



Determination of chromium(VI) in soil improvers

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SAMENVATTING

Binnen CEN/TC223/WG 4 *Soil improvers and growing media* is een nieuwe CEN-methode ontwikkeld voor de bepaling van Cr(VI) in bodemverbeterende middelen en groeimedia: prEN 00223122:2021 *Soil improvers and growing media — Determination of chromium(VI)*.

VITO heeft de toepasbaarheid van deze methode geëvalueerd door verschillende soorten bodemverbeterende middelen te analyseren, bestaande uit compost, verschillende fracties digestaten en slib. Alle monsters, als zodanig en geaddeerd met Cr(VI) en Cr(III), werden geëxtraheerd met behulp van een fosfaatbuffer met een pH tussen 7,0 en 8,0. Het Cr(VI)-gehalte werd bepaald door middel van ionenchromatografie na kolomderivatisering met 1,5-difenylocarbazide in zure oplossing en gemeten bij 540 nm.

Wat betreft de uitvoering van de methode en de beschrijving in de ontwerp EN methode was het niet mogelijk om de extracten te filtreren vanwege verstopping van de filter. Door als alternatief voorafgaandelijk een centrifugatiestap toe te passen was het mogelijk de vaste fractie van de extractieoplossing te scheiden. Vanwege de donkere kleur van het monster is het raadzaam om het monster vóór de IC-analyse minimaal 10 keer te verdunnen om de analysekolom te beschermen. Daarom was de gebruikte IC-kalibratie een factor 10 lager dan die beschreven in de ontwerp EN-methode. Beide aspecten, centrifugeren en verdunnen voorafgaand aan IC-analyse, samen met een geschikt kalibratiebereik, dienen bij voorkeur in de ontwerp EN-methode te worden geïntroduceerd.

Wat betreft de analyseresultaten wordt duidelijk aangetoond dat de aanwezigheid van Cr(VI) in het monster sterk afhankelijk is van de matrixsamenstelling. Er bleef geen Cr(VI) achter in de Cr(VI) verrijkte monsters van de verschillende slibmonsters en dikke/ruwe digestaatmonsters, zelfs niet na analyse binnen 60 min na extractie. Het is onwaarschijnlijk dat in dit soort monsters Cr(VI) te verwachten is. Voor de andere onderzochte monsters varieerde de Cr(VI) terugvinding tussen 32% en 94% bij meting binnen 60 minuten na extractie. Meten na 24 uur resulteerde in een extra afname van de recovery met 3-9%, afhankelijk van het geanalyseerde monster.

In de ontwerp EN-norm wordt opgemerkt dat het terugvindingspercentage van een geaddeerde Cr(VI)-oplossing tussen 80% en 120% moet liggen. Bovendien, als de toegevoegde Cr(VI) niet wordt gedetecteerd of significant lager is dan de verwachte waarden, is dit een indicatie dat de bodemverbeterende middelen en groeimedia reducerende middelen bevatten. Dit leidt tot de conclusie dat deze bodemverbeterende middelen en groeimedia geen Cr(VI)-gehalte hebben (onder detectiegrens). Dit wordt bevestigd door de uitgevoerde metingen op een selectie van bodemverbeterende middelen.

In de Meststoffenverordening is ter verificatie een grenswaarde van 2 mg/kg ds opgenomen. Voor monsters met een hoog droge stof gehalte is het haalbaar om deze grenswaarde te verifiëren. Maar voor sommige monsters kan het droge stof gehalte aanzienlijk lager zijn en dit heeft invloed op het uiteindelijke Cr(VI)-resultaat uitgedrukt in mg/kg ds. Bijvoorbeeld, bij een droge stof gehalte van 44% is de rapportagegrens < 1,0 mg/kg ds en bij een droge stof gehalte van 22% is de rapportagegrens < 2,0 mg/kg ds. Bij lagere droge stof gehalten dan 22 % komt de rapportagegrens zelfs boven de grenswaarde van 2 mg/kg ds uit. Hiermee moet rekening worden gehouden bij het bepalen van Cr(VI) in dit type van monsters. In de ontwerp EN-norm is een opmerking voorzien waarin wordt beschreven dat monsters met een laag droge stof gehalte een invloed kunnen hebben op de haalbare bepalingsgrens.

SUMMARY

Within CEN/TC223/WG 4 *Soil improvers and growing media* a new CEN method has been developed for the determination of Cr(VI) in soil improvers and growing media: prEN 00223122:2021 *Soil improvers and growing media — Determination of chromium(VI)*.

VITO has evaluated the applicability of this method by analysing different type of soil improvers consisting of compost, different fractions of digestates, and sludges. All samples, as such and spiked with Cr(VI) and Cr(III), were extracted using a phosphate buffer with a pH between 7.0 and 8.0. The Cr(VI) content was determined by ion chromatography after post-column derivatization with 1,5-diphenylcarbazide in acid solution and measured at 540 nm.

With respect to the execution of the method and the description in the draft EN method, it was not feasible to filtrate the extracts due to clogging of the filter. By applying alternatively a centrifugation step in advance, it was possible to separate the solid fraction from the extraction solution. Due to the dark colouring of the sample, it is advisable to dilute the sample at least 10 times prior to IC analysis to protect the analytical column. Therefore, the IC calibration used was a factor of 10 times lower than those described in the draft EN method. Both aspects, centrifugation and dilution prior to IC analysis together with an appropriate calibration range, should preferably be introduced in the draft EN method.

With respect to the analytical results, it is clearly demonstrated that the presence of Cr(VI) in the sample is strongly dependent on the matrix composition. No Cr(VI) was remained in the Cr(VI) spiked samples of the different sludge samples and thick/raw digestate samples, even after analysis within 60 min after extraction. It is unlikely that in these kind of samples Cr(VI) is to be expected. For the other samples under investigation Cr(VI) spike recoveries varied between 32% and 94% when measuring within 60 min after extraction. Measuring after 24 hrs resulted in an additional decrease of the recovery by 3-9%, depending on the sample analysed.

In the draft EN standard it is noted that the recovery rate of a spiked Cr(VI) solution should be between 80% and 120%. Moreover, if the added Cr(VI) is not detected or significantly lower than the expected values, this is an indication that the soil improvers and growing media contains reducing agents. This leads to the conclusion that this soil improvers and growing media has no Cr(VI) content (below detection limit). By the performed measurements on a selection of soil improvers this note can be confirmed.

In the Fertilizer Regulation a limit value of 2 mg/kg dm is included to verify. For samples having a high dry matter content it is feasible to verify this limit value. But for some samples the dry matter content can be significantly lower and this has an influence on the final Cr(VI) result as expressed in mg/kg dm. For example, when having a dry matter content of 44%, the reporting limit will be < 1.0 mg/kg dm and when having a dry matter content of 22%, the reporting limit will be < 2.0 mg/kg dm. With lower dry matter contents than 22 % ds, the reporting limit will even exceeds the limit value of 2 mg/kg dm. This fact has to be taken under consideration when determining Cr(VI) in these type of samples. In the draft EN standard a note is foreseen which describes that samples with a low dry matter content can have an influence on the achievable limit of quantification.

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1 BACKGROUND INFORMATION

1.1 Introduction

OVAM requested to evaluate the determination of hexavalent chromium (Cr(VI)) in soil improvers including compost and digestates. For this parameter there is at the moment no compendium method (CMA) available which describes the determination of Cr(VI) in soil improvers.

For the determination of Cr(VI) in soil and solid waste a procedure is described in CMA/2/II/A.24 with reference to NBN EN ISO 15192. It involves an alkaline digestion of the sample under investigation followed by ion chromatography with spectrophotometric detection. This method can be used for the determination of the Cr(VI) mass fraction in solid samples higher than 0.1 mg/kg.

It has to be noted that in case of a reducing or oxidizing tendency of the waste matrices, no reliable Cr(VI) content can be reported.

