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**Soil quality — Extraction of thallium and  
determination by electrothermal atomic  
absorption spectrometry**

*Qualité du sol — Extraction du thallium et dosage par spectrométrie  
d'absorption atomique électrothermale*

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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 20279 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

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# Soil quality — Extraction of thallium and determination by electrothermal atomic absorption spectrometry

**WARNING** — Thallium solutions are highly toxic. Appropriate measures shall be taken to avoid ingestion. Care should be taken in the disposal of these solutions.

Certain procedures, reagents and apparatus used in this International Standard pose potential hazards, especially in connection with concentrated acids, toxic solutions of thallium, and high-pressure gases. Users should ensure that they are familiar with the safety procedures necessary in such situations, and with any legal requirements (including waste disposal). If in any doubt, seek advice from the competent authorities.

## 1 Scope

This International Standard specifies methods for extraction of thallium from soil by nitric acid and hydrogen peroxide and its determination in the extract by electrothermal atomic absorption spectrometry (ETAAS).

NOTE The relevant working range of this method is approximately from 0,05 mg/kg to 100 mg/kg.

## 2 Normative references

The following referenced documents are indispensable for the application 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 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 11464:1994, *Soil quality — Pretreatment of samples for physico-chemical analyses*

ISO 11465:1993, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

ASTM E11:2004, *Standard Specification for Wire Cloth and Sieves for Testing Purposes*

## 3 Principle

Thallium is extracted from soil by a mixture of nitric acid and hydrogen peroxide, and determined in solution by electrothermal atomic absorption spectrometry, in which discrete volumes of sample solution are dispensed into a graphite tube. By increasing the temperature of this tube step by step, the processes of drying, thermal decomposition of the matrix and thermal dissociation into free atoms occur. The resulting absorption signal should (under optimum conditions) be a sharp symmetrical peak with a height proportional to the element concentration in solution. See Table 1.

Table 1 — Measurement wavelength for thallium

| Element  | Wavelength<br>nm | Spectral bandwidth<br>nm | Measurement method |
|----------|------------------|--------------------------|--------------------|
| Thallium | 276,8            | 0,2                      | ETAAS              |

**NOTE** Thallium contents in non-polluted soils are low. Therefore, a highly sensitive analytical method like ETAAS is necessary for the determination of trace concentrations. Unfortunately, severe interferences in aqua regia extracts of soils are observed using ETAAS for thallium determination. Due to a high chloride concentration in aqua regia extracts, thallium will be volatilised and lost during the pretreatment step. Therefore, in this International Standard, a mixture of nitric acid and hydrogen peroxide will be used for the extraction of thallium from soil.

Aqua regia can be used with approximately the same extraction efficiency to extract thallium from soil. However, for the determination of the element in the extract solution, other analytical methods, like inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS), shall be used.

## 4 Reagents

All reagents shall be of recognised analytical grade.

**4.1 Water**, demineralised or distilled, from an all-glass apparatus, conforming to Grade 2 of ISO 3696. The water used for blank determinations, and for preparing reagents and standard solutions, shall have element concentrations that are negligible compared with the lowest concentration to be determined in the sample solutions.

**4.2 Nitric acid**,  $w(\text{HNO}_3) = 65\%$ ;  $\rho \sim 1,40 \text{ g/ml}$ .

The same batch of nitric acid shall be used throughout the procedure.

**4.3 Nitric acid**,  $c(\text{HNO}_3) = 0,5 \text{ mol/l}$ .

Add 32 ml of nitric acid (4.2) to 500 ml of water in a 1 000 ml volumetric flask, fill to the mark with water and mix well.

**4.4 Hydrochloric acid**,  $w(\text{HCl}) = 37\%$ ;  $\rho \sim 1,185 \text{ g/ml}$ .

The same batch of hydrochloric acid shall be used throughout the procedure.

**4.5 Hydrogen peroxide**,  $w(\text{H}_2\text{O}_2) = 30\%$ .

The same batch of hydrogen peroxide solution shall be used throughout the procedure.

**4.6 Palladium/magnesium nitrate modifier solution.**

Dissolve 0,3 g of palladium nitrate  $[\text{Pd}(\text{NO}_3)_2]$  and 0,36 g of magnesium nitrate  $[\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}]$  in a 100 ml volumetric flask, fill to the mark with 0,5 mol/l nitric acid (4.3) and mix.

Alternatively, prepare the palladium/magnesium nitrate modifier solution as follows. Dissolve 0,14 g of palladium powder in a 250 ml beaker with 3,5 ml of nitric acid (4.2), add 10  $\mu\text{l}$  of hydrochloric acid (4.4), evaporate the solution to near dryness on a water bath or hot-plate, then add 0,36 g of magnesium nitrate  $[\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}]$ . Dissolve this solid residue in 50 ml of nitric acid (4.3), transfer the solution into a 100 ml volumetric flask, fill to the mark with nitric acid (4.3) and mix. 10  $\mu\text{l}$  of this solution are equal to 14  $\mu\text{g}$  of Pd and 36  $\mu\text{g}$  of  $\text{Mg}(\text{NO}_3)_2$ .

