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Description

Please find enclosed the 1st working draft on WI 00223122, Soil improvers and growing media — Determination of chromium(VI).

As agreed during the meeting of CEN/TC 223/WG 4 on 2021-11-09, the enclosed 1st working draft and the forms for the adoption of the new work item will be circulated to CEN/TC 223 as soon as the call for tender for the project leaders is completed and the project leaders are known.

CEN/TC 223

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Soil improvers and growing media — Determination of chromium(VI)

Einführendes Element — Haupt-Element — Ergänzendes Element

Élément introductif — Élément central — Élément complémentaire

ICS:

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European foreword

This document (prEN 00223122:2021) 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”.

This document is a working document.

This document has been prepared under a standardisation request given to CEN by the European Commission and the European Free Trade Association.

Introduction

1 Scope

This document specifies a method for the determination of hexavalent chromium (CrVI) 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 2 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 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13650:—[1], *Soil improvers and growing media – Digestion by aqua regia for subsequent determination of elements*

EN 13040-1:—[2], *Soil improvers and growing media – Sample preparation – Part 1: Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory bulk density*

3 Terms and definitions

For the purposes of this document the terms and definitions given in CEN/TS 00223137:— and EN 13040-1: — apply.

3.1

chromium(VI) content

amount of chromium(VI) in soil improvers and growing media determined after extraction with an aqueous salt solution at pH 7,0 to pH 8,0.

Note 1 to entry: The chromium(VI) content is reported as chromium(VI) in milligrams per kilogram (mg/kg), expressed as the dry mass of the sample.

[SOURCE: EN ISO 17075-2:2017, 3.1, modified: “leather” is replaced by “soil improvers and growing media” and “pH 7,0 to 8,0” is replaced by “pH 7,0 to pH 8,0”].

4 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 (EN 00223123:—[3]) could reduce the number of the samples where the determination of chromium(VI) is necessary

[1] Under preparation. Stage at the time of publication: prCEN/TS 00223137:20**.

[2] Under preparation. Stage at the time of publication: EN 13040-1:20**.

[3] Under preparation. Stage at the time of publication: EN 00223123:20**.

because if the content of aqua regia (total) extractable chromium is lower than the legislative limit for chromium(VI) then the determination of chromium(VI) is not necessary.

5 Reagents

All reagents used shall have at least analytical grade.

5.1 Extraction solution

Dissolve 22,8 g dipotassium hydrogen phosphate K2HPO4·3H2O in 1 000 ml water (5.7), adjusted to pH 8,0 ± pH 0,1 with phosphoric acid (5.2). 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 ± 3) °C but shall be warmed to room temperature and degassed prior to use.

5.2 Phosphoric acid solution

700 ml o-phosphoric acid, density ρ = 1,71 g/ml, made up to 1 000 ml with water (5.7).

First add approximately 200 ml of deionised water (5.7) to a 1 000 ml volumetric flask, then add the 700 ml of o-phosphoric acid and dilute to the mark with deionised water.

5.3 Potassium dichromate ($K_2Cr_2O_7$), dried for (16 ± 2) h at (105 ± 2) °C.

5.4 Chromium(VI) stock solution

Dissolve 2,829 g potassium dichromate ($K_2Cr_2O_7$) (5.3) in water (5.7) in a volumetric flask and make up to 1 000 ml with water (5.7). 1 ml of this solution contains 1 mg of chromium.

A stock solution at this concentration level of hexavalent chromium is an alternative available commercially.

5.5 Chromium(VI) standard solution

Pipette 1 ml of solution (5.4) into a 1 000 ml volumetric flask and make up to the mark with extraction solution (5.1). 1 ml of this solution contains 1 µg 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.

A stock solution of hexavalent chromium at this concentration level is an alternative available commercially.

5.6 Argon or nitrogen, oxygen-free

Preference should be given to argon as an inert gas instead of nitrogen because argon has a higher specific mass than air.