In addition, within CEN/TC223/WG4 a new European standard method is developed for the determination of Cr(VI) in soil improvers and growing media. The draft method (prEN 00223122:2021 *Soil improvers and growing media — Determination of chromium(VI)*) has been prepared by Technical Committee CEN/TC 223 “Soil improvers and growing media”, the secretariat of which is held by NEN, in collaboration with CEN/TC 260 “Fertilizers and liming materials” and CEN/TC 455 “Plant Biostimulants”.

The principle of this method is: “Extractable Cr(VI) is leached from the sample in phosphate buffer at pH 7.0 to 8.0. An aliquot of the filtered extract is analyzed for Cr(VI) using ion-exchange chromatography with UV-VIS detection.”

OVAM requested VITO to evaluate the feasibility of the European method *prEN 00223122 Soil improvers and growing media — Determination of chromium(VI)*. In this study the applicability of the method was evaluated. Moreover, spiking experiments with Cr(VI) and Cr(III) were conducted on a range of samples (compost, digestates, sludge,...) to verify the interconversion from Cr(VI) to Cr(III).

1.2 European Fertilising Regulation (EU 2019/1009)

The European Committee for Standardization (CEN) has been requested by the European Commission to draft European standardization deliverables in support of the European Fertilising Product Regulation (FPR; EU 2019/1009). The FPR aims to promote an increased use of recycled nutrients to further aid the development of a circular economy and allow a more resource efficient general use of nutrients, while reducing the dependency of nutrients from countries not within the European Union. It lays down rules on the requirements of different sorts of fertilising products. Fertilising products bearing CE marking may freely be traded within the European Union. As different kinds of fertilising products warrant different product safety and quality requirements, suitable to their intended uses, fertilising products have been classified into different product function categories (PFCs). A global overview of the PFCs defined in the FPR are listed in Table 1.

Table 1 Global overview of product function categories (PFCs) defined in the Fertilising Product Regulation (EU 2019/1009).

Number	Product function category
1	Fertilisers
2	Liming materials
3	Soil improvers
4	Growing media
5	Inhibitors
6	Plant biostimulants
7	Fertilising product blends

To enable the market to justify the use of the CE mark, CEN is requested by the European Commission to develop a series of European Standards described in Standardization Request M/564 amendment 1. These European Standards will enable the implementation of the FPR; the commercialisation of the soil improvers, growing media and other fertilising products listed in Table 1 within the EU Single market; and provide a uniform and reliable way of assessing the compliance to the requirements laid down in the FPR. The deliverables under this standardization request are handled by three CEN Technical Committees (TCs):

- CEN/TC 223 'Soil improvers and growing media'
- CEN/TC 260 'Fertilizers and liming materials'
- CEN/TC 455 'Plant biostimulants'

VITO is involved in the development of the European standards within CEN/TC223/WG 4 'Analytical Methods'. Related to the determination of Cr(VI) in soil improvers and growing media, within CEN/TC223/WG4 a new European standard method is developed for the determination of Cr(VI) in soil improvers and growing.

1.3 Background information from Germany

In Germany, Cr(VI) became an issue because questions arose from organic farming. A broad screening has been performed in 2002 for the determination of Cr(VI) in German compost, but this could not be determined in any sample¹. The samples examined were taken as part of an external monitoring for a quality mark of the Federal Compost Quality Association. Both fresh and finished compost were sampled. Furthermore, composts of different compositions were included in the investigation (pure organic waste composts, pure green waste composts and mixtures of both) as well as production plants of different sizes.

According to the analysis results, Cr(VI) was not detectable in any of the samples examined. The limit of quantification of 0.03 mg/kg dry matter was not reached in any case. According to the experts, it could thus be shown that normal organic and green waste composts from ongoing quality monitoring do not show any contamination with Cr(VI).

Chromium(VI) is also not to be expected in compost from separate collection. Chromium(VI) is not present as the cation Cr⁶⁺, but always as an oxyanion such as chromate or dichromate (depending on the pH value). It is therefore negatively charged and is therefore not bound by the predominantly negatively charged clay and humus components. Free chromates are

¹ Kein Chrom (VI) in Kompost. Untersuchung der BGK zur EU-Öko-Verordnung, 24.02.2002, https://www.kompost.de/publikationen/aktuelle-nachrichten/detail-ansicht?tx_news_pi1%5Baction%5D=detail&tx_news_pi1%5Bcontroller%5D=News&tx_news_pi1%5Bnews%5D=93&cHash=4e0ebf1032edd01f0fa3579384987260.

strong oxidizing agents and therefore react with the relatively easily oxidized humus components. In the process, they are reduced to Cr(III) and in the moist compost they precipitate as insoluble compounds in the aqueous solution. For the reasons mentioned, the chemical equilibrium reaction is constantly shifted and Cr(VI) - if present at all in the starting materials - is consumed quantitatively. These reactions are accelerated by the elevated temperatures during composting. Even if input materials contaminated with Cr(VI) were accepted, contamination of the finished compost with Cr(VI) would hardly be possible.

In the literature, exposure to Cr(VI) is usually associated with specific locations (e.g. tanneries, industrial landfills, etc.). It is pointed out that at old sites chromium is present almost exclusively as Cr(III).

Also, studies of the Federal Institute for Materials Research and Testing (BAM) on behalf of the German Federal Environmental Agency (UBA)² on the applicability of analytical methods on fertilizers and sewage sludge ashes proved only low recovery rates e.g. in increase experiments in sewage sludge samples with Cr(VI). This is due to the reducing effect of the organic matter content of the samples.

“Due to the reducing effect of sample matrices for the performed methodno reliable values for Cr(VI) were found. The applied method is DIN EN 15192, 2007, describing the alkaline extraction method. This does not mean, conversely, that these samples contain Cr(VI), which could not be detected with the method used. Rather, only no reliable values for Cr(VI) can be determined using the method.”

1.4 Chromium(VI) method according to EN 15192

Within CEN/TC444/WG 3 *Environmental solid matrices* another analytical method (EN 15192) was developed for the determination of Cr(VI) in waste and soil samples. It involves an alkaline extraction instead of an extraction in a phosphate buffer at pH 7,0 to pH 8,0.

EN 15192 *Soil and waste - Determination of Chromium(VI) in solid material by alkaline digestion and ion chromatography with spectrophotometric detection (ISO 15192:2021)* is applied to determine Cr(VI) in waste and soil samples and uses an alkaline digestion solution as extracting medium. The extraction solution is made of 0.5 mol/l of sodium hydroxide (NaOH) and 0.28 mol/l of sodium carbonate (Na₂CO₃). A quantity of 0.5 ml of phosphate buffer (0.5 mol/l dipotassium hydrogen phosphate, K₂HPO₄, and 0.5 mol/l potassium dihydrogen phosphate, KH₂PO₄, at pH 7.0) and 1 ml of magnesium chloride (MgCl₂) solution (4.2 mol/l) are added during digestion to prevent oxidation of Cr(III) which may be present in samples. The extraction is performed at 92.5 ± 2.5 °C for at least 60 minutes.

This method also uses an ion chromatographic separation to determine Cr(VI), which is measured spectrophotometrically either at 365 nm (direct UV detection) or after post-column derivatization with 1,5-diphenylcarbazide in acid solution at 540 nm.

In paragraph 4 some selected samples were analysed according to EN 15192, in comparison to the extraction with a phosphate buffer at pH 7,0 to pH 8,0.

² Source: Lufa Nord-West, Institute of Soil and Environment

2 ANALYTICAL METHOD (prEN 00223122)

The draft method *prEN 00223122 (2021) Soil improvers and growing media — Determination of chromium(VI)* was evaluated in this study. The major aspects of this methods are summarized below.

2.1 Scope

The document specifies a method for the determination of hexavalent chromium (Cr(VI)) in soil improvers and growing media.

The method described is suitable to quantify the Cr(VI) content in soil improvers and growing media down to 1 mg/kg dry matter.

