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Limitation requirements of toxic and harmful substance in fertilizers

肥料中有毒有害物质的限量要求

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Limitation requirements of toxic and harmful substance in fertilizers

1 Scope

This standard specifies the limit requirements, test methods, inspection rules for toxic and harmful substances in fertilizers.

This standard applies to commercial fertilizers produced by various processes.

2 Normative references

The following documents are essential to the application of this document. For the dated documents, only the versions with the dates indicated are applicable to this document; for the undated documents, only the latest version (including all the amendments) are applicable to this standard.

GB/T 2441.2 Determination of urea - Part 2: Biuret content - Spectrophotometric method

GB 5085.1 Identification standards for hazardous wastes - Identification for corrosivity

GB 5085.2 Identification standards for hazardous wastes - Screening test for acute toxicity

GB 5085.3 Identification standards for hazardous wastes - Identification for extraction toxicity

GB 5085.4 Identification standards for hazardous wastes - Identification for ignitability

GB 5085.5 Identification standards for hazardous wastes - Identification for reactivity

GB 5085.6 Identification standards for hazardous wastes - Identification for toxic substance content

GB/T 8170-2008 Rules of rounding off for numerical values & expression and judgement of limiting values

GB/T 19524.1 Determination of fecal coliforms in fertilizers

5 Test method

5.1 Corrosion identification

It is performed according to GB 5085.1.

5.2 Acute toxicity identification

It is performed according to GB 5085.2.

5.3 Identification of leaching toxicity

It is performed according to GB 5085.3.

5.4 Identification of flammability

It is performed according to GB 5085.4.

5.5 Identification of reactivity

It is performed according to GB 5085.5.

5.6 Identification of toxic substance content

It is performed according to GB 5085.6.

5.7 Total cadmium, total mercury, total arsenic, total lead, total chromium

It is performed according to GB/T 23349 or ISO 17318; GB/T 23349 is used as the arbitration method.

5.8 Total nickel, total cobalt, total vanadium, total antimony, total thallium

It is performed according to Appendix B.

5.9 Biuret

It is performed according to GB/T 22924 or GB/T 2441.2 or ISO 18643; GB/T 22924 is used as the arbitration method.

5.10 Benzo[a]pyrene

It is performed according to GB/T 32952.

5.11 Total petroleum hydrocarbons

It is performed according to GB 5085.6.

5.12 Total phthalates

Appendix A

(Normative)
Terrestrial plant growth test

A.1 Test substance information

The test substance information includes but is not limited to: water solubility, vapor pressure, structural formula, solubility in organic solvents, n-octanol/water partition coefficient, absorption behavior, purity, stability in water and light, results of biodegradation tests .

A.2 Introduction to test

A.2.1 Test purpose

Used to evaluate the potential toxic effects of solid and liquid chemicals in the soil on plant seedlings and early growth after one-time application.

A.2.2 Test principle

This Appendix is used to evaluate the effects of applying the test substance in the soil (or other suitable soil substrate) on the emergence of seedlings and the early growth of higher plants. The seeds are planted in the soil treated with the test product and evaluated within 14 d ~ 21 d after the emergence rate of the control group reaches 50%. The end-point measurement is the visible emergence rate, the dry weight of the seedling (or fresh weight), in some cases the height of the seedling; it shall also evaluate the harmful effects visible on different parts of the plant. These measurements and observations are compared with untreated controls.

According to the possible exposure pathways, the test product is mixed into the soil (or possible artificial soil substrate) or sprayed on the soil surface. These pathways shall represent the potential exposure pathways of chemicals as accurately as possible. When the soil is mixed, a large amount of loose soil is mixed first, then it is put in a pot, the selected plant seeds are planted into the soil. When applying the pesticide on the surface, put the soil in the pot first, plant the seeds, then spray the pesticide. The test system (control and treated soil and seeds) is placed in an environment suitable for plant growth.