5.7 Distilled or **deionised water,** with a specific conductivity not higher than 0,2 mS/m at 25 °C, free from the elements to be determined.

5.8 Magnesium chloride hexahydrate ($MgCl_2·6H_2O$)

Dissolve 85,4 g in a 100 ml volumetric flask, dilute with water (5.7), close and mix thoroughly.

6 Apparatus

Usual laboratory equipment and, in particular, the following.

6.1 Suitable mechanical orbital shaker, (100 ± 10) min^{-1}.

6.2 Conical flask, of capacity 250 ml, with stopper.

6.3 Aeration tube and **flow meter**, suitable for a flow rate of (50 ± 10) ml/min.

6.4 pH meter, with glass electrode.

6.5 Membrane filter, 0,45 µm pore size [polytetrafluoroethylene (PTFE) or polyamide 66].

6.6 Common laboratory glassware and pipettes.

6.7 Vacuum device, suitable for filtration of extraction solution, mobile phase, and sample extracts.

6.8 Ion-exchange chromatograph, with UV detector or high-performance liquid chromatography (HPLC) with anion-exchange column and UV detector. A photo diode array detector (DAD) is recommended.

6.9 Analytical balance, capable of weighing to 0,1 mg.

6.10 Syringe membrane filters of nylon, 0,45 µm pore size, for filtration of standards.

6.11 Suitable vials for HPLC.

7 Procedure

7.1 Sampling and preparation of samples

Sampling and sample preparation is described in EN 12579:—[4] and EN 13040-1:—.

7.2 Preparation of analytical solution

7.2.1 Solid and shear resistant pasty samples

The operator shall weigh (6.9) approximately (10 ± 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.

Following tasks shall be performed:

- Pipette 100 ml (V_0) of degassed solution (5.1) into a 250 ml conical flask (6.2). If the sample is expected to contain a significant amount of chromium(III), 1 ml of magnesium chloride solution (5.8) may be added. Displace oxygen by passing oxygen-free argon (or nitrogen) (5.6) into the flask for 5 min with a volume flow of (50 ± 10) ml/min. Remove the aeration tube (6.3), add the sample and close the flask with a stopper.

[4] Under preparation. Stage at the time of publication: EN 12579:20**.

- Shake the conical flask with the sample for 30 min on a mechanical orbital shaker at (100 ± 10) min^{-1} (6.1) 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 (6.11). 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.

7.2.2 Liquid and aqueous pasty samples

The operator shall weigh (6.9) approximately (10 ± 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 solution (5.1) into a 250 ml conical flask (6.2). If the sample is expected to contain a significant amount of chromium(III), 1 ml of magnesium chloride solution (5.8) may be added. Displace oxygen by passing oxygen-free argon (or nitrogen) (5.6) into the flask for 5 min with a volume flow of (50 ± 10) ml/min. Remove the aeration tube (6.3), 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} (6.1) 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 (6.11). 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.

7.3 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 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.

The method used should be verified using the recovery rate determination (7.5).

Record the injection volume as V_M and record the area of the chromate peak as A.

7.4 Calibration

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

The operator shall prepare calibration solutions from the standard solution (5.5). The Cr(VI) concentration in these solutions should cover the expected range of measurement.

The following tasks shall be performed:

- Plot a suitable calibration curve by using at least five standards, within the range 1 ml to 25 ml of standard solution (5.5). Pipette the given volumes of standard solution (5.5) into 25 ml volumetric flasks. Make up to volume with the extraction solution (5.1), mix well, filter (6.10) and transfer a suitable aliquot volume into a vial (6.11).

- Transfer an aliquot to a suitable vial (6.11) corresponding for the chromatographic system (6.8).

- Inject the standards in the chromatographic system (6.8). Introduce the same volume for each standard. It is recommended to inject equal volume for samples. Record the volume injected as V_c in µl.

