Methods Book

for the Analysis of Compost

in addition with:

Results of the Parallel Interlaboratory Test 1993

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Preface

Essential prerequisites for a workable quality assurance system have been created with the development of a binding methods book for the investigation of composts within the scope of the outside monitoring of the compost quality by the Federal Compost Quality Assurance Organization FCQAO and the realization of the 1993 interlaboratory tests with about 100 laboratories. The necessity of codifying standardized and reproducible investigation methods in order to be able to compare the results of compost analyses is demonstrated not least in the short period of time in which the second edition of the methods book was out of print. The third revised edition of the methods book is now being published.

Through the broad distribution that the methods book has had in the meantime and the realization of the 1993 interlaboratory test, a series of competent replies with fruitful criticism of individual methods, regarding feasibility and practicality, have come in at the Federal Quality Association.. Modification and improvement suggestions were discussed by the Federal Quality Association and are reflected in this third edition of the methods book. For the determination of the conductivity, for example, the simpler extraction with distilled water was fallen back on again. Uncertainties that were still existing, such as the calculation of the C/N relationship or the correct designation of the individually determined nitrogen fractions, for instance, were able to also be clarified through additions or explanations. Further supplemental methods for the analysis of composts were proposed to the Federal Compost Quality Assurance Organization and are under discussion at present. These methods will become established in Chapter III in the course of the updated continuation of the method book.

The prerequisites for the qualified analysis of compost have been improved further with the third edition of the method book. Sound and competent quality assurance of composts and compost products can consequently be guaranteed now and in the future.

Cologne, November, 1994

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Carrying out the taking of sample

1 Preliminary remark

In order to be able to get representative analytical findings, the taking of the sample may only be burdened with incidental, i.e. unavoidable, errors. According to Garvert, the sample taking should fulfill three conditions to the extent possible.

"It should a. supply a representative sample
b. be able to be carried out with low effort and
c. not require a major technical expenditure."

Compost samples that are examined by the Federal Compost Quality Assurance Organisation within the scope of the outside monitoring of the compost quality may in principle only be taken from goods ready for sale !

If the goods ready for sale have already been classified, the classification is to be indicated. If they have not been classified, they are to be classified at the taking of the sample. Sieves with a mesh width of at least 10 mm, 40 mm at the most, though, have to be used. The mesh width is to be indicated (see Chap. II, Method 2).

2 Materials

No devices or materials may be used for the sample taking, processing and packing that could pass on one of the materials to be analyzed to the samples.

3 Carrying out the taking of the sample

3.1 Taking a sample from a profile section

- the profile section is to be dug out with a wheel loader
- the entire profile section height is to be sampled equally
- the minimum amount of the partial sample per section wall should be 30 liters

3.2 Taking a sample from a dormant deposit

- bore in the respective pit section to the pit floor (screw borer)
- cross section: at least 5 borings of the same type

3.3 Taking a sample from agitated compost

- see Table 1.1 for the number of individual samples
- the minimum amount of the partial sample should be 30 liters

4 Remarks

Definitions:

- An **individual sample** is an amount of substance taken out in one work step.
- A **collective sample** consists of several individual samples that were thoroughly homogenized.

4.1 Individual samples

The minimum number of required individual samples depends on the mean grain size of the compost or waste and on the amount to be evaluated. Table 1.1 gives a basis for the establishment of the minimum number of individual samples.

Table 1.1: Minimum number of individual samples in dependence on the grain and condition of the compost batch

Grain size of the compost or of the waste	**Minimum number** of individual samples				
	from agitated substances dependent on the volume flow		from dormant composts or wastes		
			in vehicles	in deposits	
	up to 50 t	**> 50 t**		**50 - 150 t**	**>150 t**
> 20 mm	10	1 per 5 t	10 per	1 per 5 t	15
< 20 mm	5	1 per 10 t	vehicle	1 per 10 t	10

The minimum volume of an individual sample should be 5 liters for a grain size of > 20 mm and 3 liters for < 20 mm.

The minimum amount of an individual sample can also be calculated according to the following formula:

G [kg] = 0.06 x d [mm]

The coarser and the less uniform the material, the larger the individual sample and the collective sample have to be selected.

4.2 Collective samples

The collective sample gotten from the individual samples is well mixed on a plastic foil (flat spreading and a joining of sectors lying across from one another). The reduction of the collective sample takes place by throwing out a quarter to a third of the material. Following this, mixing takes place again and a portion of the sample is thrown out anew.

This procedure is repeated until the desired amount of sample is left (see Garvert).

In the case of a collective sample of more than 100 l, the mixing method described above can only be carried out with substantial difficulties under certain circumstances. The case can also arise with very damp material that the sample can no longer be sufficiently homogenized. The homogenization of the sample is to be carried out through repeated heaping in a cone and pulling the material apart. The mixing has to take place on a secure and clean foundation (concrete floor, asphalt) or on a solid foil.

4.3 Transport:

- the samples are transported into the laboratory in well-sealed PE containers
- the sample amount should be at least 20 liters
- the sample has to be in the laboratory after 24 h, if possible, and be cooled if necessary
- deviations from the described methods have to be carefully documented

5 Literature

Anonymous; LAGA Guidelines; Garbage Handbook Volume 2

Garvert, U.; The technique of taking samples and annual variations of important parameters of garbage-slurry composts; Dissertation 1977.

Meyer-Spasche, H.; General rules for taking a compost sample; Working regulation of the Institute for Soil Ecology and Environmental Assessment; Bohlsen 1992.

Sample preparation in the laboratory

1 Preliminary remark

The sample taker delivers fresh compost samples to the laboratory. They are designated as the original sample in the following. The original samples are prepared and treated further in the laboratory.

The preparation and homogenization steps can be taken from the procedure diagram on page 8.

2 Materials

- Sieve with a mesh width of 10 mm, 2 mm and 0.25 mm
- Suitable grinders
- Scales (0.1 g reading)
- Drying chamber (adjustable, 40°C and 105°C)

3 Procedure steps for the sample preparation

3.1 Analyses in the fresh substance

Screening the fresh original sample

For all analyses that are carried out in the fresh substance (see Chap. II, Methods 3, 4, 5, 6, 7, 8, 9, and Chap. III, Methods 1, 2, 3, 4), a portion of the original sample has to be screened down to < 10 mm (approx. 20 l sieve through fraction).

The amounts from the sieve overflow and sieve through fraction are to be determined with a gravimetric method during this and are to be stated in connection with the total mass.

$STF_r = [STF / (STF + SOF)] \times 100$ [%]
$SOF_r = [SOF / (STF + SOF)] \times 100$ [%]

STF_r : Sieve through fraction in [%]
SOF_r : Sieve overflow in [%]
STF : Sieve through fraction in [g]
SOF : Sieve overflow in [g]

Adjusting to an optimum water content using a fist test

For the determination of the degree of rotting on the basis of self-heating or exchange activity of the sample material (see Chap. II, Method 4 and Chap. III, Method 1), a portion of the fresh sieved substance (approx. 5 liters) has to be adjusted to an optimum and standardized water content. The adjustment to the optimum water content takes place using the so-called 'fist test'; the execution is described in Chap. II, Method 4.

3.2 Analyses in the dry substance

Drying the unscreened original sample at 105°C

For the determination of the water content and of the parameters with regard to the dry substance, approx. 5 liters of the unscreened original sample are dried at 105°C up to a constant weight.

A portion of the dried material is kept as a reserve sample (approx. 1 liter).

For the determination of the foreign matter and stone content, 1-3 liters of material are necessary, depending on the grain of the original sample (see Chap. II, Method 10).