**4.7 Preparation of stock and standard solutions of individual elements.**

Two sources of stock solutions are available:

- commercially available stock solutions;
- stock solutions prepared in the laboratory from pure elements or stoichiometrically defined salts or oxides.

**NOTE** Commercially available stock solutions have the advantage that they remove the need to handle toxic metals, especially thallium, directly. However, special care needs to be taken to ensure that these solutions are supplied with a certified composition from a reputable source and are checked on a regular basis.

**4.8 Thallium stock solution**, corresponding to  $\rho$  (Tl) = 1 000 mg/l.

**4.9 Thallium standard solution**, corresponding to  $\rho$  (Tl) = 100 mg/l.

Pipette 50,00 ml of the thallium stock solution (4.8) into a 500 ml volumetric flask, add 5 ml of nitric acid (4.2), fill to the mark with water and mix well.

**4.10 Thallium standard solution**, corresponding to  $\rho$  (Tl) = 1 mg/l.

Pipette 1,00 ml of the thallium standard solution (4.9) into a 100 ml volumetric flask, add 2 ml of nitric acid (4.2), fill to the mark with water and mix well. Prepare this solution on the day of use.

**4.11 Blank calibration solution.**

Dilute 5 ml of nitric acid (4.2) in a 100 ml volumetric flask and fill to the mark with water.

Cleaning of glassware: All glassware used in the determination of small amounts of this element shall be cleaned carefully before use, e.g. by immersion in aqueous nitric acid solution,  $w(\text{HNO}_3) = 5\%$ , for a minimum of 6 h, followed by rinsing with water before use. The nitric acid shall be replaced each week. It can be helpful to keep a separate set of glassware exclusively for these determinations.

## 5 Apparatus

Usual laboratory apparatus and the following.

**5.1 Grinding device**, capable of grinding dried soils to  $< 150\ \mu\text{m}$  particle size without element contamination.

**5.2 Test sieve**, in accordance with ASTM E11, with an aperture of  $150\ \mu\text{m}$  (100 mesh).

**5.3 Drying oven and desiccator**, for the determination of dry matter in accordance with ISO 11465.

**5.4 Nitric acid/hydrogen peroxide extraction device.**

Temperature-controlled heating apparatus, and a 250 ml round-bottomed flask with reflux condenser, straight-through type, and a non-return-type absorption vessel filled with 10 ml of nitric acid (4.3), capable of heating the nitric acid/hydrogen peroxide mixture to reflux temperature.

The use of an absorption vessel is recommended, due to vigorous reaction of reagents with samples having a high organic-matter content.

Alternatively, a pressure digestion system (up to 50 bar) with sample vessels made of PTFE-TFM, PFA, quartz or another suitable material, and thermal heating equipment or a microwave oven may be used.

**5.5 Filter papers**, cellulose-based ashless types for quantitative work, with a medium open texture and with a diameter of approximately 100 mm to 150 mm. Alternatively, use a membrane filtration equipment with cellulose-based membrane filters of approximately  $8\ \mu\text{m}$  pore size.

**5.6 Atomic absorption spectrometer**, equipped with an electrothermal atomiser, an automated sample introduction system, a thallium hollow cathode lamp or electrodeless discharge lamp operated at a current recommended by the lamp and instrument manufacturer, an automatic background correction device (preferably Zeeman background correction) and a computerised readout.

## 6 Procedure

### 6.1 Test portion

#### 6.1.1 General

Grind a representative portion of air-dried sample (prepared in accordance with ISO 11464) until it passes entirely through the 150 µm aperture sieve (5.2), so as to obtain a subsample of approximately 20 g. Use a separate portion of the subsample to determine the water content in accordance with ISO 11465.

#### 6.1.2 Nitric acid/hydrogen peroxide extraction for thallium — Reflux technique

Weigh  $(1,000 \pm 0,001)$  g of this ground subsample into a round-bottomed flask, and add 5 ml of nitric acid (4.2). Add 10 ml of nitric acid (4.3) to the absorption vessel. Connect the cooling system with the trap, and allow to react for 16 h at room temperature. Then add 10 ml of hydrogen peroxide (4.5) to the round-bottomed flask. Raise the temperature slowly to reflux conditions and maintain for 4 h, ensuring that the condensation zone is lower than 1/3 of the height of the condenser, then allow to cool. Add the contents of the absorption vessel to the reaction vessel, via the condenser, rinsing both the absorption vessel and the condenser with a further 10 ml of nitric acid (4.3). Allow the reaction vessel to stand so that most of any insoluble residue settles out of suspension. Decant the sediment-free supernatant carefully onto a filter paper (5.5), and collect the filtrate in a 100 ml volumetric flask. Wash the residue carefully with a minimum of nitric acid (4.3) and add the washings to the volumetric flask. Fill to the mark with water and mix well.

