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Soil quality — Determination of perchlorate in soil using ion chromatography

Qualité du sol — Détermination du perchlorate des sols en utilisant la chromatographie ionique

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical and physical characterization*.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Although perchlorate occurs naturally, it is mainly a manmade anion (ClO_4^-). Usually, it is combined with NH_4^+, Na^+ and K^+ to form ammonium perchlorate, potassium perchlorate, and sodium perchlorate, respectively. It was reported that more than 90 % of perchlorate is used in military activities. Due to the excellent oxidizing capacity of perchlorate, it is added into propellant of rocket, missile, and satellite. We can presume some routes of manmade perchlorate exposure to soil and groundwater. For example, complete or incomplete explosion of the signal bomb (containing about 2 000 μg of perchlorate) in target or impact area, oversupplying of perchlorate for complete combustion in firing point, grand scale of fireworks could be the route of perchlorate exposure to soil and groundwater. In addition to these, other route could come from waste treatment process. Because perchlorate in missile is naturally deteriorated according to time, it should be recharged with a new one. In the past, incineration was preferred for the treatment of deteriorated perchlorate. When the incineration process was carried out in open space and kept as ash on site without any caution, it could be an important route of soil and groundwater contamination. Perchlorate is very stable in water and is not adsorbed easily on soil particle. From that view, surface water or groundwater could be contaminated more often than soil due to surface runoff or leaching process. However, perchlorate can also contaminate soil and vegetation. This kind of contamination could affect high level organisms in food chain. Perchlorate contamination of drinking water and food chain potentially affect human health because it can interfere with iodide uptake by the thyroid gland. Through this kind of interference, thyroid hormone production is decreased and it cause hyperthyroidism. The permitted level of perchlorate concentration in drinking water is below 15 ppb in Korea. Some states in the USA have an advisory level for perchlorate in drinking water. It is very difficult to find a country to regulate perchlorate level in soil because it seems that perchlorate contamination of soil is very rare in normal areas. However, perchlorate could be one of the major contaminants at a target area or firing point in military field and it is needed to manage the perchlorate concentration of soil to protect the vegetation, surface water, and groundwater. For this purpose, a standard method for perchlorate analysis in soil has been developed.

Soil quality — Determination of perchlorate in soil using ion chromatography

1 Scope

This document specifies a method for the determination of perchlorate in soil and soil materials.

Under the conditions specified in this document, a concentration as low as 0,1 mg/kg can be determined.

The working range is restricted by the ion-exchange capacity of the separator column. Dilution of the water extracts to the working range can be necessary.

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.

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

4 Principle

A dried and sieved soil sample is used as the test portion. Perchlorate is extracted by distilled or deionised water from the soil sample. Extraction is conducted by mechanical shaking and centrifugation.

After filtering the extract with a 0,45 µm membrane filter (e.g. cellulose acetate, hydrophilic polypropylene or polyethersulphone filter), the filtrate is analysed by ion chromatography to determine perchlorate.

If the adverse effects of anions, cations or organics are not negligible, appropriate pre-treatment for the elimination of these effects should be applied. Selective removal of interfering elements using a cartridge is one of the applicable pre-treatments.

The method requires the application of high-capacity separator columns, which allow the injection of sample volumes up to 1 ml.

Perchlorate is separated by ion chromatography (IC). Detection is conducted by suppressed conductivity (CD).

An anion-exchange resin is used as the stationary phase and an aqueous solution of salts of weak monobasic acids and dibasic acids is used as an eluent for isocratic or gradient elution (e.g. carbonate-, hydrogen carbonate-, hydroxide-eluent, and organic modifiers such as acetone, acetonitrile).

The concentration of perchlorate is determined after calibration of the overall procedure according to ISO 8466-1 or ISO 8466-2.

Control experiments are necessary to check the validity of the calibration function. Replicate determinations can be necessary. Use of a standard addition method can be required if matrix interferences are expected.

NOTE The results of interlaboratory validation study can be found in Annex B.

5 Interferences

Any substance that has a retention time coinciding with perchlorate and producing a detector response can interfere. Co-elution can be solved by changing columns, eluent strength (e.g. gradient elution), modifying the eluent with organic solvents or by selective removal of the interference with sample pre-treatment.

In the case of saline soil, a high concentration of chloride, sulfate, and carbonate in soil extracts can cause interference with the determination of perchlorate. It was reported that an injection of 800 mg/l of chloride, sulfate, and carbonate (about 6 mS/cm as of electrical conductivity) in perchlorate standard solution (0,025 mg/l) resulted in 80 % of recovery for perchlorate (1). Additionally, metals like iron or aluminium in soil extracts can have adverse effects on the performance of ion chromatograph due to binding with the resin material of the separator or suppressor column. These interference can be reduced by sample dilution, with the aid of special cation exchangers (e.g. Na-form, Ag-form, Ba-form, H-form) or resolved by the application of advanced inline cutting or re-injection techniques (see Annexes C, D and E).