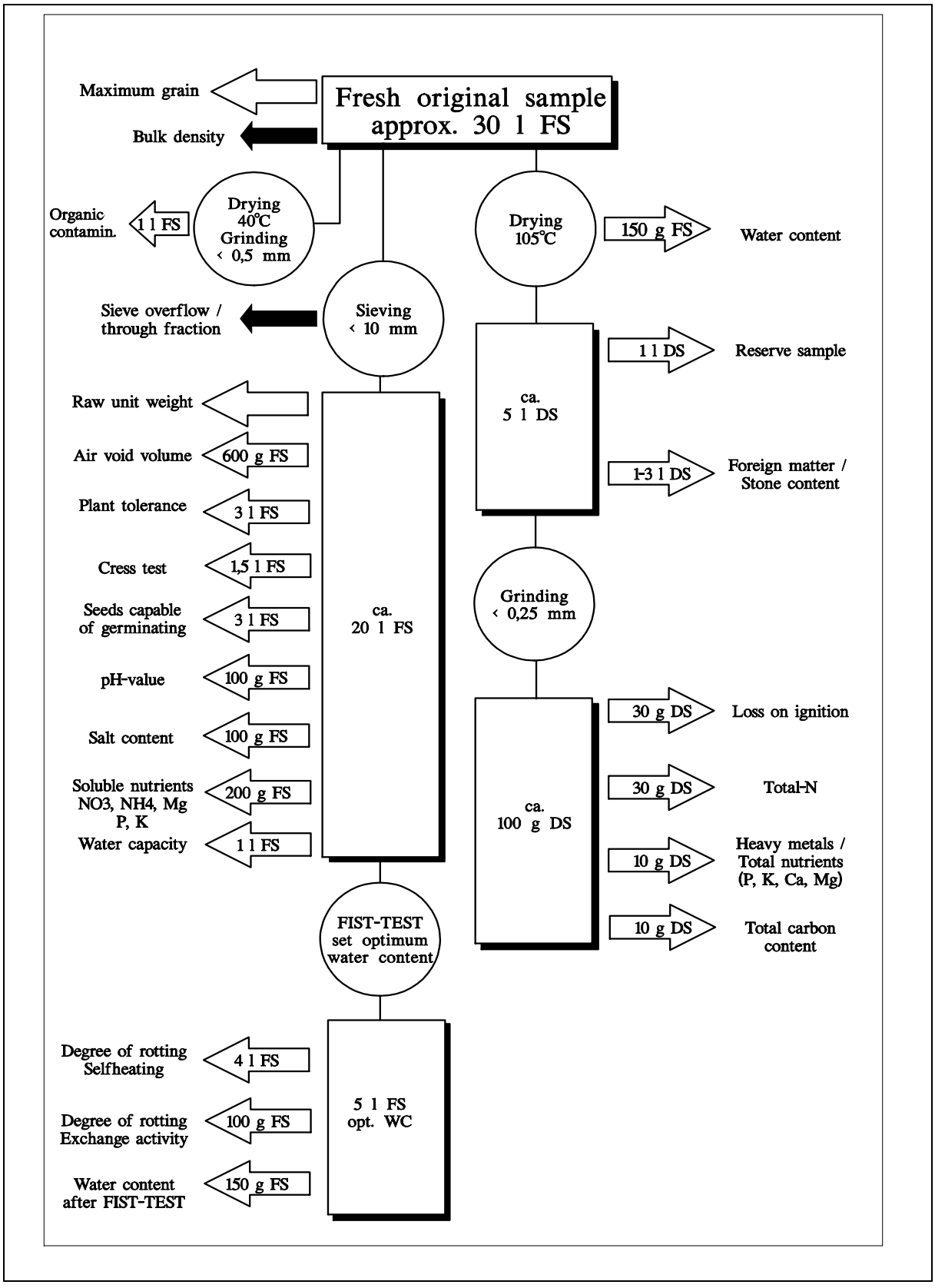
Grinding the dried sample material

At least 100 g of the dried sample are ground with suitable grinders to < 0.25 mm for further analyses (see Chap. II, Methods 11, 12, 13.1, 13.2 and Chap. III, Method 6).

No contamination of the sample with the heavy metals to be determined may take place during the preparation of the heavy metal analysis (see Chap. II, Method 12). Planetary ball grinders (fused corundum, zirconium oxide) or flywheel type belt grinders (tungsten carbide) suggest themselves as suitable tools.

Drying the unscreened original sample at 40°C

A portion of the fresh material (approx. 1 liter) is dried at 40°C for the determination of the organic contaminants (see Chap. III, Method 5) and subsequently ground to < 0.5 mm.



PROCEDURE DIAGRAM

Determination of the water content

1 Preliminary remark

A portion of the fresh original sample has to be dried for the execution of various analyses (foreign matter content, loss on ignition, heavy metal and total nutrient contents). The water content is simultaneously determined during this. A portion of the dried material (approx. 1 l DS) is to be kept as a reserve sample (RS).

2 Sample preparation

A portion (approx. 3 - 5 l FS) of the fresh, unscreened original sample is used for the drying of sample material and for the determination of the water content.

3 Materials

- Scales (0.1 g reading)
- Drying chamber for 105°C
- Suitable vessels (large glass, porcelain or aluminum basins) or suitable plates

4 Carrying out the testing

A representative sample is weighed in for the determination of water content, spread out in a thin layer on plates of the drying chamber or loaded into suitable vessels and dried at 105°C up to a constant weight (24 hours as a rule). The sample is weighed back in directly after the removal from the drying chamber with suitable scales.

5 Calculation of the results

The water content is related to the fresh mass. The result is to be stated in [% DS], accurate to one decimal place.

$$WG = [(M_{moist} - M_{dry}) / (M_{moist} - M_{tara})] \times 100 [\%]$$

$$DS = [(M_{dry} - M_{tara}) / (M_{moist} - M_{tara})] \times 100 [\%]$$

WG : Water content in [% DS]

DS : Dry substance in [% DS]

M_{tara} : Mass of the empty basin (plate) in [g]

M_{moist} : Mass of the moist sample + M_{tara} in [g]

M_{dry} : Mass of the dried sample + M_{tara} in [g]

6 Remarks

The total amount of the sample to be dried depends on the grain of the original sample, because different amounts of dry sample mass are required for the determination of the foreign matter and stone content (Method 10), depending on the grain.

The total sample to be dried does not necessarily have to be used for the purely analytical determination of the water content. The drying of a small representative amount of sample (at least 150 g DS) appears to be sufficient, especially with fine-grained material (0 - 10 mm).

In order to be able to relate parameters, that are determined in the < 10 mm sieved fresh substance (soluble nutrients, salt content, raw unit weight), to the dry substance, the water content of a correspondingly prepared sample (sieving < 10 mm) has to additionally be determined.

7 Literature

VDLUFA, Methods Book, Volume I (1991): The investigation of soils

DIN 38 414 (S2), German uniform proc. for water, waste water and slurry investigation; slurry and sediments: Determination of the water content and of the dry residue

Determination of the maximum grain size

1 Preliminary remark

In the case of a known pre-screening (classification), the statement of the sieve mesh width suffices. Otherwise, the maximum grain of the fresh original sample is to be determined after sieve analysis.

2 Sample preparation

Fresh original sample, dry, if appropriate to the sieve capability.

3 Materials

- Suitable sieve (gradation of the sieve mesh widths: 5 mm)

4 Carrying out the testing

Sieve analysis up to finding the smallest sieve mesh width, for which no material remains any longer as sieve overflow.

5 Calculation of the results

Statement of the sieve mesh width in [mm].

Determination of the raw unit weight

1 Preliminary remark

Different parameters of composts are related to the volume of the fresh substance (salt content, soluble nutrients). The determination of the raw unit weight of the fresh compost substance is necessary for the conversion of the value related to the fresh mass at first. For the determination of the raw unit weight, the material has to be prepared in the same way as for the determination of the above-mentioned parameters. The material that is used for the determination of the raw unit weight can still be used for further investigations (e.g.: plant tolerance, seeds capable of germinating, self-heating tests, etc.).

