# INTERNATIONAL STANDARD

# ISO 12782-1

First edition
2012-06-01

# Soil quality — Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials —

## Part 1:
## Extraction of amorphous iron oxides and hydroxides with ascorbic acid

*Qualité du sol — Paramètres pour la modélisation géochimique de la lixiviation et de la spéciation des constituants des sols et des matériaux —*

*Partie 1: Extraction des oxydes et hydroxydes de fer amorphe à l'acide ascorbique*

Reference number
ISO 12782-1:2012(E)

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Published in Switzerland

# Foreword

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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 12782-1 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 7, *Soil and site assessment*.

ISO 12782 consists of the following parts, under the general title *Soil quality — Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials*:

— *Part 1: Extraction of amorphous iron oxides and hydroxides with ascorbic acid*

— *Part 2: Extraction of crystalline iron oxides and hydroxides with dithionite*

— *Part 3: Extraction of aluminium oxides and hydroxides with ammonium oxalate/oxalic acid*

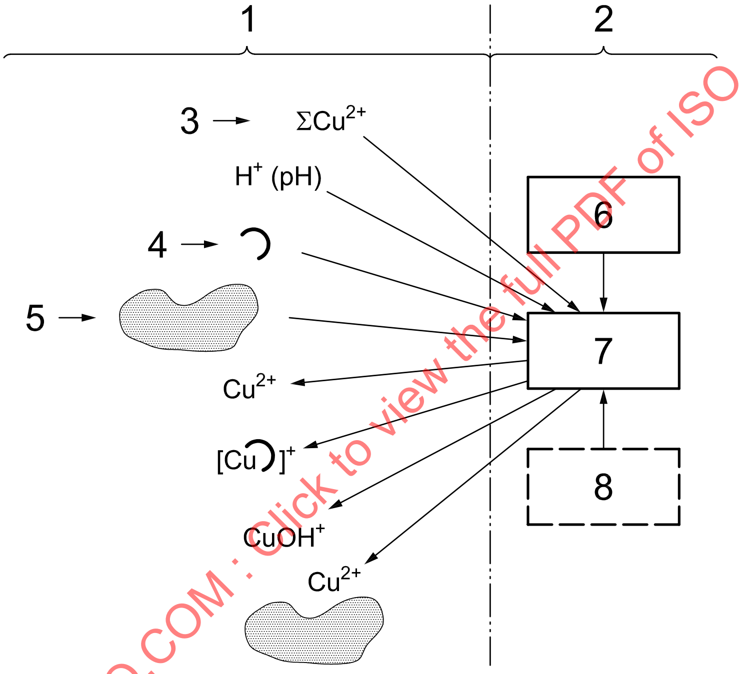
— *Part 4: Extraction of humic substances from solid samples*

— *Part 5: Extraction of humic substances from aqueous samples*

# Introduction

In addition to leaching procedures for subsequent chemical and ecotoxicological testing of soil and other materials including waste, predictive models are becoming indispensable tools in the environmental risk assessment of these materials. Models are particularly required when the results of laboratory leaching tests are to be translated to specific scenarios in the field, with regard to assessing the risks of both contaminant migration and bioavailability.

In the past few years, geochemical models have been shown to be valuable tools to be combined with the data obtained from characterization leaching standards, such as pH-dependence and percolation tests. These models have the advantage of being based on fundamental thermodynamic parameters that have general validity. In order to enable extrapolation of laboratory leaching data to the mobility and/or bioavailability of a constituent in a specific field scenario, these models require additional input parameters for specific soil properties (see Figure 1).