The results obtained from this method are strictly dependent on the extraction conditions. Results obtained by using other extraction procedures (extraction solution, pH of the extraction solution, extraction time, extraction temperature, etc.) are not comparable with the results produced by the procedure described in this document.

2.2 Principle

Extractable Cr(VI) is leached from the sample in phosphate buffer at pH 7,0 to pH 8,0. An aliquot of the filtered extract is analysed for Cr(VI) using ion-exchange chromatography with UV-VIS detection.

A preliminary determination of the total chromium in aqua regia extracts by ICP-AES could reduce the number of the samples where the determination of Cr(VI) is necessary because if the content of aqua regia (total) extractable chromium is lower than the legislative limit for Cr(VI) then the determination of Cr(VI) can be omitted..

2.3 Procedure

2.3.1 Reagents

Extraction solution

Dissolve 22,8 g dipotassium hydrogen phosphate $K_2HPO_4 \cdot 3H_2O$ in 1 000 ml water, adjusted to $pH 8,0 \pm pH 0,1$ with phosphoric acid. Degas this solution with either argon or nitrogen (5.6) or ultrasonic bath.

Standard practice is to make up a fresh solution each day. However, the solution may be kept for up to one week in a refrigerator at $(4 \pm 3) ^\circ C$ but shall be warmed to room temperature and degassed prior to use.

Phosphoric acid solution

700 ml o-phosphoric acid, density $\rho = 1,71$ g/ml, made up to 1 000 ml with water.

First add approximately 200 ml of deionised water to a 1 000 ml volumetric flask, then add the 700 ml of o-phosphoric acid and dilute to the mark with deionised water.

Potassium dichromate ($K_2Cr_2O_7$), dried for (16 ± 2) h at $(105 \pm 2) ^\circ C$.

Chromium(VI) stock solution

Dissolve 2,829 g potassium dichromate ($K_2Cr_2O_7$) in water in a volumetric flask and make up to 1 000 ml with water. 1 ml of this solution contains 1 mg of chromium.

Commercially available stock solutions at this concentration level of hexavalent chromium can be used for the same purpose.

Chromium(VI) standard solution

Pipette 1 ml of the Cr(VI) stock solution into a 1 000 ml volumetric flask and make up to the mark with extraction solution. 1 ml of this solution contains 1 μ g of chromium.

The solution may be kept for up to one week in a refrigerator at (4 ± 3) °C but shall be warmed to room temperature prior to use.

Commercially available stock solutions at this concentration level of hexavalent chromium can be used for the same purpose.

Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$)

Dissolve 85,4 g in a 100 ml volumetric flask, dilute with water, close and mix thoroughly.

2.3.2 Preparation of the analytical solution

2.3.2.1 Solid and shear resistant pasty samples

The operator shall weigh approximately $(10 \pm 0,1)$ g of fresh sample of soil improvers and growing media to the nearest 0,01 g.

NOTE A higher sample intake may be considered for coarse samples to keep the liquid to solid ratio during the extraction.

The following tasks shall be performed:

- Pipette 100 ml (V_0) of degassed extraction solution into a 250 ml conical flask. If the sample is expected to contain a significant amount of Cr(III), 1 ml of magnesium chloride solution may be added. Displace oxygen by passing oxygen-free argon (or nitrogen) into the flask for 5 min with a volume flow of (50 ± 10) ml/min. Remove the aeration tube, add the sample and close the flask with a stopper.
- Shake the conical flask with the sample for 30 min on a mechanical orbital shaker at (100 ± 10) min^{-1} at room temperature to extract the Cr(VI).
- Shake the suspension in a smooth circular movement to keep the sample from adhering to the wall of the flask and avoid shaking faster than specified.
- Immediately after completing the 30 min of extraction, filter the contents of the conical flask through a membrane filter into a glass or plastic vessel with lid. Check the pH of the solution. The pH of the solution shall be between 7,0 and 8,0. If the pH of the solution is not within this range, start the complete procedure again and consider using a smaller sample mass.
- Transfer an aliquot of the filtered extract into a vial. Instrumental determination of Cr(VI) should be performed as soon as possible and no later than 60 min after the extraction phase to avoid risks of reduction.

2.3.2.2 Liquid and aqueous pasty samples

The operator shall weigh approximately $(10 \pm 0,1)$ g of sample of soil improvers and growing media to the nearest 0,01 g.

The following tasks shall be performed:

- Pipette 100 ml (V_0) of degassed extraction solution into a 250 ml conical flask. If the sample is expected to contain a significant amount of Cr(III), 1 ml of magnesium chloride solution may be added. Displace oxygen by passing oxygen-free argon (or nitrogen) into the flask for 5 min with a volume flow of (50 ± 10) ml/min. Remove the aeration tube, add the sample and close the flask with a stopper.
- Shake the conical flask with the sample for (10 ± 1) min on a mechanical orbital shaker at (100 ± 10) min⁻¹ at room temperature to extract the Cr(VI).
- Shake the suspension in a smooth circular movement to keep the sample from adhering to the wall of the flask and avoid shaking faster than specified.
- Immediately after completing the 10 min of extraction, filter the contents of the conical flask through a membrane filter into a glass or plastic vessel with lid. Check the pH of the solution. The pH of the solution shall be between 7,0 and 8,0. If the pH of the solution is not within this range, start the complete procedure again and consider using a smaller sample mass.
- Transfer an aliquot of the filtered extract into a vial. Instrumental determination of Cr(VI) should be performed as soon as possible and no later than 60 min after the extraction phase to avoid risks of reduction.

2.3.3 Chromatographic conditions

Determination of Cr(VI) is performed using the ion chromatographic technique. As the instrumental equipment of the laboratories may vary, no specific applicable instructions can be provided for analysis. However, the operating parameters and examples of the ion chromatographic analysis for Cr(VI) listed in Annex A and Annex B of prEN 00223122 have been successfully tested and used. Annex A determines Cr(VI) by direct detection of chromate peak at 372 nm. Annex B determines Cr(VI) after a post-column reaction with 1,5-diphenylcarbazide by measuring the absorption peak at 540 nm.

2.3.4 Calibration

The content of Cr(VI) in the sample of soil improvers and growing media is determined with an external standard calibration.

2.3.5 Determination of the recovery rate

The determination of the recovery rate is important to provide information about possible matrix effects which can influence the results.

The operator shall spike an aliquot of the solution obtained in § 2.3.2 with a suitable volume of Cr(VI) solution to increase the Cr(VI) concentration by 10 mg/kg.

The following tasks shall be performed:

- Inject the same volume of this solution as the volume injected in the calibration (recording the area as A_s).
- Spike an aliquot of the extraction solution (the same volume as that taken before of the solution obtained in 2.3.2) with a suitable volume of Cr(VI) solution to increase the Cr(VI) concentration by 10 mg/kg, so that the final volume of this solution is the same as that of the above spiked solution with Cr(VI) solution. Inject the same volume of this solution as the volume injected in the calibration (recording the area as A_{st}).

The area of the chromate peak of these solutions shall be within the range of the calibration curve, otherwise repeat the procedure using a smaller aliquot. The recovery rate shall be between 80 % and 120 %.

NOTE If the added Cr(VI) is not detected or significantly lower than the expected values, this is an indication that the soil improvers and growing media contains reducing agents. This leads to the conclusion that this soil improvers and growing media has no Cr(VI) content (below detection limit).

2.3.6 Calculation and expression of results

2.3.6.1 Calculation of Cr(VI) content

The mass fraction of soluble Cr(VI) in the soil improvers and growing media $w_{Cr(VI)}$ expressed in mg/kg dry matter shall be calculated according to formula:

$$w_{Cr(VI)} = \frac{(A-b) \cdot (V_0 + m \cdot W_m) \cdot V_C}{V_M \cdot m \cdot D_M \cdot F}$$

where

- A is the area of the peak of chromate in the chromatogram of the extract of the sample;
- F is the slope of calibration curve (y/x), in ml/ μ g;
- b is the intercept of calibration curve (y/x);
- m is the mass of the sample of organic or organo-mineral fertilizer taken, in g;
- V_0 is the volume of the added extraction solution, in ml;
- V_C is the injection volume in the calibration, in μ l;
- V_M is the injection volume in the sample analysis, in μ l;
- W_m is the moisture content expressed as a percentage by mass;
- D_M is the dry matter content expressed as a percentage by mass.