- Plot the Cr(VI) concentrations in micrograms of chromium per milliliter (µg/ml) against the measured areas of the peaks of chromate. Plot the Cr(VI) concentration on the x-axis and the area on the y-axis.

7.5 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 7.2 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 7.2) 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).

8 Calculation and expression of results

8.1 Calculation of chromium(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 (1).

$$w_{Cr(VI)} = \frac{(A-b)\cdot(V_0+m\cdot W_m)\cdot V_C}{V_M\cdot m\cdot D_M\cdot F} \quad (1)$$

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/µg;
- 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 µl;
- V_M is the injection volume in the sample analysis, in µl;
- W_m is the moisture content expressed as a percentage by mass, according to EN 13040-1:—, clause 11.3.2;
- D_M is the dry matter content expressed as a percentage by mass; according to EN 13040-1:—, clause 11.3.1.

8.2 Recovery rate (according to 7.5)

The recovery rate η expressed in percent (%) shall be calculated according to formula (4).

$$\eta = \frac{A_s \times (V_1+V_2) - A \times V_1}{A_{st} \times (V_1+V_2)} \times 100 \quad (4)$$

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) as determined in (7.5);
- A is the area of chromate peak in the original sample as determined in (7.3);
- A_{st} is the area of chromate peak of extraction solution after adding Cr(VI) as determined in (7.5).

8.3 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, determined according to EN 13040-1:—, is given in percent (%) rounded to the nearest 0,1 %.

9 Test report

The test report shall include the following information:

a) the Cr(VI) content(s) obtained from 8.1 to the nearest 0,1 mg/kg;

b) a reference to this document (prEN 00223122:20**);

c) a description of the sample tested;

d) a brief description of the chromatographic technique (i.e., direct detection technique or whether a post-column reaction was used);

e) the dry matter content of the soil improvers and growing media in percent (%) to the nearest 0,1 %;

f) the recovery rate in percent (%);

g) details of any deviations from the procedure.

Annex A
(informative)

Chromatographic conditions for direct detection method

A.1 General

As the instrumental equipment of the laboratories may vary, no generally applicable instructions can be provided for the ion chromatographic analysis. The following parameters have been successfully tested and used.

The method used should be verified using the recovery rate determination (7.5).

A.2 Example of ion chromatographic conditions

A.2.1 Mobile phase reagents

All reagents used shall have at least analytical grade purity.

A.2.1.1 Anhydrous ammonium sulfate, $(NH_4)_2SO_4$ (CAS 7783-20-2).

A.2.1.2 Sodium hydroxide, NaOH (CAS1310-73-2).

A.2.1.3 Mobile phase stock solution

Dissolve 33,00 g of anhydrous ammonium sulphate and 0,40 g of sodium hydroxide in a volumetric flask and make up to 1 000 ml with water (5.7). This solution contains 250 mmol of ammonium sulphate and 10 mmol of sodium hydroxide. Its pH is 8,2. From this solution the eluent for chromatography (A.2.1.4) is prepared weekly. The shelf life is up to four months at 4 °C.

A.2.1.4 Mobile phase

Transfer 100 ml of mobile phase stock solution (A.2.1.3) into a 1 000 ml volumetric flask and make up to the mark with water (5.7). This solution contains 25 mmol of ammonium sulphate and 1 mmol of sodium hydroxide. Check that pH is (8,0 ± 0,2). Filter the solution through a membrane filter. The shelf life is up to one week at room temperature.