**Key**

| | |
|---|---|
| 1 | experiment |
| 2 | geochemical speciation modelling |
| 3 | available metal concentration |
| 4 | dissolved humic substances |
| 5 | reactive (solid) surfaces |
| 6 | database with stability constants |
| 7 | computer program |
| 8 | assumptions |

**Figure 1 — Relationships between experimental data, as obtained from laboratory leaching/extraction tests, and geochemical modelling of the speciation of a heavy metal in the environment (modified after M. Gfeller & R. Schulin, ETH, Zürich)**

Characterization leaching standards provide information on the concentrations of the contaminant of interest as a function of, in particular, pH and liquid/solid (L/S) ratio. In addition, a more complete analysis of the leachates also provides information on the major ion composition and dissolved organic carbon (DOC), parameters that are particularly important for the chemical speciation of constituents through processes such as precipitation, complexation and competition for adsorption on reactive mineral and organic surfaces in the soil. As illustrated in Figure 1 for the example of copper, geochemical modelling enables calculation of the metal distribution among these different chemical species in the system of interest. This provides necessary information for risk-assessment purposes, as these different chemical forms play distinct roles in the mobility and bioavailability of the metal in the soil. In addition to information obtained from the leaching standards (in their current state of development/definition), the following two additional types of information are required.

a) The "available" (sometimes also referred to as "active" or "exchangeable") concentration of the constituent in the solid phase, as opposed to the total concentration determined by acid destruction of the solid matrix. This "available" concentration can be obtained by leaching at low pH, a condition that can be obtained by extending the pH range in the pH-dependent leaching test (ISO/TS 21268-4) down to pH ≈ 0,5 to pH ≈ 1.

b) The concentration of reactive organic and mineral surfaces in the soil, which constitute the major binding (adsorption) sites for most constituents in the soil matrix.

The major reactive surfaces that control the binding of constituents by sorption processes to the soil matrix are particulate organic matter and iron and aluminium (hydr)oxides. It is generally accepted that the reactivity of these mineral and organic surfaces can strongly vary as a function of their specific surface area/crystallinity [iron and aluminium (hydr)oxides] and composition (organic matter). When the results are intended to be used for the above-described purposes of geochemical modelling in conjunction with leaching tests, it is important that the methods be selective for reactive surfaces for which generic thermodynamic adsorption parameters are also available for the most important major and trace elements.

This part of ISO 12782 aims to determine the content of "reactive" iron in the form of *amorphous* iron oxides and hydroxides in soil and materials using an ascorbic acid extract. The procedure is based on Reference [5], described in Reference [6], while generic thermodynamic adsorption parameters for amorphous iron (hydr) oxide are available in Reference [7].

Thermodynamic parameters for adsorption models other than those used in Reference [7] are also available in the literature and may also be used to model the binding of constituents to amorphous iron (hydr)oxides.

Iron can be present in several forms in soils, of which the most important for the binding of trace constituents are well-crystallized and insoluble oxides and hydroxides (e.g. goethite, haematite, magnetite) and the poorly ordered, more soluble oxides and hydroxides (e.g. ferrihydrite, hydrous ferric oxide). Amorphous and crystalline forms have a different reactivity towards binding of trace constituents as a result of differences in specific surface areas and characteristics of the binding "sites" on the surface.

# Soil quality — Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials —

# Part 1:
# Extraction of amorphous iron oxides and hydroxides with ascorbic acid

## 1 Scope

This part of ISO 12782 specifies the determination of the content of “reactive” iron in the form of amorphous iron oxides and hydroxides in soil and other materials by extraction with ascorbic acid. Other materials also include waste. The content of “reactive” iron can be used as input in geochemical models to represent the content of amorphous iron (hydr)oxides.

NOTE Although the ammonium oxalate/oxalic acid extraction (ISO 12782-3) is commonly used to estimate “reactive” iron in the form of iron oxides and hydroxides, this part of ISO 12782, in conjunction with ISO 12782-2, has been shown to be more specific for the extraction of amorphous and crystalline iron (hydr)oxides, respectively.

## 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, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 10381-1, *Soil quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 10381-2, *Soil quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 10381-3, *Soil quality — Sampling — Part 3: Guidance on safety*

ISO 10381-4, *Soil quality — Sampling — Part 4: Guidance on the procedure for investigation of natural, near-natural and cultivated sites*

ISO 10381-5, *Soil quality — Sampling — Part 5: Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination*

ISO 10381-6, *Soil quality — Sampling — Part 6: Guidance on the collection, handling and storage of soil under aerobic conditions for the assessment of microbiological processes, biomass and diversity in the laboratory*

ISO 11464, *Soil quality — Pretreatment of samples for physico-chemical analysis*

