay soil" (CRM041, Merck, Darmstadt, Germany) was used. San Joaquim Soil (SRM 2709, National Institute of Standards & Technology, Gaithersburg, USA) was used to evaluate the accuracy of the method for determining total chromium and other elements. These CRM were submitted to the same treatment as the samples (decomposition or extraction for Cr(VI) determination), without any other previous treatment.

Chromium extraction from samples

Tests for extracting chromium from fertilizers and CRM041 were carried out with solutions of NaOH, Na_2CO_3 and a mixture of NaOH and Na_2CO_3. Furthermore, the effect of temperature, time and the ratio of sample mass to extractor solution volume on the extraction efficiency of Cr(VI) species was studied.

All parameters were optimized in a univariate way. To study the effect of temperature, extraction time and extractor solution composition, the sample mass was set at 10 mg and the extractor volume at 10 mL. When the best condition for one of the parameters was achieved, it was fixed, and the effect of another parameter was studied. The study was carried out for all samples, however, the experimental data were shown only for sample A (tanning residue),

since the concentration of Cr(VI) is higher, which facilitates analysis. When the extractions were performed under heating, the extracts were left to stand for approximately 60 min for cooling and decantation of the solid material. Subsequently, part of the supernatant was removed to carry out the clean-up. Florisil and activated charcoal were tested to clean-up the extract. Experiments for clean-up were done at pH 12, pH 2.0 and after Cr(VI) complexation with DFC. The pH of the filtered extract was adjusted with the KCl/HCl (pH 2.0) and H_2SO_4 1:3 solutions. Finally, the DFC solution was added in order to form the complex with Cr(VI), the volume adjusted to 10 mL with purified water and the measurement of absorbance was carried out at 540 nm.

Determination of total chromium and major elements in organic fertilizers

For the determination of total Cr and major element concentration, samples and CRM were decomposed with acid in a closed system, using a microwave oven from Berghof (model Speedway, Germany). Aliquots of 150 mg of the sample were weighed and transferred to the decomposition flask and 5.0 mL of 14.4 mol L^{-1} HNO_3, 0.5 mL of 12 mol L^{-1} HCl and 0.5 mL of 25 mol L^{-1} HF were added. Flasks were properly closed and heated. The heating program consisted of a 15 min ramp with a dwell time of 35 min, with maximum pressure, temperature and microwave radiation power of 40 bar, 150 °C and 1500 W, respectively, as suggested by the equipment manufacturer. After cooling, the solution was transferred to a polypropylene flask and the volume adjusted to 50 mL with purified water.

Total Cr was determined by ICP OES using the 267.716 nm emission line; 1400 W RF power; 15, 0.20, and 0.70 L min^{-1} for plasma, auxiliary and nebulizer gas flow rate, respectively.

Cr(VI) determination by spectrophotometry

Calibration solutions were prepared under the same conditions as sample solution extracts in concentrations from 10 to 2500 µg L^{-1} Cr(VI). The complexation, both for the calibration curve and for the samples (extracts), was performed by sequentially mixing 1.0 mL of Cr(VI) reference solution or 1.0 mL of the extract, 1.0 mL of the KCl/HCl solution at pH 2.0, 50 µL of H_2SO_4 diluted 1:3 and 1.0 mL of DFC, and the volume adjusted to 10 mL with purified water. The absorbance reading was done 5 min after mixing the reagents. A glass cuvette with a 10 mm optical path was used for absorbance measurement.

RESULTS AND DISCUSSION

The selective reaction of chromate or dichromate with DFC takes place at pH around 2, as previously described in the literature.[10,26] Therefore, no exhaustive study was carried out to optimize the method, except the addition of the 1:3 sulfuric acid and KCl/HCl solution to adjust the reaction medium to pH 2.0. At this condition, the oxidation of 1,5-diphenylcarbazide to 1,5-diphenylcarbazone occurs and, consequently, the reduction of Cr^{6+} to Cr^{3+}, forming a stable complex with an intense violet color, which results of a spectrophotometric method of good sensitivity, reaching limits of detection in the order of low µg L^{-1} range. The reaction is shown in Equation 1:

$$2CrO_4^{2-} + 3C_{13}H_{14}N_4O + 8H^+ \rightarrow [Cr(C_{13}H_{12}N_4O)_2]^+ + C_{13}H_{12}N_4O + 8H_2O + Cr^{3+} \quad (1)$$