2 Sample preparation

Sieving the fresh original sample to < 10 mm.

3 Materials

- Scales (1 g reading)
- 1 liter measurement cylinder made of transparent plastic, graduations in increments of 10 ml
- Wide-neck powder funnel
- Dropping device (stand, stand pincers or ring, rubber base) for setting a standardized drop height of 10 cm

4 Carrying out the testing

Counterbalance the empty measurement cylinder. Fill the sample material loosely up to the rim with the help of the powder funnel. Let the measurement cylinder drop 10 times from a height of 10 cm vertically onto the rubber base with the help of the dropping device. The dropping device has to be constructed in such a way that, with a raised measurement cylinder, the lower edge of the measurement cylinder is exactly 10 cm over the rubber base. Read the settled volume of the sample material, accurate to 10 ml, and exactly determine the mass of the filled measurement cylinder accurate to 1 g. The determination is to be carried out with threefold repetition with loosely filled sample material each time.

5 Calculation of the results

The mean value of the three repetitions is to be stated, accurate to 10 g, in the dimension [g/l]. A more exact evaluation can not be carried out on account of the insufficient reading accuracy of the volume.

$RD_{FS} = [M_{FS} / Vol_{FS}] \times 10^3$ [g/l]

RD_{FS} : Raw unit weight of the fresh substance in [g/l]
M_{FS} : Mass of the filled fresh substance in [g]
Vol_{FS} : Volume of the settled fresh substance in [ml]

6 Remarks

For any calculation of the raw unit weight of the dry substance (RD_{DS}), one is to see to it that the water content to be used in the calculation has to be determined on a sample of the same sieving (< 10 mm).

If the raw unit weight is to be determined from unscreened large-grain compost (0 - 20 or 0 - 30 mm), a 2 liter measurement cylinder is to be used for this. The described method is not appropriate for materials with an even larger grain (e.g. raw compost materials).

The piled weight of raw compost materials has to be determined by weighing a certain volume, for example with a 10 l bucket. The suitable vessel size is, in isolated cases, dependent on the nature of the raw compost material.

7 Literature

VDLUFA, Methods Book, Volume I (1991): The investigation of soils

Determination of the degree of rotting in a self-heating test

1 Preliminary remark

The self-heating capability of the fresh compost substance in the Dewar vessel makes a statement possible on the degree of rotting. The self-heating test has to be carried out with an optimum and standardized water content of the samples. Too dry or too moist sample material leads to an underestimate of the self-heating capability and consequently to an overestimate of the degree of rotting. A standardized, optimum water content, adjusted to the water capacity of the respective compost, can be set using the so-called 'fist test'.

2 Sample preparation

Sieving the fresh original sample to < 10 mm.
Adjustment of the water content using a 'fist test'.

3 Materials

- Dewar vessel (volume 1.5 liters, inside diameter 100 mm)
- Traight enclosed-scale thermometer with a maximum display or continuously writing temperature measurement device
- Drying chamber and suitable vessels for the determination of the water content (see Method 1)
- Scales (0.1 g reading)

4 Carrying out the testing

The self-heating test has to be made as soon as possible after taking the sample. If a delay of the start of testing cannot be avoided for organizational reasons, then one is to see to it, after the cool storage of the samples, that the temperature of the sample material corresponds to the room temperature at the beginning of the test.

The testing substrate (FS < 10 mm) is to be adjusted to a moisture content that is optimum for microbial events, depending on the material, before the start of the test. In the case of composts with a low content of organic substances, the favorable water content is lower than in the case of composts with a high content of organic substances.

The optimum water content is adjusted using a 'fist test'. A compost sample is pressed into the fist. If water beads escape between the fingers in the process, the sample is too wet. If the sample crumbles without further action when the fist is opened, the sample is too dry. There is a suitable moisture content if the pressed sample crumbles with light pressure; if it is only deformed, in contrast, it is too wet. This suitable moisture is also appropriately characterized by the comparison "moist like a well-squeezed sponge". During the moistening of the sample material that is too dry, the water is to be mixing into the compost evenly, sample material that is too moist is to be carefully dried.

After the adjustment of an optimum moisture content, the Dewar vessels are filled up to the rim with compost in a loose pouring, lightly shoving the test containers on a base, and the sensor of the temperature measurement device is placed in the lower third of the vessel. The vessels are set up openly at room temperature (approx. 20°C). The temperature maximum is reached after 2 to 5 days, as a rule.

The test ends after temperatures exceed the maximum and are clearly falling, at the latest, though, after 10 days.

If continuous measurement writers or devices with digital measurement value recording (measurement interval 4 hours) are not available, at least 2 measurements with a time difference of at least 8 hours are to be carried out within 24 hours.

5 Calculation and evaluation of the results

The assignment of the degree of rotting takes place on the basis of the temperature maximum (T_{max}).

Rotting degree I : T_{max} = 60 - 70°C
Rotting degree II : T_{max} = 50 - 60°C
Rotting degree III : T_{max} = 40 - 50°C
Rotting degree IV : T_{max} = 30 - 40°C
Rotting degree V : T_{max} = 20 - 30°C

Besides the temperature maximum, the area under the curve in the time period between 0 to 72 hours (F_{72}) is additionally to be stated (calculation according to M 10, LAGA).

The water content of the compost adjusted using the 'fist test' is to be determined (see Chap. II; Method 1) and likewise to be stated.

6 Remarks

Compost with **rotting degree II and III** is designated as **fresh compost**, compost with **rotting degree IV and V** as **finished compost**.

The water content of 35%, stipulated in Instruction Leaflet 10 (M 10) for carrying out the self-heating test, is to be viewed as too dry, as a rule.

7 Literature

Instruction Leaflet 10 (M10) of the State Working Group - Waste (LAGA), Hösel et al (Editor), Garbage Handbook, index number 6856, Erich Schmidt Verlag, Berlin

Determination and evaluation of the plant tolerance of compost in the germinating plant test with spring barley

1 Preliminary remark

The testing of the plant tolerance of compost takes place in a germinating plant test with spring barley. Standard soil 0 (EE0) serves as a blending component and comparison substrate. The start of the plant test has to take place directly after the arrival of the fresh compost sample. If several days lie between the arrival of the sample and the start of the test, the statements on the test are no longer in accordance
with the necessary certainty.

2 Sample preparation

Sieving the fresh original sample to < 10 mm.

3 Materials

- Plastic mixing tub
- Plastic measurement bowls (2 l, 1 l, 0.5 l)
- Plastic pots 500 ml with bottom perforation and basins underneath
- Water-soluble multi-nutrient dung
- Certified seeds from spring barley, germinating capability > 90%
- Laboratory scales (10 mg reading)
- Standard soil 0 (EE0) from the Standardized Soil Association (pH value 5.5 - 6.5) as a comparison substrate and blending component (reference address, see page 24)

4 Carrying out the testing

The test substrate (compost) and comparison substrate (EE0) are grated through a 10 mm sieve; the sieve overflow is thrown out.

Test mixtures with 25% vol. and 50% vol. test substrate proportion are produced from the test substrate and EE0. For the variation with 25% compost proportion, 0.5 l compost are mixed with 1.5 l EE0, for the variation with 50% compost proportion, 1 l compost is mixed with 1 l EE0.

After this, 400 ml each of the test mixture (3-fold striking of the measurement bowl) are filled into the corresponding vessel. Because a three-fold test start takes place for security, 3 vessels are filled (repetitions) per test mixture (variations). The contents of all pots are lightly compressed during the filling because of the 3-fold striking of the vessel. 400 ml each of comparison substrate (EE0 unmixed) are likewise filled in 3 test vessels.