2.3.6.2 Calculation of recovery rate

The recovery rate η expressed in percent (%) shall be calculated according to:

$$\eta = \frac{A_s \times (V_1 + V_2) - A \times V_1}{A_{st} \times (V_1 + V_2)} \times 100$$

where

- V_1 is the volume of sample solution in the spiked solution, in milliliters ml;
- V_2 is the volume of chromate standard in the spiked solution, expressed in ml;
- A_s is the area of chromate peak of sample solution after adding Cr(VI), see 2.3.5;
- A is the area of chromate peak in the original sample, see 2.3.5;
- A_{st} is the area of chromate peak of extraction solution after adding Cr(VI), see 2.3.5.

2.3.6.3 Expression of results

The Cr(VI) content is given in milligrams per kilogram (mg/kg) rounded to the nearest 0,1 mg. The content is based on dry matter. The dry matter content, DM, is given in percent (%) rounded to the nearest 0,1 %.

3 EVALUATION OF THE ANALYTICAL METHOD (prEN 00223122)

3.1 Samples under investigation and their sample preparation

Samples as listed in Table 2 were collected by VLACO³ in February 2022 at different locations in Flanders (Belgium) and used to evaluate the feasibility of the Cr(VI) procedure.

The samples were differentiated accordingly to their physical state. The samples under investigation could be classified as follows:

- Solid samples: these samples have an estimated dry matter content of at least 30 % m/m.
 - Sample 3: Dried digestate 1
 - Sample 6: Greencompost
 - Sample 7: Vegetable, fruit and garden waste (VFG)-compost
 - Sample 8: Vegetable, fruit and garden waste (VFG)-compost
 - Sample 10: Filter cake fermentation (solid)
- Shear resistant pasty samples: these samples have an estimated dry matter content between 15 % and 30 % m/m.
 - Sample 2: Thick fraction of a digestate 1
 - Sample 11: Aerobic sludge grain processing industry (solid)
 - Sample 13: Aerobic sludge potato processing industry (solid)
- Liquid and aqueous pasty samples: these samples have an estimated dry matter content of less than 15 % m/m, but higher the 2% m/m.
 - Sample 1: Raw digestate 1
 - Sample 9: Anaerobic sludge OBA processing (liquid)
- Liquids: these samples have an estimated dry matter content less than 2% m/m.
 - Sample 4: Thin fraction of a digestate 2
 - Sample 5: Effluent of a digestate 2
 - Sample 12: Aerobic sludge ethanol production (liquid)

Depending on their physical state a different pretreatment procedure is applicable. It also has an influence on the further procedure of the analytical method.




The following sample pretreatment were applicable and added in Table 2 for each sample individually:

- Solid samples
 - Thoroughly mix the laboratory sample, gently breaking any lump or agglomerate of the sample that has been caused, by, for example, compression during transportation. Samples are homogenized by manual conversion.
- Shear resistant paste samples
 - Shear resistant pasty laboratory samples are homogenized by manual conversion. If the pasty samples contain coarser parts, the sample must be homogenized by mechanical mixing.
- Liquid and aqueous pasty samples
 - Liquid and aqueous pasty samples containing less than 15 % of dry matter are often heterogeneous and can consist of, e.g., a sludge layer and a liquid layer.






³ Vlaco, [Vlaco in English | Vlaco](#)

These samples shall, after shaking and stirring with a spatula, be homogenized with a robust blender. Ensure that any solid sludge layer on the bottom is loosened and well mixed. Place the sample bottle under the blender, with the rotor knife approximately 3 cm from the bottom of the sample bottle. Homogenize the sample with the greatest possible rotational speed, while avoiding excessive foaming. The blender can be moved vertically back and forth during homogenization to optimize homogenization. After homogenization, the sample bottle is closed. After mixing, immediately take sub-samples and/or test samples for the analyses to be performed. If, after storage of the homogenized samples, additional sub-sample/analysis portions have to be taken, the sample must be re-homogenized with a blender.






Table 2 Overview of the collected samples

Nr	Vlaco Code Vito code	Description	Picture	Dry matter in %	Homogenisation
1	VITO/VLACO/DIG/RD/01 Vito code: 220615-0016	Raw digestate 1		8.1	Mechanical mixing with ultra turrax
2	VITO/VLACO/DIG/DIF/02 Vito code: 220615-0017	Thick fraction of a digestate 1		23.7	Manual conversion
3	VITO/VLACO/DIG/DD/03 Vito code: 220615-0018	Dried digestate 1		80.1	Manual conversion, seewed < 1 cm, twigs removed

Evaluation of the analytical method (prEN 00223122)

Nr	Vlaco Code Vito code	Description	Picture	Dry matter in %	Homogenisation
4	VITO/MLACO/DIG/DUF/04 Vito code: 220615-0019	Thin fraction of a digestate 2		1.4	Mechanical mixing with ultra turrax
5	VITO/MLACO/DIG/EFF/05 Vito code: 220615-0020	Effluent of a digestate 2		0.7	Mechanical mixing with ultra turrax
6	VITO/MLACO/GROEN/06 Vito code: 220615-0021	Greencompost		54.1	Manual conversion, seewed < 1 cm
7	VITO/MLACO/GFT/07 Vito code: 220615-0022	VFG-compost		58	Manual conversion, seewed < 1 cm
8	VITO/MLACO/GFT/08 Vito code: 220615-0023	VFG-compost		59.7	Manual conversion, seewed < 1 cm

Evaluation of the analytical method (prEN 00223122)

Nr	Vlaco Code Vito code	Description	Picture	Dry matter in %	Homogenisation
9	VITO/VLACO/SLIB/09 Vito code: 220615-0024	Anaerobic sludge OBA processing (liquid)		8.0	Mechanical mixing with ultra turrax
10	VITO/VLACO/SLIB/10 Vito code: 220615-0025	Filter cake fermentation (solid)		38.5	Manual conversion
11	VITO/VLACO/SLIB/11 Vito code: 220615-0026	Aerobic sludge grain processing industry (solid)		17.1	Manual conversion
12	VITO/VLACO/SLIB/12 Vito code: 220615-0027	Aerobic sludge ethanol production (liquid)		0.5	Mechanical mixing with ultra turrax
13	VITO/VLACO/SLIB/13 Vito code: 220615-0028	Aerobic sludge potato processing industry (solid)		16.5	Manual conversion

VFG-compost: vegetable, fruit and garden compost - OBA: organic biowaste

3.2 Description of the performed experiments

The extraction of the samples was done according to the procedure described in §2.3.2.

The extraction solution was degassed in an ultrasonic bath during 30 min. To 100 ml of degassed extraction solution 1 ml of the $MgCl_2$ solution was added. The headspace was purged for 5 min by an N_2 stream. About 10 g of wet sample was added. Solid samples and shear resistant paste samples were extracted during 30 min on a mechanical orbital shaker at $(100 \pm 10) \text{ min}^{-1}$ at room temperature, while liquid and aqueous pasty samples were extracted during $(10 \pm 1) \text{ min}$ on a mechanical orbital shaker at $(100 \pm 10) \text{ min}^{-1}$ at room temperature. Afterwards the content was centrifuged during 5 min at 4000 rpm, followed by a filtration through a membrane filter of 0.45 μm .

Note: A centrifugation of all samples was necessary as the filter otherwise clogged.

Samples were analysed within 60 min after extraction and most of them also after 24 hrs. The ion chromatography system was calibrated from 4 to 100 $\mu\text{g/l}$ of Cr(VI). Therefore, all samples could be diluted at least a factor of 10 prior to analysis.