This Appendix can determine the dose-response curve according to the purpose of the study, or a single dose/ratio as a limit test. If the single-dose/ratio test exceeds a certain level of toxicity (for example, the observed effect is higher than x%), a range screening test is required to determine the upper and lower toxicity limits; then a multiple-dose test is performed to generate a dose-response curve. Appropriate statistical analysis methods are used to analyze

the test substance is not a plant protection product, the artificial substrate can be used to replace the natural soil for the test. The matrix used shall contain inert substances, to reduce interaction with the test product, solvent carrier or both. Quartz sand, mineral wire and glass beads (such as: 0.35 mm ~ 0.85 mm in diameter) that have been washed with acid are suitable inert substances, which can reduce the absorption of the test product and ensure that the test product reaches the seedlings through the root absorption as much as possible. Unsuitable substrates include vermiculite, perlite or other highly absorbent materials. The nutrients needed for plant growth shall be provided, to ensure that the plants are not stressed by nutrient deficiency, which can be evaluated by chemical analysis or visible evaluation of control plants.

A.4.2 Test plants

The selection of plant species shall consider its taxonomic diversity in the plant kingdom, its distribution characteristics, the specific life history of the species, the regional differences in natural distribution, including the following characteristics:

- Having uniform seeds, obtained from reliable standard seed sources, can produce continuous, reliable and consistent germination, as well as consistent seedling growth;

- Plants shall be suitable for testing in the laboratory; it may obtain reliable and reproducible results in and between laboratories;

- The sensitivity of the species used shall be consistent with the plant's response to environmental exposure;

- The selected species have been used in some previous toxicity tests, meanwhile their use in such as herbicide bioassays, heavy metal screening, salinity or mineral stress tests or plant-related research shows that they are sensitive to a wide variety of stimuli;

- Be able to adapt to the growth conditions in the test method;

- Meet the test validity standard.

The number of species used in the test is determined according to the relevant management requirements. The species used in the plant test in Appendix C are for reference.

A.4.3 Application of test article

The test product shall be applied to an appropriate carrier (such as: water, acetone, ethanol, polyethylene glycol, gum Arabic, sand). It can also be tested with formulations containing active ingredients and various additives.

A.4.6 Verification of the concentration/ratio of the test substance

The concentration shall be verified by appropriate analytical methods. For soluble substances, verification of all concentrations can be confirmed by analyzing the highest concentration used for gradual dilution. Use calibration equipment (such as: calibration glassware for analysis, calibration spray equipment) for stepwise dilution. For substances that are insoluble in water, analyze the amount added to the soil. If it wants to prove the homogeneity of the test product in the soil, it is necessary to conduct a soil analysis.

A.4.7 Test conditions

The test conditions shall be similar to the normal growth conditions of the test species and varieties. The emergent plants shall be placed in a controlled climate incubator, artificial climate box or greenhouse for gardening operations to maintain normal growth. When using growth equipment, ensure that the plants grow normally and compare with the control group. It shall record such parameters as the temperature, relative humidity, carbon dioxide concentration, light (illuminance, wavelength, photosynthetically active radiation)/photoperiod, average irrigation volume and other parameters including condition control and sufficient frequency (e.g. daily); the greenhouse temperature is controlled through ventilation, heating and / or refrigeration system. The following conditions are generally recommended for greenhouse tests:

- Temperature: (22 ± 10) °C;
- Relative humidity: (70 ± 25)%;
- Photoperiod: At least 16 h illumination;
- Illuminance: (24850 ± 3550) lx. If the illuminance drops below 14200 lx and the wavelength is 400 nm ~ 700 nm, except for some species need to reduce the illuminance, additional illumination is required.

During the test, the environmental conditions shall be monitored and recorded. The container used in the test shall be a non-porous plastic or glass container, a tray or dish shall be placed under the container. Containers shall be repositioned regularly to reduce plant growth differences (because the test conditions of the growth facilities are different). The container shall be large enough to ensure normal growth.

In order to maintain good plant vitality, it can add soil nutrient solution. Judge the need and timing of adding nutrient solution by observing the control plants. It is recommended to water it from the bottom of the test container (for example, use glass fiber filament).

For test plant species and test products, specific growth conditions are suitable

whether general chemicals have phytotoxic properties, the 1000 mg/kg dry soil is usually used as the maximum dose.