If all 9 test vessels are filled, 100 ml of a liquid multi-nutrient dung is evenly poured on them. The concentration is calculated in such a way that 110 mg nitrogen make it into each vessel (corresponds to 220 mg N/l substrate, incl. cover).

50 seeds of spring barley per vessel are evenly distributed on the substrate surface. They can, as a choice, be counted out or, after a repeated determination of weight of 50 grains, weighed out (accurate to 10 mg). It is to be guaranteed by visual inspection that no broken or stunted grains make it into the seed.

After the sowing, a covering takes place with 100 ml of the respective test mixture or with EE0 in the case of the comparison substrate.

The remaining test substrate is thrown out. The well-pressed covering layer is subsequently evenly moistened with approx. 60 ml of water (pipeline water with drinking water quality). A wetting of the covering layer has to definitely be avoided, though, because otherwise the germination of the spring barley can be impeded. The test substrate in the plant test should not be moister than the fresh compost substance during the determination of the degree of rotting (fist test).

Setting up the vessels takes place in an air-conditioned room at 18-20°C and a luminous strength of at least 3,000 lux at least 12 h/day. Fluorescent tubes connected in parallel suggest themselves for the lighting.

Desalinized water has to be poured on the vessel 2 - 3 times, as a rule, in the test period of 10 - 12 days. The pouring takes place according to the needs of the plants, strong growth uses more water than weak growth. The water requirement can be estimated by experienced personnel using a 'finger sample'; otherwise, the water used in the individual vessels can be replaced corresponding to their weight loss (weigh vessels incl. the basins underneath at the start of the test and each time during watering). The substrate is to constantly be kept well moistened, without leakage water coming out. If leakage water nevertheless comes out into the basin underneath, this is to be put back.

The cutting of the test plants takes place when the majority of the second leaves have overgrown the first ones in the checkpoint (comparison substrate). The stalks are cut off pot-wise with scissors directly over the substrate surface and immediately weighed (in [g], accurate to two decimal places).

5 Calculation and evaluation of the results

The evaluation of the plant tolerance of a test substrate takes place on the basis of the mean value of the above-ground fresh mass yields of the 3 repetitions with a 25% or, as

the case may be, with a 50% compost proportion. The yields are expressed percent-wise in relation to the mean yield of the comparison substrate.

$FM(r)_{25/50\%}$ = $[FM_{25/50\%} / FM_{EE0}] \times 100$ [%]

$FM(r)_{25/50\%}$: Relative yield of the variations with respect to the comparison substrate EE0 in [%]

$FM_{25/50\%}$: Mean fresh mass yields of the variations in [g]

FM_{EE0} : Mean fresh mass yield of the comparison substrate in [g]

Compost is considered to be plant tolerant if no visible chloroses or necroses appear on the leaves and the fresh mass yield of the variation with 25% compost proportion reaches at least 90% of the yield of the comparison substrate. If these requirements are fulfilled, compost can be recommended for use as a soil improvement agent and dung.

If the variation with the 50% compost proportion also reaches at least 90% of the fresh mass yield of the comparison substrate, the tested compost can furthermore also be recommended in principle for use as a blending component in garden molds and cultivated substrates. The mixing proportions to be recommended depend, in the process, above all on the salt content, the content of soluble plant nutrients (especially potassium) and the pH value of the compost, as well as the intended plant cultivation.

6 Remarks

During the execution of the test, one is to see to it that the material is not moistened too heavily. No leakage water should come out, especially after the addition of the dung solution, the subsequent moistening of the covering layer with water and during watering.

Reference addresses for standard soil (EE0)

Gebr. Patzer KG Einheitserde- und Humuswerke, 36391 Sinntal-Jossa;
Tel.: 06665 / 8057; Fax: 06665 / 604

Balster Einheitserdenwerk GmbH, 58730 Fröndenberg;
Tel.: 02373 / 7398; Fax: 02373 / 71919

Einheitserdenwerk Uetersen, Werner Tantau GmbH & Co. KG, 25436 Uetersen;
Tel.: 04122 / 53308; Fax: 04122 / 53365

Einheitserdenwerk A. Stangenberg GmbH, 31789 Hameln;
Tel.: 05151 / 7631; Fax: 05151 / 22794

Determination of the pH value

1 Preliminary remark

The pH value is determined electrometrically in a suspension of the fresh compost substance in 0.01 molar $CaCl_2$ solution (ratio: 1 + 10).

2 Sample preparation

Sieving the fresh original sample to < 10 mm.

3 Materials and reagents

- Scales (0.1 g reading)
- Suitable vessels (e.g. beakers), glass rod
- Thermometer
- Measuring device: pH meter with a suitable pH electrode
- 0.01 molar $CaCl_2$ solution
- Suitable pH buffer solutions for the calibration of the measuring device

4 Carrying out the testing

200 ml of 0.01 molar $CaCl_2$ solution are added to 20 g of sample material (FS < 10 mm). The pH value in the suspension (stir repeatedly with a glass rod) is determined after 1 hour with a calibrated pH measuring device. The temperature of the suspension is to be taken into account during the measurement in accordance with the type of measuring device.

5 Calculation of the results

The results of the pH determination are to be stated accurate to one decimal point.

6 Remarks

A close ratio of fresh compost substance and $CaCl_2$ solution (e.g. 1 + 2.5) would ensure an approximation of the situation in the 'soil solution'. A ratio of 1 + 10 is chosen for the determination of the pH value on account of the slight change of the pH value in the case of a greater 'dilution' and of the simpler execution of the analysis.

7 Literature

VDLUFA, Methods Book, Volume I (1991): The investigation of soils

Determination of the salt content after extraction with distilled water

1 Preliminary remark

The determination of the salt content occurs after the extraction of the fresh compost substance with **distilled water** (ratio 1+10). The extraction with saturated gypsum solution still called for in the first edition of the methods book is connected with difficulties in the method and is replaced by the simpler extraction with distilled water (also see Point 6 Remarks).

2 Sample preparation

Sieving the fresh original sample to < 10 mm.

3 Materials and reagents

- Scales (0.1 g reading)
- PE shaking bottles (min. 250 ml)
- Suitable filtering vessels (e.g. beakers)
- Medium-porous folded filter and suitable funnels
- Conductivity measuring device with cell constant C = 1
- Thermometer (min. 0.5°C reading)
- Shaker
- Distilled water (conductivity < 1.0 10^{-6} S/cm)

4 Carrying out the testing

Shake 20 g of sample material (FS < 10 mm) with 200 ml distilled water in the PE bottles for 2 hours. Following this, filter and determine the conductivity and temperature in the filtrate (in so far as a conductivity measuring device with an automatic temperature compensation is not used).

5 Calculation of the results

The corresponding calcium chloride concentration is calculated from the conductivity in the extract. The basis for the calculation is the specific conductivity of a 0.01 molar calcium chloride solution (745.6 mg KCl/l H_2O) of 14.12 ≙ 10^{-4} S/cm at 25°C. The dependence of the electrical conductivity of a salt solution on the temperature has to be taken into consideration through a corresponding factor F_t (if a conductivity measuring device with an automatic temperature compensation is not used). The conversion factors F_t are published in VDLUFA, Methods Book, Volume I (1991): The investigation of soils (Method A 10.1.1). If the determination of the conductivity is carried out at a constant temperature of 25°C or using a measuring device with automatic temperature compensation (observe manufacturer details), the conversion of the conductivity into the corresponding salt concentration takes place with the constant factor $F_t = 52.80$.

The salt content relates to the volume of the fresh compost substance. The statement takes place in [g KCl/l FS], accurate to two decimal points.