The ion chromatography conditions were as follows:

- IC: Metrohm 850 Professional IC
- Analytical column: Metrosep A Supp 10 (250/4)
- Guard column: Metrosep A Supp 10 Guard HC/4.0
- Injection volume: 100 μl
- Mobile phase flow rate: 0.8 ml/min
- Eluents:
 - o Dissolve 52.8 g $(\text{NH}_4)_2\text{SO}_4$ and 11.2 ml NH_4OH in 2000 ml volumetric flask, fill to the mark with ultra pures water.
- Post-column reagent:
 - o In a 1 000 ml volumetric flask, dissolve 28 ml of sulphuric acid in about 700 ml of ultra pure water and let it stand cooling. Dissolve 0,50 g of 1,5-diphenylcarbazide in 100 ml of methanol. When the acidic solution is cooled, stirring with a magnetic stirrer and mix the diphenylcarbazide solution with the acidic solution and fill to the mark with ultra pure water.
- Calibration standards: 4 – 10 – 30 – 50 and 100 $\mu\text{g Cr(VI)/l}$, prepared from a stock solution of 1000 m/l CrO_4 (Merck).

The following protocol was applied for these experiments:

- Analysis of the blank extraction solution
- Analysis of the extraction solution after spiking with Cr(VI) (1000 $\mu\text{g/l}$ or 10 mg/kg)
- Analysis of the extraction solution after spiking with Cr(III) (10000 $\mu\text{g/l}$ or 100 mg/kg)
- Analysis of all samples
- Analysis of all samples after spiking with Cr(VI) (1000 $\mu\text{g/l}$ or 10 mg/kg). The spiking solution was added to the extraction solution, afterwards the sample was added.
- Analysis of all samples after spiking with Cr(III) (10000 $\mu\text{g/l}$ or 100 mg/kg). The spiking solution was added to the extraction solution, afterwards the sample was added.

3.3 Analytical results

The obtained results are summarized in Table 3 for the solid and shear resistant pasty samples and in Table 4 for the liquid and aqueous pasty samples.

When analyzing the blank extraction solution spiked with 100 µg/l of Cr(VI), it is clear that a good recovery rate of the Cr(VI) spike is obtained with values between 96-100%, even for measurements after 24 hrs. When analyzing the blank extraction solution spiked with 10000 µg/l of Cr(III), all results are below 40 µg/l (the lowest limit of the calibration range, taking into consideration a dilution of 10). So there is no (detectable) conversion observed from Cr(III) to Cr(VI).

When analyzing the solid and shear resistant pasty samples no Cr(VI) and Cr(III) is measured in the extracted solutions of the original samples. For all samples, the recovery of Cr(VI) is calculated for the results measured within 60 min after extraction and also after 24 hrs after extraction.

As shown in the tables, for some samples the intake needed to be reduced to obtain after extraction a pH value between 7,0 and 8,0.

Table 3 Cr(VI) results determined on solid and shear resistant pasty samples using an extraction time of 30 min and with Cr(VI) and Cr(III) spiking of the analyses samples

Sample code	Description sample	Dry matter in % m/m	Intake in g	pH (after extraction)	Results (< 60 min) µg/l	% Rec (< 60 min)	Results (after 24 hrs) µg/l	% Rec (after 24 hrs)
Blank extraction solution	Extraction solution			8,12	< 40	-	< 40	-
Blank extraction solution+CrVI spike	Extraction solution			8,12	1000	100%	1000	100%
Blank extraction solution+CrIII spike	Extraction solution			8,10	< 40	-	< 40	-
220615-0018	Dried digestate 1	80,1	10,03	8,00	< 40	-	< 40	-
220615-0018+CrVI spike	Dried digestate 1	80,1	9,99	7,90	810	81%	780	78%
220615-0018+CrIII spike	Dried digestate 1	80,1	10,01	7,80	< 40	-	< 40	-
220615-0021	Greencompost	54,1	9,05	7,90	< 40	-	< 40	-
220615-0021+CrVI spike	Greencompost	54,1	8,78	7,90	920	92%	880	88%
220615-0021+CrIII spike	Greencompost	54,1	8,77	7,80	43	0,43%	42	0,42%
220615-0022	VFG-compost	58,0	8,15	7,90	< 40	-	< 40	-
220615-0022+CrVI spike	VFG-compost	58,0	8,19	7,90	480	48%	390	39%
220615-0022+CrIII spike	VFG-compost	58,0	7,17	7,80	< 40	-	< 40	-
220615-0023	VFG-compost	59,7	8,12	7,16	< 40	-	< 40	-
220615-0023+CrVI spike	VFG-compost	59,7	8,24	7,06	870	87%	800	80%
220615-0023+CrIII spike	VFG-compost	59,7	8,36	7,02	< 40	-	< 40	-
Blank extraction solution	Extraction solution (duplo)			7,06	< 40	-	-	-
Blank extraction solution+CrVI spike	Extraction solution (duplo)			7,05	980	98%	1000	100%
Blank extraction solution+CrIII spike	Extraction solution (duplo)			7,05	< 40	-	-	-

Evaluation of the analytical method (prEN 00223122)

Sample code	Description sample	Dry matter in % m/m	Intake in g	pH (after extraction)	Results (< 60 min) µg/l	% Rec (< 60 min)	Results (after 24 hrs) µg/l	% Rec (after 24 hrs)
220615-0025	Filter cake fermentation (solid)	38,5	9,24	7,13	< 40	-	-	-
220615-0025+CrVI spike	Filter cake fermentation (solid)	38,5	9,99	7,12	870	87%	800	80%
220615-0025+CrIII spike	Filter cake fermentation (solid)	38,5	10,07	7,08	< 40	-	-	-
220615-0017	Thick fraction of a digestate 1	23,7	8,99	7,17	< 40	-	-	-
220615-0017+CrVI spike	Thick fraction of a digestate 1	23,7	8,38	7,17	< 40	-	-	-
220615-0017+CrIII spike	Thick fraction of a digestate 1	23,7	8,67	7,15	< 40	-	-	-
220615-0026	Aerobic sludge grain processing industry (solid)	17,1	8,57	7,30	< 40	-	-	-
220615-0026+CrVI spike	Aerobic sludge grain processing industry (solid)	17,1	9,12	7,30	< 40	-	-	-
220615-0026+CrIII spike	Aerobic sludge grain processing industry (solid)	17,1	8,87	7,30	< 40	-	-	-
220615-0028	Aerobic sludge potato processing industry (solid)	16,5	8,93	7,05	< 40	-	-	-
220615-0028+CrVI spike	Aerobic sludge potato processing industry (solid)	16,5	8,81	7,04	< 40	-	-	-
220615-0028+CrIII spike	Aerobic sludge potato processing industry (solid)	16,5	8,41	7,03	< 40	-	-	-

Table 4 Cr(VI) results determined on liquid and aqueous pasty samples using an extraction time of 10 min and with Cr(VI) and Cr(III) spiking of the analyses samples