Users of this document’s method should check their system individually for the significant interfering concentration of anions and cations.

In case of agricultural soil containing phosphate fertilizer, pyrophosphate ($P_2O_7^{4-}$) or tripolyphosphate ($P_3O_{10}^{5-}$) could be coeluted with perchlorate depending on the conditions of ion chromatography (2). This kind of interference could be avoided by using an optimized eluent.

Clay particles (e.g. aluminosilicates) or organic compounds (e.g. humic acids) can plug the column even though the centrifugation and filtering processes are applied. It is recommended to use a pre-column to protect the analytical separator column.

6 Reagents

Use only reagents of pro-analysis grade free of compounds containing perchlorate. Weigh the reagents with an accuracy of ±1 % of the nominal mass, unless stated otherwise. Prepare alternative concentrations or volumes of solutions as described in 6.2 to 6.9, if necessary. Alternatively, use commercially available solutions of the required concentration.

6.1 **Water**, with a resistivity of ≥18,2 MΩ cm (25 °C).

6.2 **Potassium perchlorate**, $KClO_4$.

6.3 **Sodium hydrogen carbonate**, $NaHCO_3$.

6.4 **Sodium chloride**, NaCl.

6.5 **Sodium sulfate**, Na_2SO_4.

6.6 **Sodium nitrate**, $NaNO_3$.

6.7 **Eluents**.

6.7.1 General

Degas all eluents used. Take steps to avoid any renewed air pick-up during operation (e.g. by helium sparging and inline degassing).

The choice of eluent (e.g. potassium hydroxide, sodium hydrogen carbonate, sodium carbonate, sodium hydroxide solutions; mixed with organic modifiers if needed) depends on the choice of column and detector. Seek advice from the column supplier. Apply eluents that were prepared manually, automatically or *in situ* electrochemically prepared. The chosen combination of separator column and eluent should conform to the resolution requirements stated in Clause 9. Use eluents as long as the requirements in 8.3.3 and in Clause 9 are met.

One example for an appropriate manually prepared eluent is given in 6.7.2. Additionally, another example for an appropriate eluent prepared using a generating device is given in 6.7.3.

6.7.2 **Sodium hydroxide**, $\rho(\text{NaOH}) = 65$ mmol/l.

Prepare 65 mmol/l of NaOH by putting 5,2 g of 50 % (mass fraction) aqueous NaOH from the middle portion of the reagent bottle into a 1 000 mL volumetric flask containing about 500 ml of degassed water. Fill it up to the mark with degassed water. Mix this solution gently and degas by sparging with argon or helium or sonicating under a vacuum for 10 min. For the preparation of 50 % (mass fraction) aqueous NaOH, weigh 50 g of sodium hydroxide and transfer into a 100 ml volumetric flask. Dissolve by adding water (6.1) and fill to the mark with water (6.1). Do not shake the 50 % (mass fraction) NaOH bottle to avoid forming carbonate.

NOTE Solutions of sodium hydroxide can be susceptible to carbonate contamination resulting from the adsorption of carbon dioxide from the atmosphere. This contamination can lead to irreproducible perchlorate retention times, elevated instrument background conductivity and increased baseline noise/drift.

6.7.3 **Potassium hydroxide**, $\rho(\text{KOH}) = 65$ mmol/l.

If the ion chromatographic system has a generating device for KOH eluent, generate 65 mmol/l of KOH eluent according to the manufacturer's recommendations.

Depending on the column's properties the eluent composition can be different. According to the manufacturer's instructions, check which kind of eluent is appropriate for analysing perchlorate.

6.8 **Standard solutions**.

6.8.1 **Perchlorate stock standard solution**, $\rho(\text{ClO}_4^-) = 1\,000$ mg/l.

Dry potassium perchlorate in the oven at 100 °C for 2 h. Weigh (1,393 ± 0,001) g and transfer quantitatively into a 1 000 ml volumetric flask. Dissolve by adding water (6.1) and fill to the mark with water (6.1). Store this stock standard solution in the refrigerator at 2 °C to 8 °C using polyethylene or glass bottles. This stock standard solution is stable for 12 months.

The use of commercially available certified stock standard solution is also possible.

Other alternative perchlorate compounds (e.g. sodium perchlorate, ammonium perchlorate) may also be used in the preparation of (stock) standard solution.

6.8.2 Perchlorate standard solution I, $\rho(\mathrm{ClO_4^-}) = 100$ mg/l.

Add 10 ml of stock standard solution (6.8.1) into a 100 ml volumetric flask and fill it up to the mark with water (6.1). Store this working standard solution in the refrigerator at 2 °C to 8 °C using polyethylene or glass bottles. This standard solution would be stable for 6 months.

In addition, a working standard solution can be made through the dilution of commercially available certified stock standard solution with water (6.1).