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

EN 14899, *Characterization of waste — Sampling of waste materials — Framework for the preparation and application of a sampling plan*

EN 15002, *Characterization of waste — Preparation of test portions from the laboratory sample*

CEN/TR 15310-3, *Characterization of waste — Sampling of waste materials — Part 3: Guidance on procedures for sub-sampling in the field*

## 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

**3.1**
**water content**
**mass fraction**
$w_W$
mass of water evaporating from one soil sample when dried to constant mass at 105 °C, divided by the dry mass of the soil sample

[ISO 11074:2005]

**3.2**
**laboratory sample**
sample intended for laboratory inspection or testing

NOTE 1 When the laboratory sample is further prepared (reduced) by subdividing, mixing, grinding, or by combinations of these operations, the result is the test sample. When no preparation of the laboratory sample is required, the laboratory sample is the test sample. A test portion is removed from the test sample for the performance of the test or for analysis.

NOTE 2 The laboratory sample is the final sample from the point of view of sample collection but it is the initial sample from the point of view of the laboratory.

NOTE 3 Several laboratory samples may be prepared and sent to different laboratories or to the same laboratory for different purposes.

[ISO 11074:2005]

**3.3**
**test sample**
sample, prepared from the laboratory sample, from which the test portions are removed for testing or for analysis; this portion of material, resulting from the laboratory sample by means of an appropriate method of sample pretreatment, and having the size (volume/mass) necessary for the desired testing or analysis

NOTE Adapted from ISO 11074:2005.

**3.4**
**test portion**
**analytical portion**
quantity of material, of proper size, for measurement of the concentration or other property of interest, removed from the test sample

NOTE 1 The test portion may be taken from the primary sample or from the laboratory sample directly if no preparation of sample is required (e.g. with liquids), but usually it is taken from the prepared test sample.

NOTE 2 A unit or increment of proper homogeneity, size, and fineness, needing no further preparation, may be a test portion.

[ISO 11074:2005]

**3.5**
**material**
excavated soil, dredged material, manufactured soil, treated soil and fill material, and other relevant materials, including soil amendments and waste materials

## 4 Principle

The extraction principle is based mainly on the reduction of Fe(III) phases to the more soluble Fe(II) phases, as well as on the complexing affinity of ascorbate to extract iron from short-range ordered materials.

The analysis should be carried out using the ICP-AES technique, e.g. in accordance with ISO 11885.

## 5 Apparatus

The following apparatus shall be used. All materials that come into contact with the sample (material or reagents) should not contaminate the compounds to be determined or adsorb the compounds of interest.

**5.1 Centrifuge tubes**, e.g. polycarbonate, of appropriate size, rinsed in accordance with ISO 5667-3.

**5.2 Centrifuge**, preferably at 3 000$g$. For other appropriate conditions, see Annex A.

**5.3 End-over-end shaking machine** (5 $\text{min}^{-1}$ to 10 $\text{min}^{-1}$ )

NOTE Other shaking methods can be used provided they can be shown to provide equivalent results.

**5.4 Filter holders for syringes**, 0,2 µm, cellulose acetate, diameter 30 mm, cleaned with at least 10 ml of distilled water before use.

**5.5 Usual laboratory glass or plastic ware**, rinsed in accordance with ISO 5667-3.

**5.6 Plastic syringe**, 50 ml, rinsed in accordance with ISO 5667-3.

**5.7 Balance**, with an accuracy of at least 1 mg.

**5.8 Sieving equipment**, with a nominal screen size of 2 mm or 4 mm.

NOTE Due to sieving, contamination of the sample may occur to an extent which affects the leaching of some constituents of concern, e.g. cobalt and tungsten from tungsten carbide equipment or chromium, nickel and molybdenum from stainless-steel equipment.

**5.9 Sample splitter**, for sub-sampling of laboratory samples (optional).

**5.10 Crushing equipment**: jaw crusher or cutting device.

NOTE Due to crushing, contamination of the sample may occur to an extent which affects the leaching of some constituents of concern, e.g. cobalt and tungsten from tungsten carbide equipment or chromium, nickel and molybdenum from stainless-steel equipment.