Sample code	Description sample	Dry matter in % m/m	Intake in g	pH (after extraction)	Results (< 60 min) µg/l	% Rec (< 60 min)	Results (after 24 hrs) µg/l	% Rec (after 24 hrs)
Blank extraction solution	Extraction solution			7,05	< 40	-	< 40	-
Blank extraction solution+CrVI spike	Extraction solution			7,05	990	99%	960	96%
Blank extraction solution+CrIII spike	Extraction solution			7,05	< 40	-	< 40	-
220615-0016	Raw digestate 1	8,1	10,03	7,12	< 40	-	< 40	-
220615-0016+CrVI spike	Raw digestate 1	8,1	10,03	7,10	< 40	-	< 40	-
220615-0016+CrIII spike	Raw digestate 1	8,1	10,05	7,09	< 40	-	< 40	-
220615-0019	Thin fraction of a digestate 2	1,4	10,08	7,04	< 40	-	< 40	-
220615-0019+CrVI spike	Thin fraction of a digestate 2	1,4	10,08	7,00	320	32%	< 40	-
220615-0019+CrIII spike	Thin fraction of a digestate 2	1,4	10,07	7,00	< 40	-	< 40	-
Blank extraction solution	Extraction solution (duplo)			7,04	< 40	-	< 40	-
Blank extraction solution+CrVI spike	Extraction solution (duplo)			7,03	990	99%	970	97%
Blank extraction solution+CrIII spike	Extraction solution (duplo)			7,03	< 40	-	< 40	-
220615-0020	Effluent of a digestate 2	0,7	10,04	7,20	< 40	-	< 40	-
220615-0020+CrVI spike	Effluent of a digestate 2	0,7	8,86	7,20	940	94%	890	89%
220615-0020+CrIII spike	Effluent of a digestate 2	0,7	9,00	7,15	< 40	-	< 40	-
220615-0024	Anaerobic sludge OBA processing (liquid)	8,0	7,65	7,05	< 40	-	< 40	-
220615-0024+CrVI spike	Anaerobic sludge OBA processing (liquid)	8,0	7,74	7,04	< 40	-	< 40	-

Evaluation of the analytical method (prEN 00223122)

Sample code	Description sample	Dry matter in % m/m	Intake in g	pH (after extraction)	Results (< 60 min) µg/l	% Rec (< 60 min)	Results (after 24 hrs) µg/l	% Rec (after 24 hrs)
220615-0024+CrIII spike	Anaerobic sludge OBA processing (liquid)	8,0	8,16	7,03	< 40	-	< 40	-
220615-0027	Aerobic sludge ethanol production (liquid)	0,5	8,11	7,15	< 40	-	< 40	-
220615-0027+CrVI spike	Aerobic sludge ethanol production (liquid)	0,5	7,60	7,14	< 40	-	< 40	-
220615-0027+CrIII spike	Aerobic sludge ethanol production (liquid)	0,5	7,79	7,13	< 40	-	< 40	-

In Figure 1 the results are presented of the Cr(VI) spike recovery of the solid and shear resistant pasty samples, measured within 60 min after extraction and after 24 hrs. In the blank extraction solution, spiked with Cr(VI), the spike recovery values remain the same after 24 hrs, so there is no conversion from Cr(VI) to Cr(III) observed within 24 hrs.

For the spiked samples, the results show that a measurement within 60 min after extraction is important because for most of the samples a fraction of Cr(VI) is converted to Cr(III) within several hours. The degree of conversion is dependent from sample to sample. The Cr(VI) spike recovery was additionally reduced within a range of 3 to 9% when analysing after 24 hrs instead of within 60 min after extraction. According to the draft EN standard prEN 00223122 the recovery rate should be between 80 % and 120 %. For four solid and shear resistant pasty samples this criteria is fulfilled.

For the samples 'Thick fraction of a digestate', 'Aerobic sludge grain processing industry (solid)' and 'Aerobic sludge potato processing industry (solid)' no Cr(VI) is detected in the samples spiked with Cr(VI) and analysed within 60 min after extraction, so all Cr(VI) is immediately converted to Cr(III). This is likely due to the reducing effect of the organic matter content of the samples. In these matrices Cr(VI) will most likely not be present due to the reactivity of the samples. The results of these samples are not included in Figure 1.

The 'Greencompost' sample showed the highest Cr(VI) spike recovery of 92% (measurement within 60 min after extraction) which further reduced to a recovery of 88% after 24 hrs.

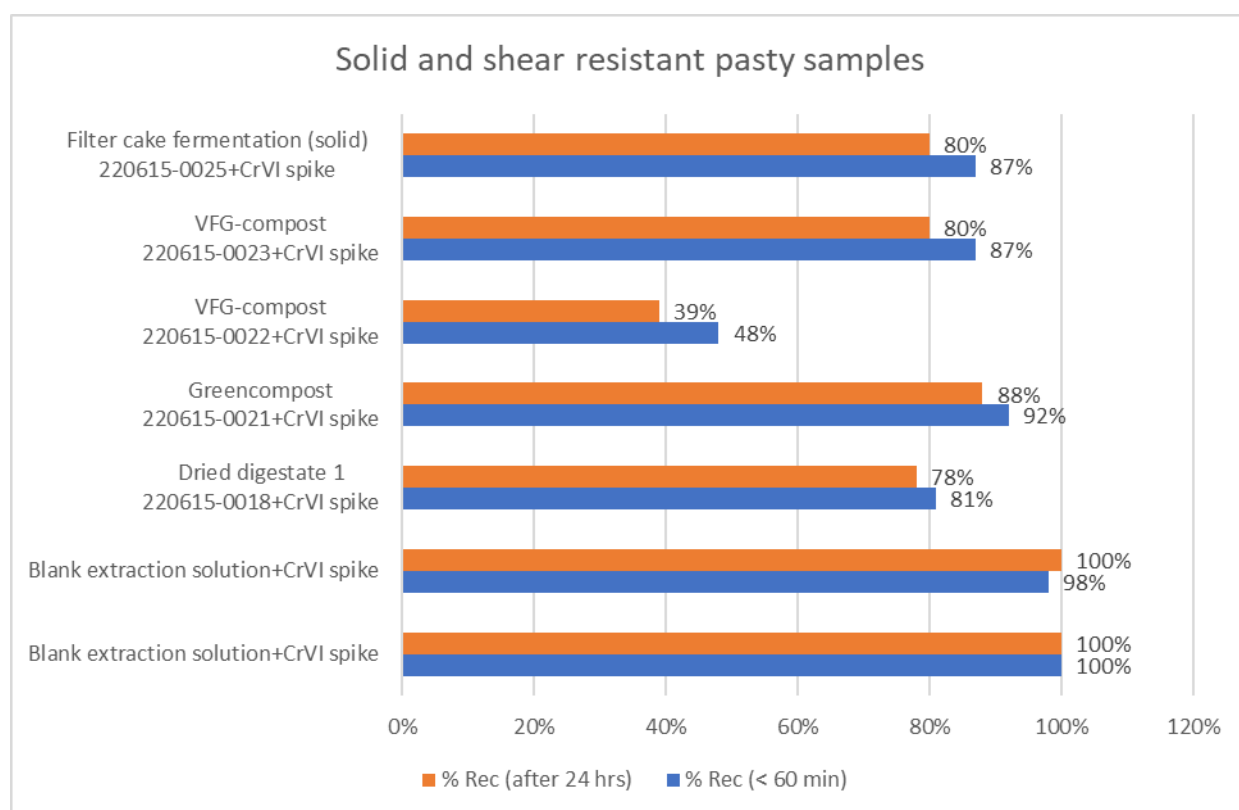


Figure 1 Cr(VI) spike recovery of the solid and shear resistant pasty samples, measured within 60 min after extraction and after 24 hrs

Two VFG-compost samples were analysed and the results showed 2 different Cr(VI) spike recovery values i.e. 48% and 87% (measurement within 60 min after extraction). These differences are most likely attributed to the stability of the compost itself. Higher Cr(VI) spike recoveries are to be expected in more stable samples.

In Figure 2 the results are presented of the Cr(VI) spike recovery of the liquid samples, measured within 60 min after extraction and after 24 hrs. In the blank extraction solution, spiked with Cr(VI), the spike recovery values remain the same after 24 hrs, so there is no conversion from Cr(VI) to Cr(III) observed within 24 hrs.

For the samples 'Raw digestate 1', 'Anaerobic sludge OBA processing (liquid)' and 'Aerobic sludge ethanol production (liquid)' no Cr(VI) is detected in the samples spiked with Cr(VI) and analysed within 60 min after extraction, so all Cr(VI) is immediately converted to Cr(III). In these matrices Cr(VI) will most likely not be present due to the reactivity of the samples. The results of these samples are not included in Figure 2.