6.8.3 Perchlorate standard solution II, $\rho(\mathrm{ClO_4^-}) = 1$ mg/l.

Add 1,0 ml of perchlorate standard solution I (6.8.2) into a 100 ml volumetric flask and fill it up to the mark with water (6.1). Store this working standard solution in the refrigerator at 2 °C to 8 °C using polyethylene or glass bottles. This standard solution is stable for 3 months.

6.8.4 Perchlorate calibration standard solution.

Prepare the calibration standard solutions through the dilution of perchlorate standard solution I (6.8.2) or perchlorate standard solution II (6.8.3). At least, five levels of concentration should be prepared over the expected working ranges as evenly as possible (e.g. 0,05, 0,1, 0,2, 0,4, 0,8 and 1 mg/l).

6.8.5 Perchlorate system check solution, $\rho(\mathrm{ClO_4^-}) = 0{,}5$ mg/l.

Add 0,5 ml of perchlorate standard solution I (6.8.2) into a 100 ml volumetric flask and fill it up to the mark with water (6.1). Prepare the solution on the day of use.

6.8.6 Matrix check stock solution, $\rho(\mathrm{HCO_3^-}, \mathrm{Cl^-}, \mathrm{SO_4^{2-}}, \mathrm{NO_3^-})$ each of 1 g/l.

Place 3,44 g of sodium hydrogen carbonate (6.3), 4,13 g of sodium chloride (6.4), 3,72 g of sodium sulfate (6.5) and 3,42 g of sodium nitrate (6.6) in a 100 ml volumetric flask. Dissolve these compounds in approximately 80 ml of water (6.1) and fill the flask up to the mark with water (6.1). This solution is stable for 1 year.

Dilute 4 ml of this solution in 100 ml of water (6.1) to obtain the 1 g/l-stock solution. This solution would be stable for 6 months.

6.8.7 Perchlorate matrix check stock solutions, $\rho(\mathrm{ClO_4^-})$, 2 mg/l.

Depending on the laboratory internal conditions chosen (e.g. separation characteristics), prepare a check solution spiked with an appropriate perchlorate concentration. The composition of this check solution should cover the actual conditions of samples as closely as possible. For example, to make samples with chloride and sulfate concentrations of up to 50 mg/l each and a presumed perchlorate concentration of 2 mg/l, follow the process described below:

Pipette 5 ml of the matrix check stock solution (6.8.6) and 2 ml of the perchlorate standard solution I (6.8.2) into a 100 ml volumetric flask and fill it up to the mark with water (6.1).

The concentrations in this solution are: 50 mg/l of carbonate, chloride, sulfate, and nitrate, respectively, and 2 mg/l of perchlorate. Prepare the solution on the day of use.

6.9 Blank solution.

Fill a volumetric flask (e.g. 100 ml) with water (6.1).

7 Apparatus

7.1 Horizontal mechanical shaker, maintaining a frequency of 100 cycles/min and offering a shaking width of about 10 cm.

7.2 Centrifuge, should be used at a speed setting of 3 000 rpm.

7.3 Membrane filters, with 0,45 µm pore size or smaller (e.g. hydrophilic polypropylene or polyethersulphone filter).

7.4 Cartridges, Ag-form, Ba-form, H-form and Na-form for the selective removal of chloride, sulfate, carbonate and cations (e.g. iron, aluminium), respectively.

7.5 Analytical balance, being capable of making precise measurements of ±0,1 mg.

7.6 Ion chromatographic system.

7.6.1 Eluent reservoir, equipped with a degassing unit.

7.6.2 Pumping system, having an accurate flow rate and pulse-free flow and suitable for the isocratic or gradient technique.

7.6.3 Injection valve, appropriate for reproducible injections into the high-pressure flow path, equipped with sample loop which allow the injection of sample volumes up to 1 ml.

7.6.4 Separator column, with the specified separating performance (9.1).

7.6.5 Pre-column, having the capability to protect the analytical separator column.

NOTE In general, pre-columns contain the same as or similar resin materials to the analytical separator column or non-functionalised resin.

7.6.6 Conductivity detector, thermally controlled and sensitive with a suppressor device.

7.6.7 Recording device.

8 Procedure

8.1 Pre-treatments

General pre-treatments include drying and sieving. The field moist sample is dried in the air or oven. In the case of air drying, spread the soil sample no thicker than 5 cm on the tray. The tray should not absorb any moisture from the soil. Additionally, direct sunlight should be avoided. For oven drying, the temperature in the oven should not exceed 40 °C and a ventilation device should be equipped.

The dried sample is passed through a 2 mm sieve and then it is used as a test portion.

For other details of pre-treatments, refer to ISO 11464.

8.2 Extraction

Weigh (10 ± 0,1) g of dried and sieved soil sample into a 50 ml centrifuge tube. Add 30 ml of deionized water. Shake it using a mechanical shaker (7.1) for 1 h at 100 cycles/min. After the shaking process, centrifuge the mixture at 3 000 rpm for 1 h (Annex A). Filter the supernatant through a 25 mm