$SA_m = LF_p \times F_t$ [mg/100 g]

SA_m : Salt content with regard to the fresh mass in [mg KCl/100 g FS] (with an extraction ratio of 1 + 10, the value corresponds to the KCl concentration of the solution in [mg/l])

LF_p : Conductivity of the sample extract in [10^{-4} S/cm]

F_t : Factor for the calculation of the salt concentration from the conductivity, taking the temperature into consideration

At 25°C : F = 745.6 [mg/l] / 14.12 [10^{-4} S/cm]

= 52.80 [mg/l] / [10^{-4} S/cm]

Conversion of the volume of the fresh substance

$SA_{vol} = SA_m \times RD_{FS} \times 10^{-5}$ [g/l]

SA_{vol} : Salt content with regard to the volume of the fresh substance in [g KCl/l FS]

RD_{FS} : Raw unit weight of the fresh substance (< 10 mm) in [g/l]

During the conversion of the salt content from [mg KCl/100 g FS] to [g KCl/l FS], all dimensionally dependent changes in the factor 10^{-5} are integrated, so only the numerical values of SA_m and RD_{FS} have to be used in the formula.

6 Remarks

The influence of weak electrolytes is to be made impossible during the determination of the salt content through the extraction with saturated gypsum solution (1st edition of the methods book). Only the strong electrolytes with osmotic relevance should specifically be recorded, therefore, for the evaluation of the plant tolerance of the material. This procedure has proven itself for many garden soils for the evaluation of the conductivity (of the salt content) for the plant tolerance. A simple transfer to composts and compost substrates is not practical, however; the portion actually relevant for the plant tolerance can, for example, be overestimated for strong electrolytes (Na+ and K+ ions) through the strengthened exchange of cations with the use of saturated gypsum solution.

In addition, difficulties with the method can arise with the use of saturated gypsum solution as the extraction agent that can lead to an erroneous determination of the conductivity stemming from the compost sample.

The salt content derived from the conductivity measurement with the use of distilled water as the extraction agent can also only be a first, crude (and above all simple to determine) parameter for the evaluation of the plant tolerance of the examined compost material. The direct determination of the ions Na+, K+ and Cl- with osmotic effectiveness in the extract is substantially more convincing. The determination of the ions mentioned can be carried out without a problem when the equipment is available (flame photometer, chloride meter). Rules for the determination in the watery extract can be taken from the methods book, volume I of the VDLUFA.

7 Literature

VDLUFA, Methods Book, Volume I (1991): The investigation of soils

Determination of nitrate, ammonia and magnesium in the $CaCl_2$ extract

1 Preliminary remark

The soluble content of nitrate, ammonia and magnesium is determined after extraction of the fresh compost substance with 0.0125 molar $CaCl_2$ solution (ratio 1 + 10). In the extract, nitrate and ammonia are measured with a spectrophotometer (or with a comparable method), and magnesium using AAS. The nitrogen fractions determined in this way are designated as **soluble mineral nitrogen**. The **soluble organic nitrogen compounds** likewise obtained in the extract are not recorded with the described methods. No statement on the total nitrogen available to the plants can be made by the sole determination of nitrogen and ammonia either. As a crude rule of thumb, approx. 10% of the total nitrogen content determined according to Method 13.1 can be assessed for the nitrogen available to plants in a vegetation period.

2 Sample preparation

Sieving the fresh original sample to < 10 mm.

3 Materials and reagents

- Scales (0.1 g reading)
- PE shaking bottles (min. 250 ml)
- Suitable filtering vessels (e.g. conical flasks)
- Medium-porous folded filter and suitable funnels
- Shaker
- Measuring devices (spectrophotometer, AAS)
- 0.0125 molar $CaCl_2$ solution
- Standard solutions of the nutrients to be determined

4 Carrying out the testing

Shake 20 g of sample material (FS < 10 mm) with 200 ml of 0.0125 molar $CaCl_2$ solution in the PE bottles for 2 hours. Following this, filter and determine the nitrate and ammonia in the filtrate with a spectrophotometer and determine magnesium using AAS. The determination of the individual nutrients in the extract can also take place through comparable methods (e.g. titration for the determination of the ammonia content).

5 Calculation of the results

The soluble nutrient content is related to the volume of the fresh compost substance. The statements take place as Nitrate-N, Ammonia-N and Mg as whole numbers in [mg/l FS].

$$NS_{vol} = NS_m \times RD_{FS} \times 10^{-2} \text{ [mg/l FS]}$$

NS_{vol} : Nutrient content with regard to the volume of the fresh substance in [mg/l FS]

NS_m : Nutrient content with regard to the fresh mass in [mg/100 g FS] (with an extraction ratio of 1 + 10, the value corresponds to the nutrient concentration of the solution in [mg/l])

RD_{FS} : Raw unit weight of the fresh substance (< 10 mm) in [g/l]

6 Remarks

The nutrients in the extract are determined in accordance with the methods mentioned in the methods book VDLUFA, Volume I (1991), A 6.1.4.1 and A 6.2.4.1 or using comparable methods.

Possibly arising dilution steps or the mixing of an aliquot of the extract with reagents are to be correspondingly taken into consideration in the determination of NS_m.

The self-coloring of the extracts can lead to substantial problems during the determination of the nitrate, especially with low nitrate content. That is why an examination of the nitrate determination with the spectrophotometer using nitrate indicator rods is to be recommended. As a rule, these quick nitrate determinations alone already supply sufficiently accurate results for most compost applications. Strongly colored extraction solutions can be compensated by suitable decolorizing agents (e.g. activated charcoal), by blind measurements of the extracts or by alternative nitrate determination methods (more on this in the methods book of VDLUFA, Volume I (1991), Method A 6.1.4.1, Point 8 Remarks).

Besides the purely analytical problems mentioned for the determination of the soluble mineral nitrogen fractions, the **sample preparation and conservation** or, as the case may be, the **rapid execution of the analyses** have an outstanding significance! The soluble mineral nitrogen contents are subject to a strongly temperature-dependent dynamic. That is why the samples have to be examined directly after the taking of the sample for their soluble nitrogen contents. If delays that are not avoidable arise during the analysis, the samples have to be conserved by freezing. In connection with this, it is pointed out that the determination of the soluble mineral nitrogen contents can characterize compost charge ready for sale only at a certain point in time (that of the taking of the sample); the dynamic addressed takes its course further, of course, during the storage of the compost.

7 Literature

VDLUFA, Methods Book, Volume I (1991): The investigation of soils
DIN 38 406 Section 5 (1988)

Determination of phosphorus and potassium in the CAL extract

1 Preliminary remark

The soluble content of phosphorus and potassium is determined after extraction of the fresh compost substance with a solution of calcium acetate, calcium lactate and acetic acid buffered to pH 4.1 in the ratio 1 + 10. In the extract, phosphorus is measured with a spectrophotometer and potassium with flame photometry.

2 Sample preparation

Sieving the fresh original sample to < 10 mm.

3 Materials and reagents

- Scales (0.1 g reading)
- PE shaking bottles (min. 250 ml)
- Suitable filtering vessels (e.g. conical flasks)
- Medium-porous folded filter and suitable funnels
- Shaker
- Measuring devices (spectrophotometer, AAS)
- CAL solution (statements on the production in VDLUFA, Methods Book, Volume I (1991), Method A 6.2.1.1)
- Standard solutions of the nutrients to be determined
- Color reagents for the determination of phosphates (statements on the production in VDLUFA, Methods Book, Volume I (1991), Method A 6.2.1.1)

4 Carrying out the testing

Shake 20 g of sample material (FS < 10 mm) with 200 ml CAL solution in the PE bottles for 2 hours. Following this, filter and determine the phosphorus in the filtrate with a spectrophotometer and determine potassium with flame photometry.