Clean-up of the extract

Fertilizer extracts have a slight yellowish/brown color, which absorbs in the same region as the Cr-DPC complex. In this way, the analytical performance of the method is compromised, especially the limit of quantification. Therefore, Florisil and activated charcoal were evaluated as adsorbents to remove color from the solution in order to improve the analytical characteristics of the method. Tests were carried out with a reference solution of Cr(VI) and with the extract solution from the samples. For this purpose, a 1.0 mg L^{-1} Cr(VI) solution at pH 12 and 2 was used, since the chromium extraction and complexation reactions are carried out at these pH, respectively. Experiments were carried out before and after the reaction of the analyte with the complexing agent in order to verify the efficiency of color removal and the possible loss of the analyte. For the clean-up study, masses of 10, 25 and 50 mg of the adsorbent were added to 10 mL of the solutions to be evaluated. After addition of the adsorbent, the solution was manually shaken and allowed to stand for 1 min and then filtered through 0.22 µm polytetrafluoroethylene (PTFE) filters.

Figure 1a shows the effect of the adsorbent Florisil and activated charcoal on the adsorption of Cr(VI) present in a solution at 1.0 mg L^{-1} and at pH 12. As can be seen, there is almost complete removal of chromium from the solution by using Florisil at this condition, while it is not retained by the activated charcoal. Therefore, subsequent experiments were performed only with activated charcoal. As can be observed in Figure 1b, the Cr-DPC complex and the Cr(VI) standard are adsorbed on activated charcoal at pH 2.0, with removal close to 100% from the solution. On the other hand, Cr(VI) is not removed when clean-up is done at pH 12. After establishing the condition for the standard solution of Cr(VI), experiments were applied to remove the color from the sample extract. It was verified that this procedure proved to be efficient in removing the color from the solution, where the absorbance at 540 nm of the extract reduced from around 0.35 to close to zero after treatment with activated charcoal. Furthermore, the procedure is very simple and quick compared to cloud point extraction,

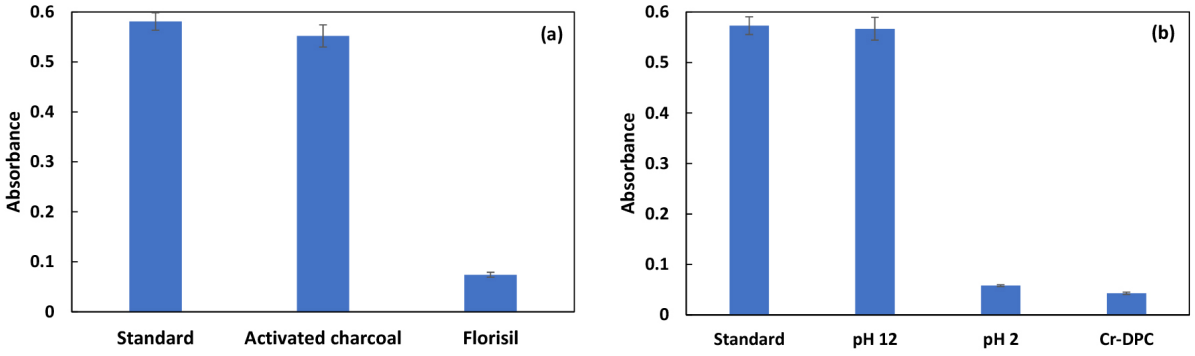

Figure 1. *(a) Effect of the adsorbents on the adsorption of Cr(VI), 1.0 mg L^{-1}, at pH 12; (b) effect of the pH (12 and 2) on the adsorption of Cr(VI), 1.0 mg L^{-1}, and the complex Cr-DPC*

for example.[11] In short, by adopting this clean-up procedure, the limit of quantification (LOQ) of the method is improved.