A.4.8.3 Pre-test

Before conducting a formal multi-concentration dose-response study, it is necessary to conduct a preliminary test to determine the dose range. The concentration interval of the pre-test shall be wide (such as: 0.1 mg/kg, 1.0 mg/kg, 10 mg/kg, 100 mg/kg, 1000 mg/kg dry soil). The concentration of crop protection products shall be determined according to the recommended or maximum use concentration or application rate, such as 1/100, 1/10, 1/1 of the recommended/maximum concentration or application ratio.

A.4.8.4 Multiple concentration/ratio test

The purpose of the multi-concentration/ratio test is to establish a dose-response relationship and determine the germination rate, the EC_x or ER_x value of the biomass and/or the observable effect compared with the untreated control group.

The number and spacing of the test concentration/ratio shall be sufficient to produce a credible dose-response relationship and regression linear equation and an estimated EC_x or ER_x value. The number of selected concentrations shall be at least five geometric levels plus the control; the two adjacent concentration gradients shall not exceed 3 geometric levels. Each treatment and control have at least four parallels; the total number of seeds shall be at least 20. For some plants with low germination rate or plants with diversified growth characteristics, increase the number of parallels to improve statistical power.

A.4.8.5 Observation

During the observation period, that is, within 14 d ~ 21 d after the emergence rate of the control (solvent control) reached 50%, regularly (at least 1 week, if possible, daily) observe whether the plant emerges and there is visible plant poisoning death. At the end of the test, record the emergence rate, the biomass of surviving plants and the visible toxic effects in different parts of the plant. The latter includes morphological abnormalities of emerging seedlings, growth retardation, withering, discoloration, death, effects on plant development. The final biomass is completed by measuring the average dry weight of the final surviving plants. The plants above the soil surface are harvested and dried at 60 °C to a constant mass. It can also choose to use fresh weight as the final biomass. If there are special requirements, the seedling height can be used as another key indicator. A unified scoring system can be used to score visible injuries to evaluate observable toxicity action.

results graphs and summaries. It usually includes the following:

a) Test product:

- Chemical identification data, characteristics of related substances (if possible, the partition coefficient lgP_{OW} of n-octanol/water, water solubility, vapor pressure, environmental fate and behavior information);

- The preparation details of the test solution and the verification of the test concentration.

b) Test plant species:

- Detailed information of the test organism: Species/subspecies, plant family, scientific name and common name, source and history as detailed as possible (i.e.: provider's name, germination rate, seed size level, batch number, year of production or selected growing season, budding stage level), viability, etc.;

- The number of monocot and dicot species tested;

- Reasons for choosing this type;

- Description of seed storage, handling and maintenance.

c) Test conditions:

- Test facilities (e.g. growth chamber, artificial climate chamber and room temperature);

- Description of the test system (e.g. container diameter, container material and soil volume);

- Soil characteristics (soil texture or type: soil particle distribution and classification, physical and chemical characteristics, including organic matter content, organic carbon content, pH value);

- Preparation of soil/substrate (such as soil, artificial soil, sand and others) before the test;

- If nutrient solution is used, formula description;

- Application of the test product: application method, equipment, exposure load and volume (including chemical verification, calibration method), description of environmental conditions during application;

- Growth conditions: Illumination, photoperiod, maximum/minimum temperature, watering schedule and method, fertilization;

Appendix B

(Normative)
Determination of total nickel, total cobalt, total vanadium, total antimony, total thallium in fertilizers -- Inductively coupled plasma emission spectrometry

Warning - The hydrochloric acid used in this Appendix is corrosive, the nitric acid is corrosive and oxidizing, so the test personnel shall take appropriate protection. This Appendix does not indicate all possible security issues. The user is responsible for taking appropriate safety and health measures and ensuring compliance with the conditions stipulated by relevant national laws and regulations.

B.1 Method summary

The total nickel, total cobalt, total vanadium, total antimony, total thallium in the specimen are digested and extracted with aqua regia, determined by inductively coupled plasma emission spectrometry. When manganese and other elements interfere with the determination, the total thallium is determined using aqua regia sample; after the methyl isobutyl ketone is extracted and enriched, the extract is evaporated to dryness, the residue is digested with nitric acid, then it is determined by the inductively coupled plasma emission spectrometry.