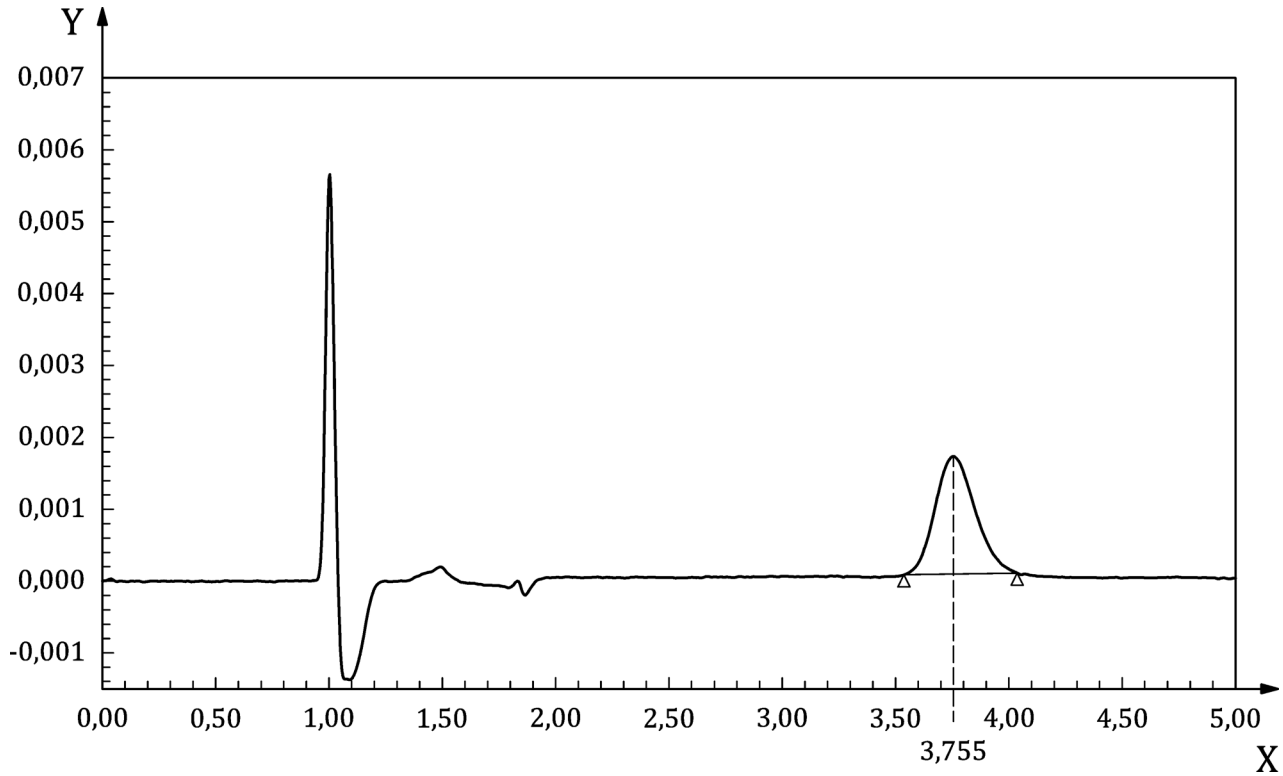
A.2.2 Instrumental conditions

- Column oven: 30 °C
- Mobile phase: 25 mmol ammonium sulphate and 1 mmol sodium hydroxide (A.2.1.4)
- Column: Anion-exchange column (polymethacrylate resin with quaternary ammonium functional groups), 4,6 × 75 mm, with 1 mm pre-column
- Range of wavelength (only for DAD): record the UV spectrum in the range 200 nm to 550 nm
- Wavelength of extracted chromatogram: 372 nm
- Flow rate: 0,9 ml/min

- Injection volume: 50 µl
- Run time of chromatogram: 5 min
- Equilibrate between injections: 6 min

A DAD diode array detector allows the reliable confirmation of chromate identity by comparing the UV spectrum of the detected peak with a standard chromate spectrum. Figure A.1 shows the chromatogram obtained from one sample that contains 3,9 mg/kg of Cr(VI). Figure A.2 shows the UV spectrum of the chromate anion found in a sample.