Conditions for chromium extraction

As mentioned in Experimental section ("Chromium extraction from samples" sub-section), solutions of NaOH and Na_2CO_3 and mixtures of NaOH and Na_2CO_3 at different concentrations were tested, since the extraction of Cr(VI) is generally efficient in this medium and avoids the conversion of Cr(VI) to Cr(III).[18] Therefore, these solutions were initially tested in order to verify the efficiency of Cr(VI) extraction. Similar extraction conditions were adopted to those reported previously,[10,27,28] for extraction of chromium in solid samples, such as fly ash, soil, foodstuffs, biological samples, among others, but not in organic fertilizers. As shown in Figure 2, there is a great influence of the solutions on the extraction of the analyte in relation to the extractor used. It should be noted that extractions were performed by using 10 mg of sample A, 10 mL of extracting solution, extraction time of 60 min and temperature of 90 °C, 1.0 mol L^{-1} NaOH, 0.28 mol L^{-1} Na_2CO_3 and a mixture of 1.0 mol L^{-1} NaOH plus 0.28 mol L^{-1} Na_2CO_3.

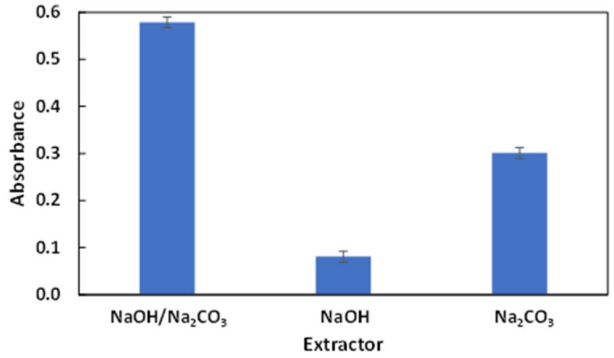

Figure 2. *Effect of the solution composition on Cr(VI) extraction from organic fertilizer. See in the text the other extraction conditions. Values represent the mean and standard deviation of three replicates (n = 3)*

As can be seen in Figure 2, the $NaOH/Na_2CO_3$ mixture provides higher Cr(VI) extraction efficiency from the fertilizer obtained from tanning residue. Similarly, this solution also proved to be better for the other organic fertilizer samples as well as the CRM.

It can be observed in Figure 3 that the temperature also has a great influence on the extraction of Cr(VI). This effect is similar for all fertilizers tested and for the CRM. Extractions were performed by using 10 mg of sample A, 10 mL of 1.0 mol L^{-1} NaOH plus 0.28 mol L^{-1} Na_2CO_3 extracting solution, and extraction time of 60 min. In general, similar behavior was also observed for Cr(VI) extraction from different kind of samples.[29,30]

However, in this work the best temperature was 90 °C, different from other studies where good Cr(VI) extraction efficiency was verified at temperatures around 50 °C.

Similar to the other evaluated parameters, time influences the extraction of Cr(VI). Thus, it was observed that at least 60 min (Figure 4) are necessary to quantitatively extract chromium, both from the organic fertilizers and CRM. Extractions were performed by using 10 mg of sample A, 10 mL of 1.0 mol L^{-1} NaOH plus 0.28 mol L^{-1} Na_2CO_3 extracting solution, and temperature of 90 °C.

Effect of extraction solution concentration and sample mass

After setting the time and temperature conditions at 60 min and 90 °C, respectively, the effect of the concentration of the

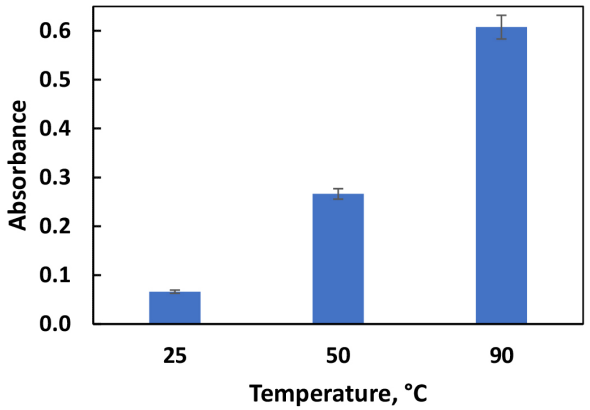

Figure 3. *Effect of temperature on Cr(VI) extraction from organic fertilizer. See in the text the other extraction conditions. Values represent the mean and standard deviation of three replicates (n = 3)*