B.2 Reagents

B.2.1 Nitric acid: Pure superior grade.

B.2.2 10% nitric acid solution: 1 volume of nitric acid is mixed with 9 volumes of water.

B.2.3 Hydrochloric acid: Pure superior grade.

B.2.4 Hydrochloric acid solution: 1 + 1.

B.2.5 Potassium iodide-ascorbic acid solution: Weigh 30 g of potassium iodide and 20 g of ascorbic acid in a beaker; add water to dissolve; transfer to a 100 mL volumetric flask; use ultrapure water to dilute it; mix it uniformly.

B.2.6 Methyl isobutyl ketone: Analytically pure.

B.2.7 Standard stock solution of nickel, cobalt, vanadium, antimony, thallium: 1.000 g/L, certified standard material.

B.2.8 High purity argon: Content ≥ 99.999%.

Add 4 mL of methyl isobutyl ketone each according to the same operation. Continue 2 more extractions. Combine the organic phase. Please the beaker on a boiling water bath to evaporate to dryness. Add 5 mL of nitric acid to the beaker. Heat and digest on a hot plate and evaporate until the solution volume is less than 1 mL (the solution cannot be evaporated to dryness). Cool to room temperature. Transfer to a 10 mL volumetric flask. Make it reach to the volume. Shake well. Prepare for use. If the test solution is turbid, filter it before measurement;

b) Remove the watch glass slightly to continue heating. When the solution is about 10 mL, remove it. Cool it down. Transfer to a 50 mL volumetric flask. Make its volume reach to the mark. Perform dry filtering. Discard the first 10 mL filtrate. Accurately pipet 20 mL of the filtrate into a 50 mL colorimetric tube. Add 3 mL of potassium iodide-ascorbic acid solution. Shake well. Add 5 mL of methyl isobutyl ketone. Shake and extract for 2 minutes. After standing for 15 minutes, use a dropper to carefully remove most of the organic phase in a 50 mL beaker. According to the same operation, add 4 mL of methyl isobutyl ketone and continue to extract 2 times. Combine the organic phases and place the beaker on a boiling water bath to evaporate to dryness. Add 5 mL of nitric acid to the beaker. Heat and digest on a hot plate and evaporate until the volume of the solution is less than 1 mL (the solution cannot be evaporated to dryness). Cool to room temperature. Transfer to a 10 mL volumetric flask. Make its volume reach to the mark. Shake well. Prepare for use. If the test solution is turbid, filter it before measurement.

B.4.3 Preparation of blank solution

Except that no specimen is added, the other steps are the same as the preparation of the specimen solution.

B.4.4 Preparation of working standard solution

Take an appropriate amount of standard stock solution of each element. Dilute it step by step and use 10% nitric acid solution (B.2.2) to make it reach to the volume. Prepare the mixed ion standard solution series according to Table B.1.

Appendix D

(Informative)
Examples of defining suitable growth conditions for specific species in terrestrial plant growth tests

The following conditions are suitable for the following 10 crop species to be tested in an incubator:

- Carbon dioxide's volume fraction: $350 \times 10^{-6} \pm 50 \times 10^{-6}$;
- Relative humidity: The relative humidity in the light cycle is about (70 ± 5)%, the relative humidity in the dark cycle is about (90 ± 5)%;
- Temperature: 25 °C ± 3 °C during the day, 20 °C ± 3 °C at night;
- Photoperiod: 16 h light/8 h dark, light wavelength is 700 nm;
- Illumination: 24850 lx ± 3550 lx, at the top of test incubator.

The 10 crop species are:

- Tomato (Solanum lycopersicon, Solanum);
- Cucumber (Cucumi ssativus, Cucumber);
- Lactuca sativa (Lactuca sativa, Lactuca);
- Soybean (Glycine max, soybean);
- Cabbage (Brassica oleracea var. capitata, Brassica);
- Carrot (Daucus carota, Daucus);
- Oats (Avena sativa);
- Ryegrass (Lolium perenne, Lolium);
- Corn (Zea mays);
- Onion (Allium cepa).

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