5 Calculation of the results

The soluble nutrient content is related to the volume of the fresh compost substance. The statements take place as **oxide compounds (P_2O_5 , K_2O)** as whole numbers in [mg/l FS].

$$NS_{vol} = NS_m \times RD_{FS} \times 10^{-2} \text{ [mg/l]}$$

NS_{vol} : Nutrient content with regard to the volume of the fresh substance in [mg/l FS]

NS_m : Nutrient content with regard to the fresh mass in [mg/100 g FS] (with an extraction ratio of 1 + 10, the value corresponds to the nutrient concentration of the solution in [mg/l])

RD_{FS} : Raw unit weight of the fresh substance (< 10 mm) in [g/l]

6 Remarks

The nutrients in the extract are determined in accordance with the methods mentioned in the methods book VDLUFA, Volume I (1991), A 6.2.1.1 or using comparable methods.

Possibly arising dilution steps or the mixing of an aliquot of the extract with color reagents for the determination of the phosphate are to be correspondingly taken into consideration in the determination of NS_m.

7 Literature

VDLUFA, Methods Book, Volume I (1991): The investigation of soils

Determination and evaluation of the content of seeds capable of germinating and plant parts capable of sprouting

1 Preliminary remark

The cultivation method is carried out for the determination of the content of seeds capable of germinating and plant parts capable of sprouting in the compost.

2 Sample preparation

Sieving the fresh original sample to < 10 mm.

3 Materials and reagents

- Plastic basin with bottom perforation or equivalent testing containers
- Pouting mats
- Pinhole foil
- Conductivity measuring device and further materials (see Method 8) for the determination of the salt content
- Suitable blending substrate (e.g. weakly replaced moor peat with approx. 4 g calcium carbonate per liter)

4 Carrying out the testing

The sieved test substrate (FS < 10 mm) is exposed to a temperature of +4°C for 3 days. Following this, 3 liters of the test substrate are diluted with a blending component in such a way that the test mixture has a salt content of < 2 g KCl/l FS.

The required dilution is to be determined by calculation from the salt content of the fresh substance and the blending component is to be assessed a salt content of 0 g KCl/l FS here! The blending component used has to be free from seeds capable of germinating and plant parts capable of sprouting. Weakly replaced moor peat with approx. 4 g of calcium carbonate per liter is suitable.

The test mixture is evenly distributed in a layer of approx. 10 mm in test basins with bottom perforation, lightly pressed down and watered to the full water capacity. A pouring mat is laid out for the test containers ahead of time and they are covered with a pinhole foil for protection against contamination.

After this, the test containers are set up over a period of 15 days with an illumination intensity of at least 1000 lux and a room temperature of 18 - 20°C without direct sunshine and the water loss is regularly compensated by spraying it. In order to prevent drying to a great extent, the basins can be covered with glass or plastic plates (leaving an air gap open).

5 Calculation and evaluation of the results

After the end of the test, the germinating plants that have accumulated are counted and calculated per liter of test substrate, if necessary, the species composition is determined and stated.

Compost is **free** of seeds capable of germinating and plant parts capable of sprouting if **fewer than 0.5 germinating plants** are determined per liter of test substrate.

Compost is **largely free** of seeds capable of germinating and plant parts capable of sprouting if **fewer than 2 germinating plants** are determined per liter of test substrate.

There is a **substantial content** of seeds capable of germinating and plant parts capable of sprouting if **more than 2 germinating plants** are determined per liter of test substrate.

6 Remarks

One proceeds according to Method 7 for the determination of the salt content of the fresh compost substance. The required salt content in the test mixture of < 2 g KCl/l FS is to be determined by way of calculation and not by measuring the conductivity of the test mixture, because the conductivity measurement would supply higher and higher values with the use of lime-white moor peat as a blending component. A salt content of 0 g KCl/l FS is to be assessed for the blending component for the calculation of the required dilution of the fresh substance.

Compost has to be **largely free** of seeds capable of germinating and plant parts capable of sprouting for the **use as a mulch and soil conditioner.**

Compost has to be **free** of seeds capable of germinating and plant parts capable of sprouting for the use as a blending component for cultivation substrates.

Determination and evaluation of the foreign matter and stone content

1 Preliminary remark

Foreign matter is all of the material that is undesired in the composting. This is in principle all inorganic materials, such as glass, plastic, metals, rubber, composite materials etc. Paper is not foreign matter.

Foreign matter is undesirable content material, because it impairs the optical appearance of compost and can be disturbing when compost is used. The degree of impurity is dependent on the optical conspicuousness of the foreign matter contained in the compost. Smaller foreign matter particles are less noticeable than larger foreign matter particles. Only foreign matter with a particle size > 2 mm is relevant for the optically-effective degree of impurity of compost.

Stones are likewise undesirable content material, but not foreign matter. The evaluation of the content of stones in compost takes place separately, therefore. Only stones with a particle size > 5 mm are relevant for the evaluation.

2 Sample preparation

Drying the unscreened fresh substance at 105°C.

3 Materials

- Scales (10 mg reading)
- Sieve with 5 mm mesh width
- Sieve with 2 mm mesh width
- Tweezers

4 Carrying out the testing

For fine-grained compost (0 to 10 mm), 1 liter of dried (105°C) test substrate is required for the examinations, for medium-grained compost (0 to 20 mm), 2 liters, and for coarse-grained compost, 3 liters.

The dry sample is weighed and subsequently grated by hand through a 5 mm sieve and the sieve through fraction through a 2 mm sieve. The sieve through fraction < 2 mm is thrown out. From the sieve fraction > 5 mm, stones are picked out and weighed. Following this, the sieve fractions 2 - 5 mm and > 5 mm are joined. This united fraction is spread out on a flat base and the foreign matter is picked out with tweezers. During the selection, portions of not more than 100 ml are to be examined each time, in the process of which the selection of the foreign matter has to take place as thoroughly as possible. The mass of the foreign matter > 2 mm is weighed and separately recorded.

5 Calculation and evaluation of the results

Foreign matter and stone content relate to the total mass of the dried sample each time (before the sieving) and to be stated in [% DS], accurate to two decimal places.

$Fs = [M_{Fs>2mm} / P_{tot}] \times 100\ [\%]$

$St = [M_{St>5mm} / P_{tot}] \times 100\ [\%]$

Fs : Foreign matter content in [% DS]

$M_{Fs>2mm}$: Foreign matter > 2 mm in [g]

St : Stone content in [% DS]

$M_{St>5mm}$: Stones > 5 mm in [g]

P_{tot} : Total mass of the examined sample before the sieving in [g]

Evaluation of the foreign matter content**:**

- Compost is **free of foreign matter** if the content of foreign matter is **less than 0.1** [% DS].

- Compost is **practically free of foreign matter** if the content of foreign matter is **less than 0.5** [% DS].

- Compost has a **noticeable content of foreign matter** if this is **more than 0.5** [% DS].

- Compost has a **substantial content of foreign matter** if the content is **more than 2** [% DS].

Evaluation of the stone content:

- Compost has a **low content** of stones if this is **less than 5** [% DS].

- Compost has a **noticeable content** of stones if this is **more than 5** [% DS].

Determination of the loss on ignition

1 Preliminary remark

The loss on ignition supplies a measure for the content of organic substances in composts. It is to be observed that inorganic compounds and water of constitution can also evaporate through this determination method and that they are added to the content of organic substances in the evaluation. During the examination of composts, this possible error is negligibly small as a rule, however, so the loss on ignition represents a practical and sufficiently accurate measure for the content of organic substance, especially on account of the simple execution of the method.

2 Sample preparation

Drying the unscreened fresh substance at 105°C.

Grinding of at least 30 g DS with a suitable grinder to < 0.25 mm.

3 Materials

- Analytical scales (1 mg reading)
- Box-type furnace
- Porcelain crucible
- Dessicator

4 Carrying out the testing

Weigh in approx. 5 g of the dried and ground sample material into a dry, weighed porcelain crucible (make red hot and keep in the dessicator) and burn up at 550°C in the box-type furnace until the weight is constant. Let the porcelain crucible cool down in the dessicator and weigh back in. The weighings are to be determined accurate to 1 mg.