For the 'Effluent of a digestate 2' sample the Cr(VI) spike recovery is high (94%) (measured within 60 min after extraction), but slightly reduces to a recovery of 89% after 24 hrs.

For the 'Thin fraction of a digestate 2' sample the matrix is very unstable and the Cr(VI) spike recovery reduces from 32% (measured within 60 min after extraction) to 0% (after 24 hrs).

According to the draft EN standard prEN 00223122 the recovery rate should be between 80 % and 120 %. For only one of the liquid samples this criteria is fulfilled.

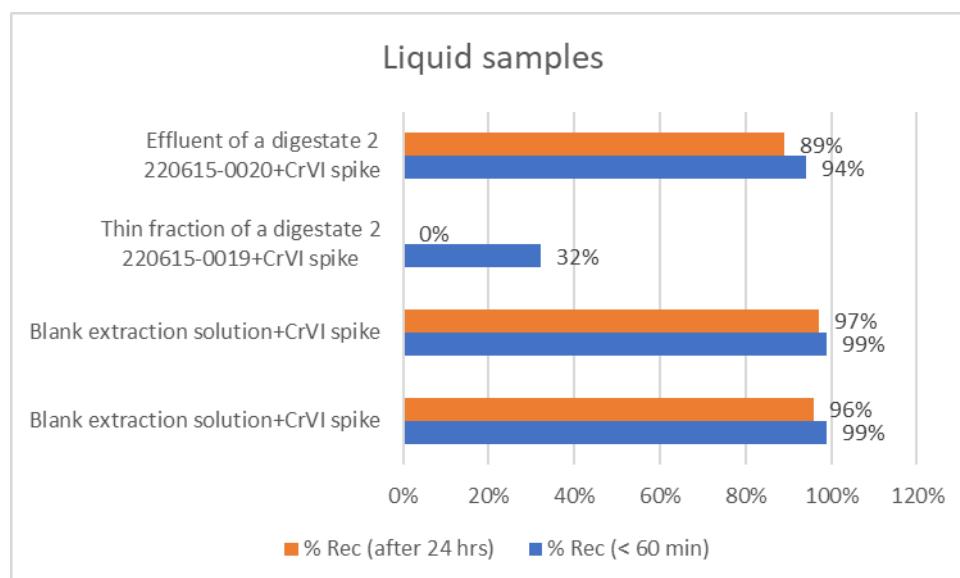


Figure 2 Cr(VI) spike recovery of the solid and shear resistant pasty samples, measured within 60 min after extraction and after 24 hrs

3.4 Results of the samples and their reporting limits

The results of the various samples analysed are in the above paragraph expressed in µg/l. For the final reporting the results needs to be expressed in mg/kg dry matter.

Considering an intake of 10 g fresh material, extraction in 100 ml solution, a reporting limit of < 40 µg/l (calibration IC starting from 4 µg/l, and 10x dilution measurement), and a dry matter content of 100%, then the reporting limit will be < 0.4 mg/kg dry matter.

But for various samples analysed the dry matter content is significantly lower than 100% and this has an influence on the final Cr(VI) result as expressed in mg/kg dm. In Table 5 the results of the analysed samples are presented as expressed in mg/kg dm. As can be deduced from the last column the reporting limit can be up to < 107 mg/kg dm when the dry matter content is only 0.5%.

Table 5 Results of the samples expressed in mg/kg dm

Vito code	Sample description	Dry matter in %	Intake in g	Results in mg/kg dm
220615-0016	Raw digestate 1	8,1	10,03	< 5,4
220615-0017	Thick fraction of a digestate 1	23,7	8,99	< 2,0
220615-0018	Dried digestate 1	80,1	10,03	< 0,5
220615-0019	Thin fraction of a digestate 2	1,4	10,08	< 31
220615-0020	Effluent of a digestate 2	0,7	10,04	< 63
220615-0021	Greencompost	54,1	9,05	< 0,9
220615-0022	VFG-compost	58,0	8,15	< 0,9
220615-0023	VFG-compost	59,7	8,12	< 0,9
220615-0024	Anaerobic sludge OBA processing (liquid)	8,0	7,65	< 7,0
220615-0025	Filter cake fermentation (solid)	38,5	9,24	< 1,2
220615-0026	Aerobic sludge grain processing industry (solid)	17,1	8,57	< 2,9
220615-0027	Aerobic sludge ethanol production (liquid)	0,5	8,11	< 107
220615-0028	Aerobic sludge potato processing industry (solid)	16,5	8,93	< 2,9

As in the Fertilizer Regulation a limit value of 2 mg/kg dm is included, it is not possible to verify this criterium for samples with a low dry matter content. For example, when having a dry matter content of 44%, the reporting limit will be < 1.0 mg/kg dm and when having a dry matter content of 22%, the reporting limit will be < 2.0 mg/kg dm. This fact has to be taken under consideration when determining Cr(VI) in these type of samples.

4 ANALYTICAL METHOD (EN 15192)

4.1 Description of the performed experiments

Within CEN/TC444/WG 3 *Environmental solid matrices* another analytical method (EN 15192) was developed for the determination of Cr(VI) in waste and soil samples. It involves an alkaline extraction instead of an extraction in a phosphate buffer at pH 7,0 to pH 8,0.

EN 15192 *Soil and waste - Determination of Chromium(VI) in solid material by alkaline digestion and ion chromatography with spectrophotometric detection (ISO 15192:2021)* is applied to determine Cr(VI) in waste and soil samples and uses an alkaline digestion solution as extracting medium. This method was also applied to the solid and shear resistant pasty samples.

The following procedure was applied: About 2.5 g of fresh sample was weighed in the digestion vessel. Add (50 ± 1) ml of the alkaline digestion solution (0.5 M NaOH and 0.28 M Na_2CO_3) to each sample using a graduated cylinder, and also add 1 ml of 4.2 M MgCl_2 solution and 0,5 ml of phosphate buffer solution (0.5 M K_2HPO_4 and 0.5 M KH_2PO_4 , at pH 7.0). All digestion vessels were covered. Using a heating block, the samples were heated to ($92,5 \pm 2,5$) °C with continuous stirring, then the samples were maintained at ($92,5 \pm 2,5$) °C for at least 60 min with stirring continuously. Each solution was cooled to room temperature. The content of the digestion vessel (also rinsed with small portions of water) was quantitatively transferred and centrifuged for 5 min at 4000 rpm. The supernatant was collected in a volumetric flask of 100 ml and fill up to the mark with ultra pure water. The determination of Cr(VI) was done with ion chromatography using post-column derivatization with 1,5-diphenylcarbazide in acid solution at 540 nm.

The ion chromatography system was calibrated from 1 to 100 µg/l of Cr(VI). Therefore, all samples could be diluted at least a factor of 20 prior to analysis.

The ion chromatography conditions were as follows:

- IC: Metrohm 850 Professional IC
- Analytical column: Metrosep A Supp 10 (250/4)
- Guard column: Metrosep A Supp 10 Guard HC/4.0
- Injection volume: 100 µl
- Mobile phase flow rate: 0.8 ml/min
- Eluents:
 - o Dissolve 52.8 g $(\text{NH}_4)_2\text{SO}_4$ and 11.2 ml NH_4OH in 2000 ml volumetric flask, fill to the mark with ultra pures water.
- Post-column reagent:
 - o In a 1 000 ml volumetric flask, dissolve 28 ml of sulphuric acid in about 700 ml of ultra pure water and let it stand cooling. Dissolve 0,50 g of 1,5-diphenylcarbazide in 100 ml of methanol. When the acidic solution is cooled, stirring with a magnetic stirrer and mix the diphenylcarbazide solution with the acidic solution and fill to the mark with ultra pure water.
- Calibration standards: 1 – 1.5 – 2.0 – 3.0 – 4.0 – 5.0 – 10 – 30 – 50 and 100 µg Cr(VI)/l, prepared from a 1000 mg/l Cr(VI) stock solution (made of $\text{K}_2\text{Cr}_2\text{O}_7$ (solid))

The following protocol was applied for these experiments:

- Analysis of the blank extraction solution
- Analysis of the extraction solution after spiking with Cr(VI) (250 µg/l)
- Analysis of the extraction solution after spiking with Cr(III) (2500 µg/l)
- Analysis of all samples
- Analysis of all samples after spiking with Cr(VI) (250 µg/l). The spiking solution was added to the extraction solution, afterwards the sample was added.
- Analysis of all samples after spiking with Cr(III) (2500 µg/l). The spiking solution was added to the extraction solution, afterwards the sample was added.