A.3 Example of a chromatogram and UV spectrum obtained in the analysis of a commercial sample



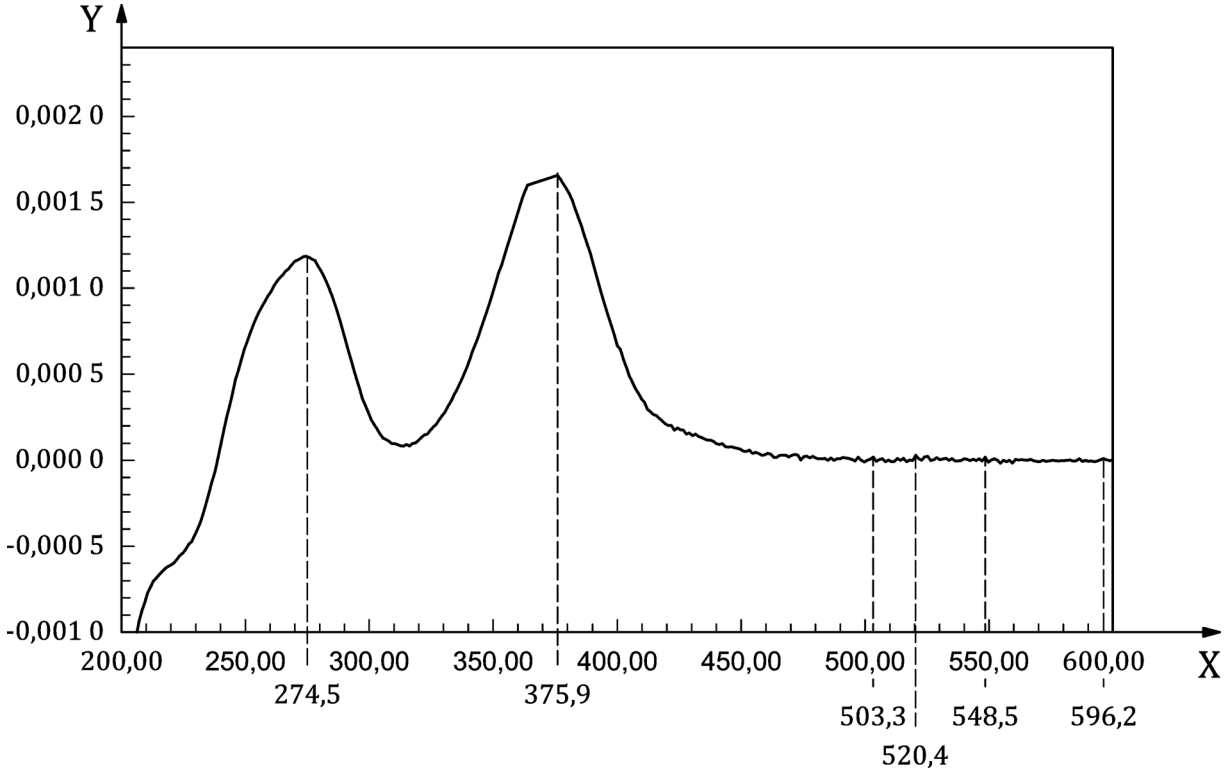
Key

X min

Y AU

NOTE Peak: Chromate, 3,755 min.

Figure A.1 — Chromatogram obtained from one sample that contains 3,9 mg/kg of Cr(VI)



Key

X mm

Y AU

Figure A.2 — Ultraviolet spectrum of chromate ion captured from the chromatogram of the sample of Figure B.1 at 3 757 min with a DAD detector

Annex B
(informative)