5 Calculation of the results

The loss on ignition relates to the dry mass. The results are stated in [% DS], accurate to one decimal place.

$$GV = [(M_{vdG} - M_{ndG}) / (M_{vdG} - M_{tara})] \times 100 [\%]$$

GV : Loss on ignition in [% DS]
M_{tara} : Mass of the empty crucible in [g]
M_{vdG} : Sample weight + M_{tara} in [g]; before the burning
M_{ndG} : Sample + M_{tara} in [g]; after the burning

6 Remarks

A generally valid time span up to point where constancy of weight is reached can not be given; in case of doubt, a sample has to be burned still further after an initial reweighing. Ventilation with approx. 2 l air/minute has proven itself for the removal of faulty oxidation.

The organic carbon content can be calculated by multiplication with the factor 0.58 from the loss on ignition as a measure of the organic substance in composts. The C/N relationship then results from the division of the carbon content calculated in this way by the total nitrogen content determined according to Method 13.1.

7 Literature

DIN 38 414 (S2), German uniform proc. for water, waste water and slurry investigation; slurry and sediments: Determination of the loss on ignition and of the burning residue

Schaller, K. (1988): Practical training for soil science and plant nutrition; Geisenheimer reports, Volume II

Determination of heavy metals in the aqua regia treatment

1 Preliminary remark

The dry compost substance is treated with aqua regia for the determination of the total content of the heavy metals lead, cadmium, chromium, copper, nickel, mercury and zinc. The elements mentioned are determined in the treatment solution with AAS or an equivalent procedure.

2 Sample preparation

Drying the unscreened fresh substance at 105°C.
Grinding of at least 30 g DS with a suitable grinder to < 0.25 mm. During the grinding procedure, no contamination of the sample may take place with the heavy metals to be determined.

3 Materials and reagents

- Scales (1 mg reading)
- Reaction vessels made of glass with suitable reflux condensers and heating devices
- 100 ml volumetric flask
- Fine to medium-porous folded filters (acid-proof, free of trace elements) and suitable glass funnels
- Sealable filtering vessel (100 ml volumetric capacity)
- Measuring device: AAS (ICP)
- Hydrochloric $acid_{conc}$ (ρ = 1.19 g/ml, degree of purity: at least to a.)
- Nitric $acid_{conc}$ (ρ = 1.40 g/ml, degree of purity: at least to a.)
- Nitric $acid_{dil}$ (c = 2 mol/l, degree of purity: at least to a.)
- Heavy metal standard solutions

4 Carrying out the testing

Approx. 5 g of the sample material is weighed into the reaction vessel (note the weigh-in in [g], accurate to 3 decimal points), subsequently 18 ml of hydrochloric $acid_{conc}$ and 6 ml of nitric $acid_{conc}$ are carefully added (aqua regia: 3 parts hydrochloric $acid_{conc}$ + 1 part nitric $acid_{conc}$). Let the reaction vessel stand at least 12 hours (over night) at room temperature. After that, render the solution soluble for 2 hours with light boiling under reflux condensation. After cooling, partially rinse the condenser with nitric $acid_{dil}$ (max. 25 ml) and subsequently transform the contents of the reaction vessel with nitric $acid_{dil}$ into a 100 ml volumetric flask (fill up to the marking with acid). Filter the contents of the volumetric flask after thorough mixing through a suitable filter into various filtering vessels.

The determination of the individual heavy metals in the treatment solution takes place using AAS (ICP) in [mg/l], applying the corresponding standard calibration series. It is to be ensured that the standard calibration solutions contain the same proportion of acid as the measurement solution.

5 Calculation of the results

The heavy metal contents relate to the dry mass, the statement takes place in [mg/kg DS], in the process of which contents < 10 mg/kg are to be given to two decimal points, contents between 10 - 100 mg/kg DS to one decimal point and contents > 100 mg/kg DS are to be given as whole numbers.

$SM = SM_{al} \times F_{dil} \times V_{mk} / E$ [mg/kg]

SM : Heavy metal content in [mg/kg DS]

SM_{al} : Heavy metal concentration in the treatment solution in [mg/l]

F_{dil}: Possibly necessary dilution factor, in so far as the standard measurement range was exceeded with individual elements and the treatment solution had to be diluted

V_{mk} : Volume of the treatment solution (volumetric flask) in [ml]

E : Weigh-in in [g]

6 Remarks

After the treatment of the dry compost substance with aqua regia, the total nutrient content of phosphorus, potassium, calcium and magnesium can also be determined in the treatment solution, in addition to the heavy metals mentioned. Phosphorus is determined using ICP (or with a spectrophotometer), the other elements using AAS.

If a different procedure than AAS is used for the determination of individual elements in the treatment solution, this is to be explicitly stated together with the respective analytical result!

A scaling of the heavy metal contents to 30% of loss on ignition (organic substance) takes place according to the formula:

$SM_{30\%} = SM_p \times 70 / (100 - GV_p)$

$SM_{30\%}$: Heavy metal content in [mg/kg DS], scaled to 30% of loss on ignition

SM_p : Heavy metal content in [mg/kg DS] in the sample

GV_p : loss on ignition in [% DS] of the sample

7 Literature

VDLUFA, Methods Book, Volume I (1991): The investigation of soils
DIN 38 414, Section 7, German uniform proc. for water, waste water and slurry investigation; slurry and sediments: Treatment with aqua regia for the subsequent determination of the acid-soluble proportion of metals
DIN 38 406, Section 12 (1988)
DIN 38 406, Section 22 (1988)

Determination of the total content of nitrogen according to Kjeldahl

1 Preliminary remark

The organically-bound total nitrogen content can be recorded through the Kjeldahl treatment of the dry compost substance. The organically-bound nitrogen is transformed with concentrated sulfuric acid in the presence of salts and suitable catalysts into the ammonia form. After alkalization, distillation and collection of the stripped ammonia in a suitable acid pattern, the ammonia content can be determined with volumetric analysis.

2 Sample preparation

Drying the unscreened fresh substance at 105°C.
Grinding of at least 30 g DS with a suitable grinder to < 0.25 mm.

3 Materials and reagents

- Scales (1 mg reading)
- Kjeldahl apparatus (heatable treatment block, treatment vessel, distillation apparatus)
- Burette or titration machine
- Suitable glass vessel for acid reception (beaker or conical flask)
- Concentrated sulfuric acid (ρ = 1.84 g/ml)
- Kjeldahl tablets or catalysts (selenium, titanium oxide) and potassium sulfate
- Soda lye (w = approx. 40%)
- Acid receiver (boric acid, hydrochloric acid) and indicator
- Suitable acid measurement solution (e.g. hydrochloric acid c = 0.1 mol/l or 0.01 mol/l)

4 Carrying out the testing

The sample amount to be weighed in depends on the nitrogen content to be expected. For composts that contain approx. 1-2% nitrogen in the dry substance as a rule, a weigh-in of approx. 250 mg DS has proven itself. With a greater content of nitrogen, the weigh-in is to be reduced in accordance with Table 12.1.1.

Table 12.1.1: Favorable sample weigh-ins based on the total N content expected in the dry substance

N content in [%]	Sample weigh-in in [mg]
1-2	200-250
3-4	100-150
5-10	50-100

The required sample amount is weighed into a treatment vessel (note accurate to 1 mg), a Kjeldahl tablet is added and treated with 15 ml concentrated sulfuric acid. The addition of the sulfuric acid is to be calculated in such a way that a residual still remains after the treatment. Instead of the Kjeldahl tablet, selenium reaction mixture (0.5 g) and potassium sulfate (0.2 - 0.3 g / ml H_2SO_4) can also be added.

The treatment takes place at 360°C until the liquid is bright and clear (duration approx. 60 - 90 min.). When the sample has cooled down to room temperature, approx. 20 ml of distilled water are carefully mixed in.