**5.11 Equipment for deaeration with nitrogen gas** ($N_2$, purity 99,999 %, $O_2 < 0{,}000\,3$ %).

Apply the nitrogen gas as a constant stream, e.g. using a pressure valve.

**5.12 pH-meter**, with a measurement accuracy of at least ±0,05 pH units.

## 6 Reagents

The reagents used shall be of analytical grade and the water used shall comply with grade 3 in accordance with ISO 3696.

**6.1 Water**: use distilled and demineralized water with a specific conductivity of at most 0,2 mS/cm at 25 °C and a pH > 5,6.

**6.2 Sodium hydrogen carbonate**, $M(\text{NaHCO}_3) = 84{,}01$ g/mol.

**6.3 Trisodium citrate dihydrate**, $M(\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}) = 294{,}1$ g/mol.

**6.4 L(+) ascorbic acid**, suitable for biochemistry, $M(\text{C}_6\text{H}_8\text{O}_6) = 176{,}13$ g/mol.

**6.6** **Nitric acid**, $c(HNO_3) = 0{,}1$ mol/l.

# 7 Sample pretreatment

## 7.1 Sample size

Sampling shall be performed in accordance with the guidelines for preparing a sampling plan for soil materials, as specified in ISO 10381-1 to ISO 10381-6 and for waste in accordance with EN 14899, in order to obtain representative laboratory samples. Obtain a representative laboratory sample of at least 200 g (dry matter) for soil and soil materials and 2 kg (dry matter) for waste material. Follow instructions for sample pretreatment:

- for soil and soil materials according to ISO 11464;
- for waste according to CEN/TR 15310-3 and EN 15002.

Use a sample splitter (5.9) or apply coning and quartering to split the sample.

NOTE The required size of the laboratory sample is dependent on the particle size distribution of the soil or material to be analysed (see ISO 11277). The specified sample size is generally adequate. In specific cases, a smaller sample size can be accepted — for instance if, for specific reasons, less material is available — provided that the test can be carried out as specified in 7.2 and 7.3.

Any deviation(s) to accommodate sample size or volume requirements shall be recorded in the test report.

## 7.2 Particle size reduction

### 7.2.1 General

The tests shall be carried out preferably on material as received.

### 7.2.2 Particle size reduction of soil and soil material

For soil and soil material, the test portion to be prepared shall have a grain size $\leq 2$ mm. If oversized material is not of natural origin and exceeds 5 % (mass fraction), the entire oversized fraction shall be separated by sieving (see 5.8) and crushed using suitable crushing equipment (5.10). On no account shall the material be finely ground. Oversized material of natural origin (e.g. stones, pebbles, twigs) in the sample shall be separated and discarded. Irrespective of any necessary size reduction, the separate fractions, with the exception of non-crushable and discarded material, shall be mixed to constitute the test sample. If the laboratory sample cannot be crushed or sieved because of its water content, it is permitted, in this case only, to reduce the water content until the laboratory sample can be sieved. The drying temperature shall not exceed 25 °C.

### 7.2.3 Particle size reduction of waste

For waste, the test shall be carried out on material with a grain size of at least 95 % (mass fraction) $< 4$ mm. Therefore, the laboratory sample shall be sieved (see 5.8). If oversized material exceeds 5 % (mass fraction), the entire oversized fraction shall be crushed using crushing equipment (5.10). On no account shall the material be finely ground. Non-crushable material (e.g. metallic parts such as nuts, bolts, scrap) in the sample shall be separated and the mass and nature of the material shall be recorded. The method of size reduction applied shall be documented and recorded in the test report. Irrespective of any necessary size reduction, the separate fractions, with the exception of the non-crushable material and the material that may be used according to the second paragraph after Note 1, shall be mixed to constitute the test sample. If the laboratory sample cannot be crushed or sieved because of its moisture content, it is permitted, in this case only, to reduce the water content until the laboratory sample can be sieved. The drying temperature shall not exceed 25 °C. Any necessary deviation in the drying procedure shall be given in the test report.