The following solid samples (these samples have an estimated dry matter content of at least 30 % m/m) were analysed:

- Sample 3: Dried digestate 1
- Sample 6: Greencompost
- Sample 7: VFG-compost
- Sample 8: VFG-compost
- Sample 10: Filter cake fermentation (solid)

4.2 Analytical results

The results for the solid and shear resistant pasty samples obtained with the alkaline digestion are summarized in Table 6.

Table 6 Cr(VI) results determined on solid and shear resistant pasty samples using an alkaline digestion and with Cr(VI) and Cr(III) spiking of the analyses samples

Sample code	Description sample	Dry matter in % m/m	Results Cr(VI) µg/l	% Rec
Blank extraction solution	Extraction solution		< 1	-
Blank extraction solution+CrVI spike	Extraction solution+250 µg/l CrVI		246	98%
Blank extraction solution+CrIII spike	Extraction solution+2500 µg/l CrIII		10	0,4%
220615-0018	Dried digestate 1	80,1	< 20	-
220615-0018+CrVI spike	Dried digestate 1+250 µg/l CrVI	80,1	< 20	-
220615-0018+CrIII spike	Dried digestate 1+2500 µg/l CrIII	80,1	< 20	-
				-
220615-0021	Greencompost	54,1	< 20	-
220615-0021+CrVI spike	Greencompost+250 µg/l CrVI	54,1	< 20	-
220615-0021+CrIII spike	Greencompost+2500 µg/l CrIII	54,1	< 20	-
				-
220615-0022	VFG-compost	58,0	< 20	-
220615-0022+CrVI spike	VFG-compost+250 µg/l CrVI	58,0	< 20	-
220615-0022+CrIII spike	VFG-compost+2500 µg/l CrIII	58,0	< 20	-
				-
220615-0023	VFG-compost	59,7	< 20	-
220615-0023+CrVI spike	VFG-compost+250 µg/l CrVI	59,7	< 20	-

Sample code	Description sample	Dry matter in % m/m	Results Cr(VI) µg/l	% Rec
220615-0023+CrIII spike	VFG-compost+2500 µg/l CrIII	59,7	< 20	-
				-
220615-0025	Filter cake fermentation (solid)	38,5	< 20	-
220615-0025+CrVI spike	Filter cake fermentation (solid)+250 µg/l CrVI	38,5	< 20	-
220615-0025+CrIII spike	Filter cake fermentation (solid)+2500 µg/l CrIII	38,5	< 20	-

In the Cr(VI) spiked blank extraction solution a recovery of about 98% is obtained, while for the Cr(III) spiked blank extraction solution a conversion rate of about 0.4% is obtained.

For all samples analysed, no Cr(VI) is detected in the Cr(VI) spiked samples. This is in contrast with the extraction using a phosphate buffer (according to prEN 00223122) where Cr(VI) spike recoveries between 48% and 92% were obtained.

Also within CEN/TC 260 *Fertilizers and liming materials* an analytical method for the determination of Cr(VI) in organic and organo-mineral fertilizers needs to be developed. Experimental laboratory trials⁴ were done for this purpose to evaluate the extraction method using a phosphate buffer on the one hand and the alkaline extraction method on the other hand. The trials performed on liquid and solid organic and organo-mineral fertilizers showed that an extraction with a phosphate buffer is the best available option. The other proposed method (alkaline extraction) was not suitable for organic and organo-mineral fertilizers, as the oxidation of Cr(III) to Cr(VI) is highly probable for samples containing significant amount of trivalent chromium.

So it can be concluded that with the alkaline extraction method according to EN 15192 false positive results for Cr(VI) in the sample can be obtained due to conversion of Cr(III) to Cr(VI). This conversion is not observed using a phosphate buffer.

⁴ Claudio Ciavatte & coll., Alma Mater Studiorum University of Bologna – UniBO, Department of Agricultural and Food Sciences, May 2021.

5 CONCLUSION

Within CEN/TC223/WG 4 *Soil improvers and growing media* a new CEN method has been developed for the determination of Cr(VI) in soil improvers and growing media.

VITO has evaluated the applicability of this method by analysing different type of soil improvers consisting of compost, different fractions of digestates, and sludges. All samples, as such and spiked with Cr(VI) and Cr(III), were extracted using a phosphate buffer with a pH between 7.0 and 8.0. The Cr(VI) content was determined by ion chromatography after post-column derivatization with 1,5-diphenylcarbazide in acid solution and measured at 540 nm.

With respect to the execution of the method and the description in the draft EN method, it was not feasible to filtrate the extracts due to clogging of the filter. By applying alternatively a centrifugation step in advance, it was possible to separate the solid fraction from the extraction solution. Due to the dark colouring of the sample, it is advisable to dilute the sample at least 10 times prior to IC analysis to protect the analytical column. Therefore, the IC calibration used was a factor of 10 times lower than those described in the draft EN method. Both aspects, centrifugation and dilution prior to IC analysis together with an appropriate calibration range, should preferably be introduced in the draft EN method.

With respect to the analytical results, it is clearly demonstrated that the presence of Cr(VI) in the sample is strongly dependent on the matrix composition. No Cr(VI) was remained in the Cr(VI) spiked samples of the different sludge samples and thick/raw digestate samples, even after analysis within 60 min after extraction. It is unlikely that in these kind of samples Cr(VI) is to be expected. For the other samples under investigation Cr(VI) spike recoveries varied between 32% and 94% when measuring within 60 min after extraction. Measuring after 24 hrs resulted in an additional decrease of the recovery by 3-9%, depending on the sample analysed.

In the draft EN standard it is noted that the recovery rate of a spiked Cr(VI) solution should be between 80% and 120%. Moreover, if the added Cr(VI) is not detected or significantly lower than the expected values, this is an indication that the soil improvers and growing media contains reducing agents. This leads to the conclusion that this soil improvers and growing media has no Cr(VI) content (below detection limit). By the performed measurements on a selection of soil improvers this note can be confirmed.

In the Fertilizer Regulation a limit value of 2 mg/kg dm is included to verify. For samples having a high dry matter content it is feasible to verify this limit value. But for some samples the dry matter content can be significantly lower and this has an influence on the final Cr(VI) result as expressed in mg/kg dm. For example, when having a dry matter content of 44%, the reporting limit will be < 1.0 mg/kg dm and when having a dry matter content of 22%, the reporting limit will be < 2.0 mg/kg dm. With lower dry matter contents than 22 %, the reporting limit will even exceeds the limit value of 2 mg/kg dm. This fact has to be taken under consideration when determining Cr(VI) in these type of samples. In the draft EN standard a note is foreseen which describes that samples with a low dry matter content can have an influence on the achievable limit of quantification.

LIST OF LITERATURE

NBN EN ISO 15192 Soil and waste - Determination of chromium(VI) in solid material by alkaline digestion and ion chromatography with spectrophotometric detection (ISO 15192:2021)

prEN 00223122:2021 Soil improvers and growing media — Determination of chromium(VI)

European Fertilizing Regulation [CEN published 82 new Technical Specifications on fertilizing products in support of the EU Circular Economy objectives - CEN-CENELEC \(cencenelec.eu\)](https://cencenelec.eu/)
– posted 2022-04-21.

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