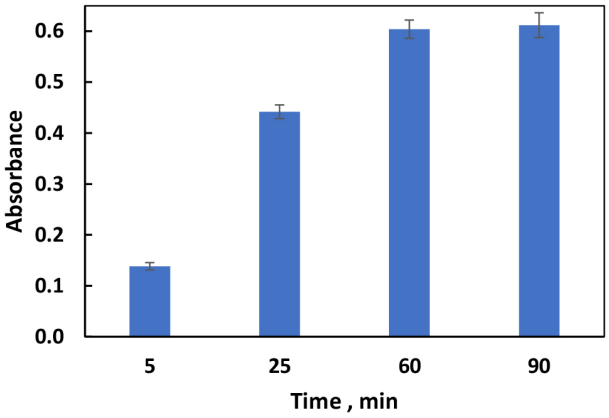

Figure 4. *Effect of time on Cr(VI) extraction from organic fertilizer. See in the text the other extraction conditions. Values represent the mean and standard deviation of three replicates (n = 3)*

$NaOH/Na_2CO_3$ extracting solution was studied. For this purpose, extractions were done by using solutions of 0.50 mol L^{-1} of NaOH plus 0.28 mol L^{-1} of Na_2CO_3, 0.25 mol L^{-1} of NaOH plus 0.14 mol L^{-1} of Na_2CO_3 and 0.125 mol L^{-1} of NaOH plus 0.07 mol L^{-1} of Na_2CO_3, with the volume of extractor and mass of the sample maintained at 10 mL and 10 mg, respectively. According to Figure 5, the extraction is similar in the three conditions evaluated.

Nevertheless, in addition to the solution consisting of 0.125 mol L^{-1}

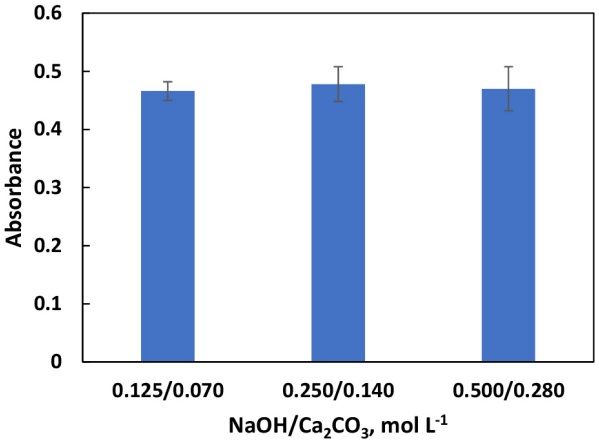

Figure 5. *Effect of $NaOH/Na_2CO_3$ solution concentration on Cr(VI) extraction from organic fertilizer. See in the text the other extraction conditions. Values represent the mean and standard deviation of three replicates (n = 3)*

of NaOH and 0.07 mol L^{-1} of Na_2CO_3 being as efficient as those with higher concentrations, at this concentration the blank values are lower, and it is easier to adjust the pH for the complexation reaction.

Finally, the effect of the sample mass, considered as the ratio of sample mass to extractor solution volume, was studied. The time, temperature and extractor were fixed at 60 min, 90 °C and 0.125 mol L^{-1} NaOH plus 0.07 mol L^{-1} Na_2CO_3, respectively. For these tests, the volume of the extracting solution was maintained at 10 mL and the sample mass was changed from 5 to 150 mg for the organic fertilizer A and 10 to 50 mg for the CRM. The effect can be observed in Table 1.

Table 1. Effect of sample mass on Cr(VI) extraction (n = 3)

Sample / mg	Volume / mL	Mass to volume ratio	Cr(VI) / (μg g^{-1})
5	10	0.0005	< LOQ[b]
10	10	0.0010	1226 ± 72
25	10	0.0025	674 ± 87
50	10	0.0050	234 ± 18
150	10	0.0150	< LOQ[b]
10[a]	10	0.0010	205 ± 10
25[a]	10	0.0025	204 ± 7
50[a]	10	0.0050	200 ± 9

[a]Obtained value for the CRM041 (certificate value: 203 ± 17 μg g^{-1}); [b]LOQ (limit of quantification): 1.62 μg g^{-1}.

As can be seen in Table 1, there is a strong influence on the Cr(VI) extraction in relation to the sample mass to volume ratio of the extracting solution, with the best condition being 0.0010. In this sample, Cr(VI) was not detected with lower sample masses (ratio of 0.0005). On the other hand, it was also not possible to determine chromium in the extraction carried out with a mass of 150 mg (ratio 0.0150), a fact attributed to the presence of interferences that inhibited the formation of the DFC-Cr complex. Similar behavior was observed for the other samples studied. No further studies have been done to identify or circumvent the interference. However, despite cleaning-up the sample solutions, remaining organic compounds could be present and thus interfere in the analysis.