#### 6.1.3 Nitric acid/hydrogen peroxide extraction for thallium — Pressurized digestion technique

Weigh  $(0,500 \pm 0,001)$  g of this ground subsample into the pressure vessel (5.4). Add 5 ml of nitric acid (4.2) and 2,5 ml of hydrogen peroxide (4.5), wait until any vigorous gaseous emission ends and then close the vessel. Raise the temperature to 160 °C and hold for 3 h. Cool the digestion vessel to room temperature, rinse with nitric acid (4.3) and filter the suspension through a paper filter or membrane filter (5.5) into a 50 ml volumetric flask. Wash the residue carefully with a minimum of nitric acid (4.3) and add the washings to the volumetric flask. Fill to the mark with water and mix well.

### 6.2 Blank test solution

Carry out a blank test at the same time as the determination and following the same procedure, using the same quantities of all the reagents for the determination, but omitting the test portion.

### 6.3 Preparation of calibration solutions for thallium

The standard solutions shall be prepared before each batch of determinations.

Pipette 0,5 ml, 2,00 ml, 4,00 ml and 6,00 ml of the thallium standard solution (4.10) into a series of 100 ml volumetric flasks. Add 2 ml of nitric acid (4.2), dilute to the mark with water and mix well. These solutions correspond to thallium concentrations of 0,005 mg/l, 0,02 mg/l, 0,04 mg/l and 0,06 mg/l, respectively.

### 6.4 Calibration and determination, electrothermal atomic absorption spectrometry (ETAAS)

**6.4.1** Set up the instrument and align the electrothermal atomiser in accordance with the manufacturer's instructions. Use of background correction is essential.

**6.4.2** Determine the optimum electrothermal atomiser parameters for the particular type of atomiser and sample size as recommended by the instrument manufacturer or normal laboratory practice (see Table 2). The temperatures given are only approximate values. The temperature programme should be optimised with the instrument used.

**Table 2 — Example of ETAAS conditions**

| Element                      | Thallium                            | Time<br>s |
|------------------------------|-------------------------------------|-----------|
| Wavelength, nm               | 276,8                               |           |
| Graphite furnace             | Pyrolytic coated tube with platform |           |
| Matrix modifier              | Palladium/magnesium nitrate (4.6)   |           |
| Drying temperature, °C       | 90/130/300                          | 5/120/20  |
| Pretreatment temperature, °C | 700                                 | 90        |
| Atomising temperature, °C    | 1 800                               | 3         |
| Clean-up temperature, °C     | 2 500                               | 5         |

Depending on the apparatus, the application of deuterium background correction systems can be limited to approximately 0,6 absorbance. Also, if structured spectral backgrounds occur, the deuterium background correction systems cannot be used. To overcome the disadvantages of the deuterium background compensation method, the application of Zeeman background correction is highly recommended for measurements in complex soil extracts. To increase the analyte-to-background signal ratio, use of a graphite tube with a pyrolytic platform, together with palladium and magnesium nitrate as matrix modifiers, is recommended.

**6.4.3** Ensure that the test solutions (6.1.2 or 6.1.3) and the calibration solutions (6.3) are within 1 °C of the same temperature. This will be reached at approximately 2 h equilibration time. Set the instrument at zero and set the baseline. Check the zero stability and lack of spectral interferences within the atomisation system, by running the pre-set heating programme for blank-firing the graphite atomiser. Repeat to ensure baseline stability.

## **6.5 Direct measurement of calibration and test solutions, ETAAS**

For each type of soil, it is mandatory to determine the corresponding extract solution at least once by means of the standard addition method. If the analytical results according to the standard addition method and the calibration curve method are equal, the calibration curve method can be applied. If the analytical results are different, matrix interferences are likely and the standard addition method shall be used for each corresponding soil extract solution.

The calibration shall be established from standard solutions which give peak absorbances lower than the maximum absorbance specified by the manufacturer for that wavelength.

Using an autosampler (5.6), inject a fixed volume of solution and atomise the calibration blank (4.11), calibration solutions (6.3), blank test solution (6.2) and test solution, in order of increasing instrument response. If the peak height or peak area of the test portion exceeds the value of the highest calibration solution, a smaller volume of the test portion shall be used.

Atomise each solution three times and, if the repeatability is good, average the readings. Check the instrument for memory effects, especially at high analyte levels, by running the blank-firing programme between determinations. Reset the baseline to zero if necessary.