Chromatographic conditions for method with post-column reaction

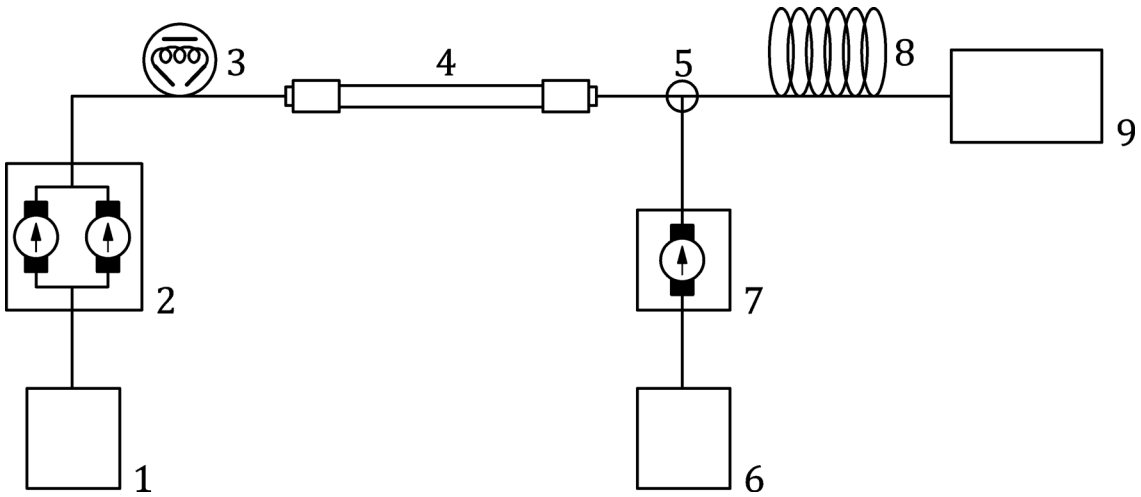
B.1 General

As the instrumental equipment of the laboratories may vary, no generally applicable instructions can be provided for the ion chromatographic analysis. The following parameters have been successfully tested and used.

The method used should be verified using the recovery rate determination (7.5).

B.2 Chromatographic system and apparatus required

The ionic chromatography method with post-column reaction is summarised in Figure B.1.



Key

1 mobile phase
2 LC pump
3 injection loop
4 analytical column
5 zero dead volume tee
6 post column reagent
7 post column reagent pump
8 reaction coil
9 detector (MWD or DAD)

Figure B.1 — Diagram of a system for ionic chromatography with post-column reaction

The Cr(VI) content is determined using chromatographic column packed with an anion exchange stationary phase.

Post-column reagent, containing 1,5-diphenylcarbazide, is added between the column and the reactor coil with the help of a zero dead volume tee.

The reaction coil ensures the proper mixing of the eluent from the column and the post column reagent and the Cr(VI) in solution oxidises 1,5-diphenylcarbazide to 1,5-diphenylcarbazone. This forms a red/violet complex with chromium, which can be quantified at 540 nm with the help of multiple wavelength detector (MWD) or a diode array detector (DAD).

B.2.1 Two suitable liquid chromatoraphy (LC) pumps. One is used to deliver the mobile phase in the system, the other is used to deliver the post-column reagent before the reaction coil.

B.2.2 Autosampler or **manual injection valve** equipped with a sample loop for the injection of a sample.

B.2.3 Thermostated column compartment.

B.2.4 Analytical column packed with an anion exchange stationary phase.

B.2.5 Zero dead volume tee.

B.2.6 Suitable reaction coil.

B.2.7 Detector, either MWD or DAD with the capability to detect at 540 nm.

NOTE In order to maintain the inertness of the configuration, the column and all the capillaries (including the injection loop) are in PEEK.

The usage of a guard column is highly recommended in order to extend the life span of the column. A guard column in PEEK packed with polystyrene-divinylbenzene particles is applicable.

B.3 Example of analytical conditions

B.3.1 Mobile phase and post-column reagents

All reagents used shall have at least analytical grade purity.

B.3.1.1 Ammonium sulfate, $(NH_4)_2SO_4$ (CAS 7783-20-2).

B.3.1.2 Ammonium hydroxide, NH_4OH (CAS 1336-21-6) as 28 % NH_3 in water.

B.3.1.3 1,5-Diphenylcarbazide, $C_{13}H_{14}N_4O$ (CAS 140-22-7).

B.3.1.4 Methanol, CH_3OH (CAS 67-56-1).