NOTE 1 Fibrous materials and plastics can often be reduced in size after cryogenic treatment.

Any drying step can change other properties of the waste. Care should be taken to minimize such changes.

In order to minimize a possible contamination during sieving, fragmentation and splitting, it is recommended, before preparing the test sample, that a portion of the laboratory sample be processed through the devices for sieving, fragmentation, splitting, discarding the material thereafter. This recommendation does not cover the possible contamination described in the Notes in 5.8 and 5.10.

NOTE 2 Important differences may occur in the leaching test results for a given material, depending on the crushing procedure and the waste material being crushed. Particle-size-related differences may be made evident by determining the particle size distribution. It is to be noted that, in the case of a very narrow size distribution, such differences in the leaching result may be enhanced, especially in the upper part of the size range.

### 7.3 Determination of the water content

Determine the water content of the sample on a separate test portion at (105 ± 5) °C in accordance with ISO 11465. If the soil sample is air-dried prior to testing, the dry matter content of the air-dried sample shall be determined as well.

## 8 Procedure

### 8.1 Preparation of the extraction solution

Prepare a solution of 50 g of sodium hydrogen carbonate (6.2) and 50 g of trisodium citrate dihydrate (6.3) per litre of water. Deaerate with nitrogen gas (5.11) for 4 h. Add 20 g of L(+) ascorbic acid (6.4) per litre. Deaerate with nitrogen gas (5.11) again until a final pH of 8,0 is reached.

Prepare this extraction solution freshly for each experiment as it cannot be stored.

### 8.2 Extraction

Using a balance (5.7), weigh a test portion equivalent to 10 g (for materials ≤ 2 mm) or 25 g (for materials < 4 mm) of dry matter and transfer it to a dry bottle. Add 200 ml (for materials ≤ 2 mm) or 500 ml (for materials < 4 mm) of the extraction solution (8.1) and close the bottle tightly. Shake (see 5.3) for 24 h at room temperature. Centrifuge an appropriate volume for analysis for 30 min at 3 000$g$ or at appropriate centrifugation conditions, as given in Annex A.

Take off the supernatant using a syringe and filtrate the supernatant through a 0,2 µm filter (5.4). Discard the first 3 ml and collect the remainder of the filtrate in a bottle. Preserve the filtrate in accordance with ISO 5667-3 and analyse (8.3).

NOTE Larger test portions can be used when there are indications that the material is too heterogeneous to obtain an adequate reproducibility of the results. If a larger test portion is used, it is necessary to increase the volume of the extraction solution (8.1) proportionally.

Include blanks of the extraction.

### 8.3 Analytical determination

Analyse the acidified filtrate (see 8.2) using the ICP-AES technique, e.g. in accordance with ISO 11885.

## 9 Calculation

Calculate the concentration of iron, in millimoles per kilogram (mmol/kg) of dry soil, using Equation (1).

$$c_{\mathrm{Fe}} = \left(\rho_{\mathrm{Fe}} - \rho_{\mathrm{Fe,b}}\right) \times \frac{V}{m} \times \frac{\left(100 + w_w\right)}{100} \times \frac{1}{55{,}85} \tag{1}$$

where

$c_{Fe}$ is the concentration of extracted iron in the sample on a dry-matter basis, in millimoles per kilogram (mmol/kg);

$\rho_{Fe}$ is the mass concentration of iron in the filtrates, in milligrams per litre (mg/l);

$\rho_{Fe,b}$ is the mass concentration of iron in the blank, in milligrams per litre (mg/l);

$V$ is the volume of the extractant used, in millilitres (ml);

$m$ is the mass of the test portion, in grams (g);

$w_w$ is the water content determined in accordance with ISO 11465, as a percentage (%) on a mass basis.

## 10 Expression of results

Report the concentration of extracted iron in the sample on a dry-matter basis, in millimoles per kilogram (mmol/kg).

## 11 Test report

The test report shall include at least the following details:

a) a reference to this part of ISO 12782;

b) any information necessary for the complete identification of the sample;

c) a reference to the method used for the analytical determination, e.g. ISO 11885;

d) the result of the determination;

e) any details that are optional or deviations from the specifications of this part of ISO 12782, and any effects which may have affected the results.