## **7 Plotting the graph**

The software in modern instruments may plot a graph having the element concentrations of the calibration solutions (from which the blank calibration readings have been subtracted), in milligrams per litre as abscissa, and the corresponding values of the peak height (or peak area) as the ordinate. If this is not possible, produce such a graph using external software or by hand.

## 8 Calculation

**8.1** By reference to the calibration graph, the software may calculate the concentrations of the elements corresponding to the absorbances of the test portion and the blank test solution. Alternatively, this can be done by hand. Calculate the content ( $w$ ) of Tl, expressed in milligrams per kilogram of dry matter, of the sample using the following formula:

$$w(\text{Tl}) = \frac{(\rho_1 - \rho_0)}{m} \cdot f \cdot V \cdot C$$

where

- $w(\text{Tl})$  is the mass fraction of thallium in the sample, in milligrams per kilogram of dry matter;
- $\rho_1$  is the element concentration, in milligrams per litre, corresponding to the absorbency of the test portion (6.1.2);
- $\rho_0$  is the element concentration, in milligrams per litre, corresponding to the absorbency of the blank test solution (6.2);
- $f$  is the dilution factor of the test portion [if the test portion (6.1) is diluted];
- $V$  is the volume, in millilitres, of the test portion taken for the analysis;
- $m$  is the mass of test sample taken, in grams;
- $C$  is the correction factor for the dry soil sample:  $C = 100/w_{\text{dm}}$ ;
- $w_{\text{dm}}$  is the dry matter content of the soil, expressed as a percentage mass fraction in accordance with ISO 11465.

## 8.2 Calculation according to the method of standard additions

The software in modern instruments may calculate the content or plot a graph, with the absorbance values on the ordinate and the element concentrations on the abscissa. The element content of the soil samples is calculated from the value of the negative intercept on the abscissa, taking into account the blank value and any dilution of the sample. Be sure that the analyte portions added do not exceed the linear region of the calibration curve. If suitable software is not available, perform this calculation by hand.

## 8.3 Expression of results

Values shall be rounded to 0,01 mg/kg, but only significant figures should be expressed.

EXAMPLE  $w(\text{Tl}) = 0,15 \text{ mg/kg}$   
 $w(\text{Tl}) = 1,5 \text{ mg/kg}$

## 9 Interferences

Potential background absorption interferences due to high salt concentrations are eliminated by the instrumental background correction system. Background signals can be reduced with appropriate matrix modifiers and application of the platform technique together with a carefully designed temperature programme.

Because of the high sensitivity of electrothermal atomic absorption, stringent precautions shall be taken to clean all glassware and avoid contamination of sample, standard and calibration solutions by foreign material and dust from the laboratory atmosphere. To reduce background values/contamination, it can help to keep a separate set of glassware for these determinations.

## 10 Precision

An interlaboratory comparison yielded the data given in Table 3. Repeatability and reproducibility were calculated according to the principles of ISO 5725-2.

**Table 3 — Precision data from an interlaboratory comparison using  $\text{HNO}_3/\text{H}_2\text{O}_2$  extraction with thallium determination by ETAAS (3 replicates)**

| Sample                                                                                                                                                                                                                                                                                                                                                                                                                                                       | $N_{\text{lab}}$ | $N_{\text{rej}}$ | $N_{\text{res}}$ | $\bar{x}$<br>mg/kg | $S_R$<br>mg/kg | $V_R$<br>% | $S_r$<br>mg/kg | $V_r$<br>% | $R$<br>mg/kg | $r$<br>mg/kg |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|------------------|------------------|--------------------|----------------|------------|----------------|------------|--------------|--------------|
| Soil 1                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 8                | 0                | 24               | 0,560              | 0,134          | 23,87      | 0,028          | 4,99       | 0,37         | 0,08         |
| Soil 2                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 10               | 3                | 30               | 21,05              | 1,576          | 7,49       | 0,585          | 2,78       | 4,37         | 1,62         |
| $N_{\text{lab}}$ is the number of accepted laboratories<br>$N_{\text{rej}}$ is the number of rejected laboratories<br>$N_{\text{res}}$ is the number of accepted results<br>$S_R$ is the reproducibility standard deviation<br>$S_r$ is the repeatability standard deviation<br>$V_R$ is the relative reproducibility standard deviation<br>$V_r$ is the relative repeatability standard deviation<br>$R$ is the reproducibility<br>$r$ is the repeatability |                  |                  |                  |                    |                |            |                |            |              |              |

## 11 Test report

The test report shall contain the following information:

- a reference to this International Standard;
- a reference to the method used;
- complete identification of the sample;
- mineralization procedure (see 6.1.2 or 6.1.3);
- the results of the determination;
- any details not specified in this International Standard or which are optional, as well as any factor which may have affected the results.