B.3.1.5 Sulphuric acid, H_2SO_4 (CAS 7664-93-9) at 98 % purity.

B.3.2 Preparation of the mobile phase

Dissolve (33,0 ± 0,1) g of ammonium sulphate (B.3.1.1) and 8,0 ml of ammonium hydroxide (B.3.1.2) in a 1 000 ml volumetric flask, fill to the mark with distilled water (5.7).

B.3.3 Preparation of post-column reagent

In a 1 000 ml volumetric flask, dissolve 28 ml of sulphuric acid (B.3.1.5) in about 500 ml of distilled water (5.7) and let it stand cooling.

During this time, dissolve (0,50 ± 0,01) g of 1,5-diphenylcarbazide (B.3.1.3) in 100 ml of methanol (B.3.1.4).

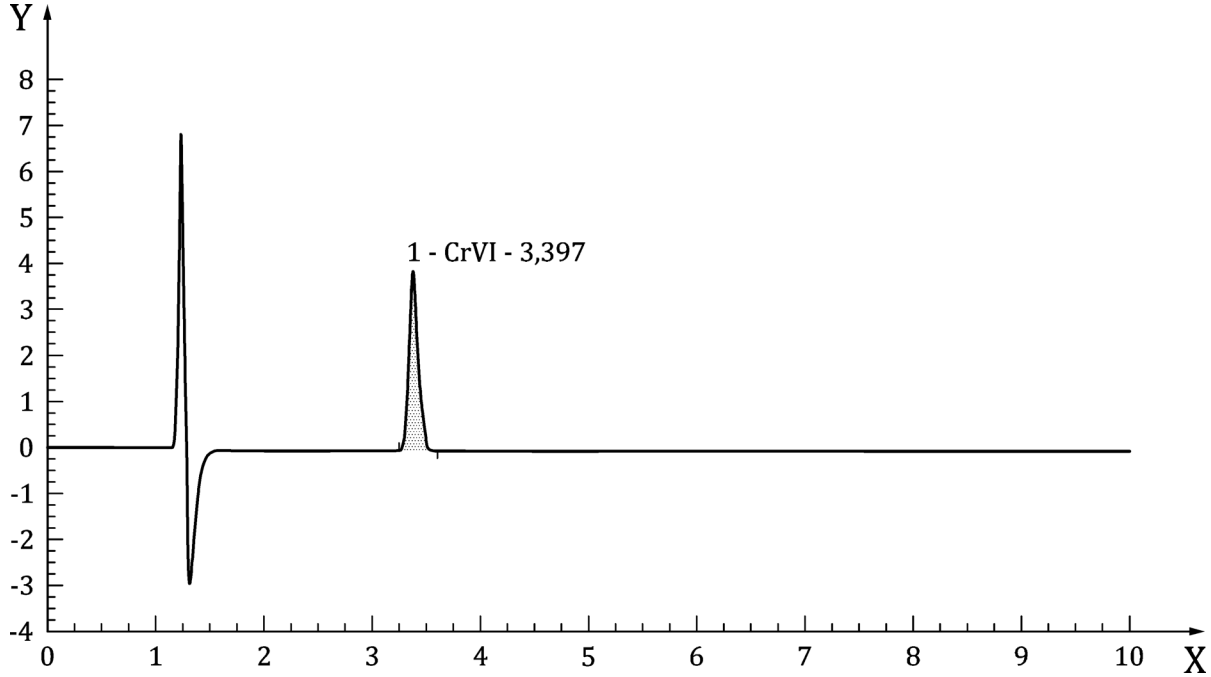
When the acidic solution is cooled, stirring with a magnetic stirrer and mix the diphenylcarbazide solution with the acidic solution and fill to the mark with water (5.7).