Through the analysis of the fertilizer samples decomposed with acid and determination by ICP OES, it was verified the presence of relatively high concentration of some elements. Total concentrations of up to 0.7 mg g^{-1} of Na, 15 mg g^{-1} of Al, Ca, Fe and Mg, 20 mg g^{-1} of S and Zn, 40 mg g^{-1} of P and 50 mg g^{-1} of K are present in the samples. Although elements such as Fe, V, Mo, Cu, and Hg form complexes with DFC,[31] interferences are only observed at high concentrations of these elements, which is not the case in the present samples.

Three conditions (ratio of 0.0050, 0.0025 and 0.0010) were also tested for Cr(VI) quantification in CRM041. As can be observed, in all conditions the values obtained are in agreement with the certified value at a confidence level of 95% (*t*-test). In addition, it was possible to quantify the analyte when a mass of 50 mg of the CRM is used (ratio of 0.0050). This indicates that the matrix of CRM041 is different from those of the organic fertilizer samples. Probably the concentration of organic matter is higher in the fertilizers.

Analytical characteristics of proposed method and application to real sample analysis

The accuracy of the proposed method was evaluated by analyzing the certified reference material CRM041, one of the few CRMs with certified values for Cr(VI). As can be seen in Table 2, the value obtained for the CRM041 agrees with the certified value at a confidence level of 95% (*t*-test). In addition, analyte recovery test was done by spiking the sample A with a Cr(VI) solution. Spike was done at the extraction step. Recovery of Cr(VI) was higher than 95%, indicating no analyte losses or species interconversion occurs.

Table 2. Results obtained for Cr(VI) in organic fertilizers and in CRM. The results correspond to the mean and standard deviation of three replicates

Sample	Cr(VI) / (μg g^{-1})	Cr total / (μg g^{-1})
A	1227 ± 73	25698 ± 1191
B	3.31 ± 0.17	60.0 ± 15.6
C	8.12 ± 0.21	34.3 ± 2.9
D	1.85 ± 0.14	11.2 ± 0.7
CRM041[a]	210 ± 7	–

[a]CRM041: 203 ± 17 μg g^{-1}.

The limit of detection (LOD) and quantification are 0.54 and 1.62 μg g^{-1} Cr(VI), respectively, which are below the maximum limit of Cr(VI) established by the Brazilian and EU legislation (2 μg g^{-1}). The LOD and LOQ values were estimated according to IUPAC recommendations (LOD = B + 3s and LOQ = B + 10s, with B being the blank value and s the standard deviation, considering the mean and standard deviation of ten determinations of the blank). The linearity of the Cr-DFC complex extends up to 2500 μg L^{-1} of Cr(VI). The accuracy of the method, expressed as relative standard deviation (RSD), is better than 5%, considering five consecutive determinations of 1000 μg L^{-1} Cr(VI).

On the other hand, it is important to note that under these conditions it is possible to determine Cr(VI) in concentrations lower than that required by Brazilian and EU legislation.

Table 2 shows the results obtained for four samples of organic fertilizer, with sample A being the fertilizer obtained from leather waste.

CONCLUSION

Monitoring chromium species, mainly the hexavalent form, in organic fertilizers, especially residues from tanning industries, is relevant due to their carcinogenic and environmental action. Therefore, a spectrophotometric method was developed that complies with Brazilian and EU legislation regarding the maximum concentration of Cr(VI) allowed in these fertilizers. The method consists of extracting Cr(VI) with a NaOH/Na_2CO_3 solution at pH 12, clean-up of the extract with activated charcoal and spectrophotometric determination of chromium as Cr-DFC complex. Quantification by spectrophotometry through Cr-DFC complexation is of low cost, quick and simple to implement, with LOD and LOQ of 0.54 and 1.62 μg g^{-1}, respectively, below the limit of 2 μg g^{-1} established in Brazil and EU legislation. In addition, under the conditions established, the method is accurate and precise and meets the conditions to be applied in routine analysis.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Process No. 310228/2021-2 and 435671/2018-9) for financial support and scholarship for the authors.

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