# Annex A
(informative)

# Conditions regarding centrifugation

## A.1 General

According to this part of ISO 12782, the first step of the solid/liquid separation shall be done by centrifugation. It is recommended centrifuging at 3 000$g$ for 30 min.

However, it is possible to get the same separation efficiency at other centrifugation conditions (shorter centrifugation time at higher centrifugation speed or extended centrifugation time at lower centrifugation speed). In order to ensure reproducibility of the centrifugation, the following principles shall be considered when deviating from the recommended centrifugation procedure.

Generally, the relative centrifugal force ($F_{\mathrm{c,r}}$, in $g$) depends on the rotor speed, $n$ (revolutions per minute, $\mathrm{min}^{-1}$), and the rotor radius, $r$ (in cm), and is calculated using Equation (A.1):

$$F_{\mathrm{c,r}} = 0{,}000\,011\,18 \times (n)^2 \times r \qquad \text{(A.1)}$$

Drawing on this, each rotor has a specific $k$-factor that describes its pelleting efficiency. The lower the $k$-factor, the more efficient the pelleting will be.

This factor can be used to determine the time required for reproducible centrifugation at different rotor speeds. The $k$-factor can be calculated using Equation (A.2):

$$k = \frac{2{,}53 \times (\ln r_{\mathrm{max}} - \ln r_{\mathrm{min}})}{(n)^2} \times 10^{11} \qquad \text{(A.2)}$$

where

$k$ is the rotor-specific factor;

$r_{\mathrm{max}}$ is the maximum radius from the axis, in centimetres (cm);

$r_{\mathrm{min}}$ is the minimum radius from the axis, in centimetres (cm);

$n$ is the rotor speed, in revolutions per minute ($\mathrm{min}^{-1}$).

To calculate the time needed at different rotor speeds to get the same centrifugation result, the $k$-factors for both rotor speeds shall be calculated. Using Equation (A.3), the times can be determined:

$$t_{\mathrm{a}} = t_{\mathrm{b}} \cdot \frac{k_{\mathrm{a}}}{k_{\mathrm{b}}} \qquad \text{(A.3)}$$

where

$k_{\mathrm{a}}$ is the rotor-specific factor at rotor speed a;

$k_{\mathrm{b}}$ is the rotor-specific factor at rotor speed b;

$t_{\mathrm{a}}$ is the centrifugation time for rotor speed a, needed to achieve the same separation efficiency as for rotor speed b in the time $t_{\mathrm{b}}$, in minutes (min);

$t_{\mathrm{b}}$ is the centrifugation time for rotor speed b, in minutes (min).

## A.2 Example for calculation

Rotor dimension: $r_{\text{max}} = 9$ cm, $r_{\text{min}} = 3$ cm, $\bar{r} = 6$ cm

$n$ needed for $F_{\text{c,r}} = 3\,000g$ [see Equation (A.1)]:

$$n = \sqrt{\frac{3\,000}{0{,}000\,011\,18 \times 6}} = 6\,694 \text{ min}^{-1}$$

Desired $n$: 3 000 min$^{-1}$

Question: 6 694 min$^{-1}$ for 30 min correspond to 3 000 min$^{-1}$ for $x$ min.

Calculation of $k$-factors [see Equation (A.2)]:

a) 6 694 min$^{-1}$:

$$k_{6694} = \frac{2{,}53 \times (\ln 9 - \ln 3)}{6694^2} \times 10^{11} = 6203$$

b) 3 000 min$^{-1}$:

$$k_{3000} = \frac{2{,}53 \times (\ln 9 - \ln 3)}{3000^2} \times 10^{11} = 30883$$

Time needed at 3 000 min$^{-1}$ [see Equation (A.3)]:

$$t_{3000} = 30 \times \frac{30883}{6203} = 149{,}4 \text{ min}$$

Answer: at 3 000 min$^{-1}$ the centrifugation time shall be 149 min.

Figure A.1 shows a plot of the centrifugation time, $t$, versus the rotation speed, $n$, for the rotor dimension described above (based on 3 000$g$ for 30 min):