B.3.4 Instrumental conditions

- Analytical column: Anion exchange column with alkyl quaternary ammonium as functional group. Length: 250 mm. Internal diameter: 4 mm
- Guard column of length 35 mm and internal diameter 4 mm
- Reaction coil volume: 750 µl
- Injection volume: 100 µl
- Mobile phase flow rate: 1 ml/min
- Post-column reagent flow rate: 0,33 ml/min
- Run time: 10 min

B.4 Examples of chromatograms

Figure B.2 shows the chromatogram of a 20 µg/l standard and Figure B.3 shows a chromatogram of a real sample of organo-mineral fertilizer NPK 6-5-13.

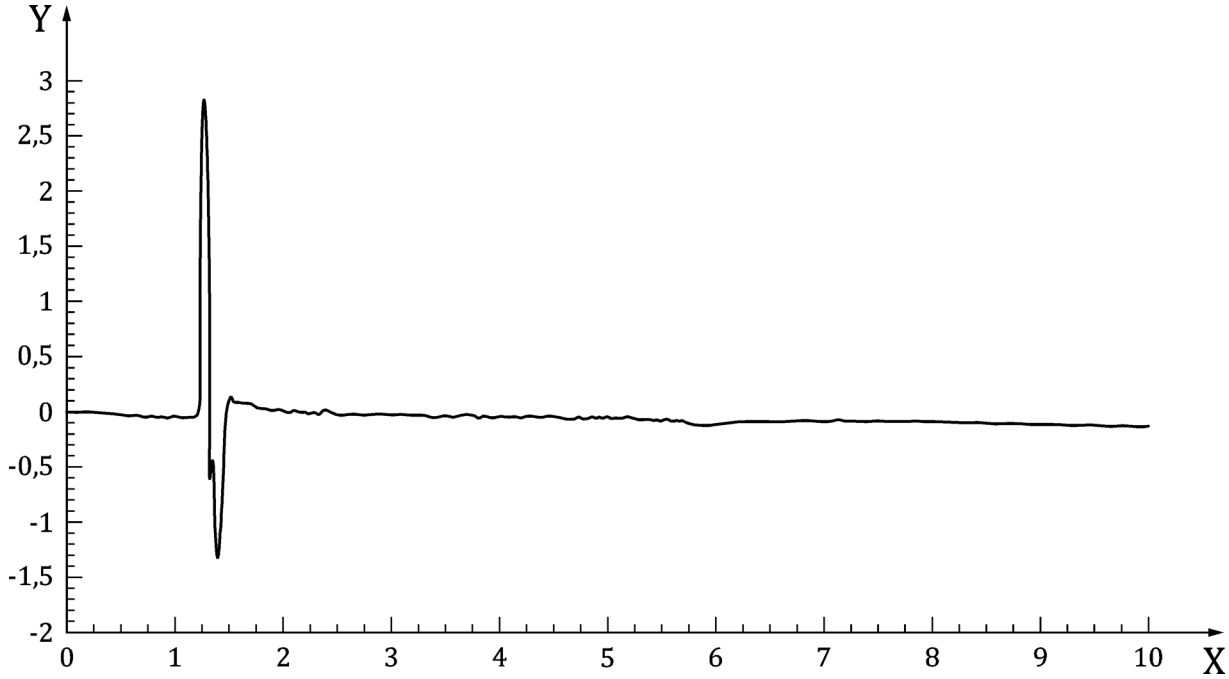


Key

X min

Y mAU

Figure B.2 — Chromatogram of a 20 µg/l standard



Key

X min

Y mAU

Figure B.3 — Chromatogram of a real sample of organo-mineral fertilizer NPK 6-5-13

Bibliography

[1] CEN/TS 00223137:—, *Soil improvers and growing media – Terminology*

[2] EN ISO 17075-2:2017, *Leather – Chemical determination of chromium(VI) content in leather – Part 2: Chromatographic method (ISO 17075-2:2017)*

[3] EN 12579:—, *Soil improvers and growing media – Sampling*

[4] EN 00223123:—, *Soil improvers and growing media – Determination of mercury in aqua regia extracts*