In so far as a direct distillation is possible from the treatment vessels, soda lye is carefully added in a clear surplus (approx. 30 ml) (otherwise transfer the content of the treatment vessel quantitatively into a suitable distillation vessel beforehand). Following this, the distillation of the ammonia takes place with water steam into an acid receiver.

The ammonia amounts collected in the acid receiver are titrated with a suitable measurement solution with the help of a burette of a titration machine up to the transition of the indicator.

A reagent blind value is also to be determined for every sample series.

5 Calculation of the results

The weighed-in sample amount is to be noted accurate to 1 mg and the measurement solution used is to be noted in ml accurate to 2 decimal places. The results are to be stated in [% DS], accurate to two decimal places.

$$N = (Ml_p - Ml_b) \times 100 \times F_N / E \; [\%]$$

N : Nitrogen content in [% DS]

Ml_p : Measurement solution used in [ml] for the sample treatment

Ml_b : Measurement solution used in [ml] for the blind value

F_N : Factor (in [mg/ml]) for the calculation of the nitrogen equivalent in mg of 1 ml of measurement solution used. F_N is dependent on the concentration of the measurement solution used (1.4 for 0.1 molar or 0.14 for 0.01 molar HCl solution).

E : Sample weigh-in in [mg].

6 Remarks

Only the **organically-bound total nitrogen** can be determined with the described method, strictly speaking, because ammonia - nitrogen is stripped through the drying at 105°C and nitrates are not, or only insufficiently, recorded through the Kjeldahl treatment. **Nevertheless (in accordance with the definition), the designation total nitrogen is used for the characterization of composts.** The soluble mineral nitrogen compounds determined according to Method 8.1 are **not** calculated in with the Kjeldahl nitrogen determined here and remain disregarded in the calculation of the C/N ratio as well.

7 Literature

VDLUFA, Methods Book, Volume I (1991): The investigation of soils

Determination of P, K, Ca, Mg in the aqua regia treatment

1 Preliminary remark

The total content of phosphorus, potassium, calcium and magnesium are determined together with the heavy metals after treatment of the dry compost substance with aqua regia. Phosphorus is determined in the treatment solution using ICP (or with a spectrophotometer), the other elements are determined using AAS.

2 Sample preparation

See Method 12.

3 Materials and reagents

- Standard solutions of the elements to be determined
- Otherwise see Method 12

4 Carrying out the testing

The treatment of the sample and the determination of the individual elements in the treatment solution takes place in accordance with Method 12.

5 Calculation of the results

The total content of phosphorus, potassium, calcium and magnesium relate to the dry substance. The statement takes place each time as an **oxide compound (P_2O_5 , K_2O, CaO, MgO)** in [% DS], accurate to two decimal points.

$$NS = NS_{al} \times F_{dil} \times V_{mk} \times 10^{-4} / E \; [\%]$$

NS : Nutrient content in [% DS]

NS_{al} : Nutrient concentration in the treatment solution in [mg/l]

F_{dil} : Possibly necessary dilution factor, in so far as the standard measurement range was exceeded with individual elements and the treatment solution had to be diluted

V_{mk} : Volume of the treatment solution (volumetric flask) in [ml]

E : Weigh-in in [g]

6 Remarks

If a different procedure that AAS or ICP (phosphorus) was used for the determination of individual elements in the treatment solution, this is to be explicitly stated together with the respective analytical result!

7 Literature

VDLUFA, Methods Book, Volume I (1991): The investigation of soils

DIN 38 414, Section 7, German uniform proc. for water, waste water and slurry investigation; slurry and sediments (1983): Treatment with aqua regia for the subsequent determination of the acid-soluble proportion of metals

DIN 38 406, Section 22 (1988)

Determination of the degree of rotting through the exchange activity with the help of a respirometer

1 Preliminary remark

The exchange activity allows a statement on the content of biologically degradable materials in composts. An assessment of the degree of rotting takes place on the basis of the oxygen consumption.

2 Sample preparation

Sieving the fresh original sample to < 10 mm.

3 Materials

- Respirometer
- Scales
- Drying chamber

4 Carrying out the testing

The determination of the exchange activity takes place in the respirometer. The fresh compost sample is adjusted with the help of the 'fist test' (see Chap. II, Method 4) and allowed to stand for approx. 1 hour while being repeatedly turned. Following this, approx. 30 - 50 g of this mixture (depending on the respirometer) are weighed into the reaction vessels. The reaction vessels are placed into the respirometer into a water bath at 20°C and connected.

The registration of the oxygen used should take place in a 6 hour rhythm. The testing runs over 4 days (AT_4).

5 Calculation and evaluation of the results

A conversion of the units given in mg O_2/l is necessary. With an estimate of 166 ml of waste water required specific to the device, 1 counter unit (CU) = 0.166 mg O_2 consumption.

The result after 4 days is to be given in mg O_2 /g ODS as AT_4, taking the dry substance and the loss on ignition of the sample into consideration.

Calculation (following the determination of waste water samples):

AT_4 = CU after 4 d x 0.166 mg / (weigh-in DS in g x BL in %) x 100
Units : mg O_2 /g ODS

AT_4 : Exchange activity after 4 days
CU : Counter units
BL : Loss on ignition
DS : Dry substance
ODS : Organic dry substance

6 Literature

Notices of the State Working Group, Waste (LAGA), Instruction Leaflet 10 (M 10) "Quality criteria and application recommendations for compost from garbage and garbage/sewage sludge"; Erich Schmidt Verlag

Cress test

1 Preliminary remark

The chemical-physical examinations of the compost for carbon, nitrogen, self-heating and biological oxygen needs only give insights into the degree of aging (rotting). They say nothing about its plant tolerance, however. For this reason, a vegetation test is carried out (see plant tolerance with barley, Chap. II, Method 5).

The garden cress (Lepidium sativum) growing quickly in the sprouting-leaf stage has proven itself for a quick orientation, because the result is already available after 5 - 7 days.

2 Sample preparation

The fresh compost sample is sieved to < 10 mm.

3 Materials

- Plant basins (dia. 12 cm, height 7 cm)
- Standard soil EE0
- Multi-nutrient dung (see Chap. II, Method 5)

4 Carrying out the testing

The basins (dia. 12 cm, height 7 cm) are loosely filled with the substrate, almost up to the rim, patted smooth and watered. After a short period of waiting, in which an even moistening takes place and surplus water can run off, 1 g of cress is evenly scattered over the surface of the seed.

The seed should have contact with the bottom overall, if necessary, press down.

The basins are covered with a glass plate (evaporation protection), in the process of which a small gap should remain, that ensures the exchange of gas. The plant basins remain in the greenhouse approx. 7 days (the day of the sowing is included in the counting); the glass plates are removed if the germination plants touch them.

The plants are cut off exactly between the root and stalk for the harvest. The harvest should take place quickly, because the plants start to dry out immediately at the cutting surfaces. Following this, the plants are dried at 105°C and the water content is determined in the process.

The burning residual is determined at 550°C in the box-type furnace with the dried plant mass (see Chap. II, Method 11).

A cress cultivation on standard soil EE0 with corresponding additions of dung serves as a comparison.

5 Calculation and evaluation of the results

First, an observation is made as to whether the cress even starts to sprout. In the process, it can quickly be recognized whether the compost is an impediment to germination for sensitive plants or not. The cress reacts with a low capability for germinating or poor growth in the case of raised salt content. In comparison with the cultivation on EE0 substrate, it can be recognized how strong the impediment to sensitive plants is with the examined compost.

6 Literature

Abfall-Now, Number 1, PP. 14 - 16, Stuttgart

Determination of the air void volume in compost

1 Preliminary remark

For the determination of the air void volume in compost input materials and in composts.

2 Sample preparation

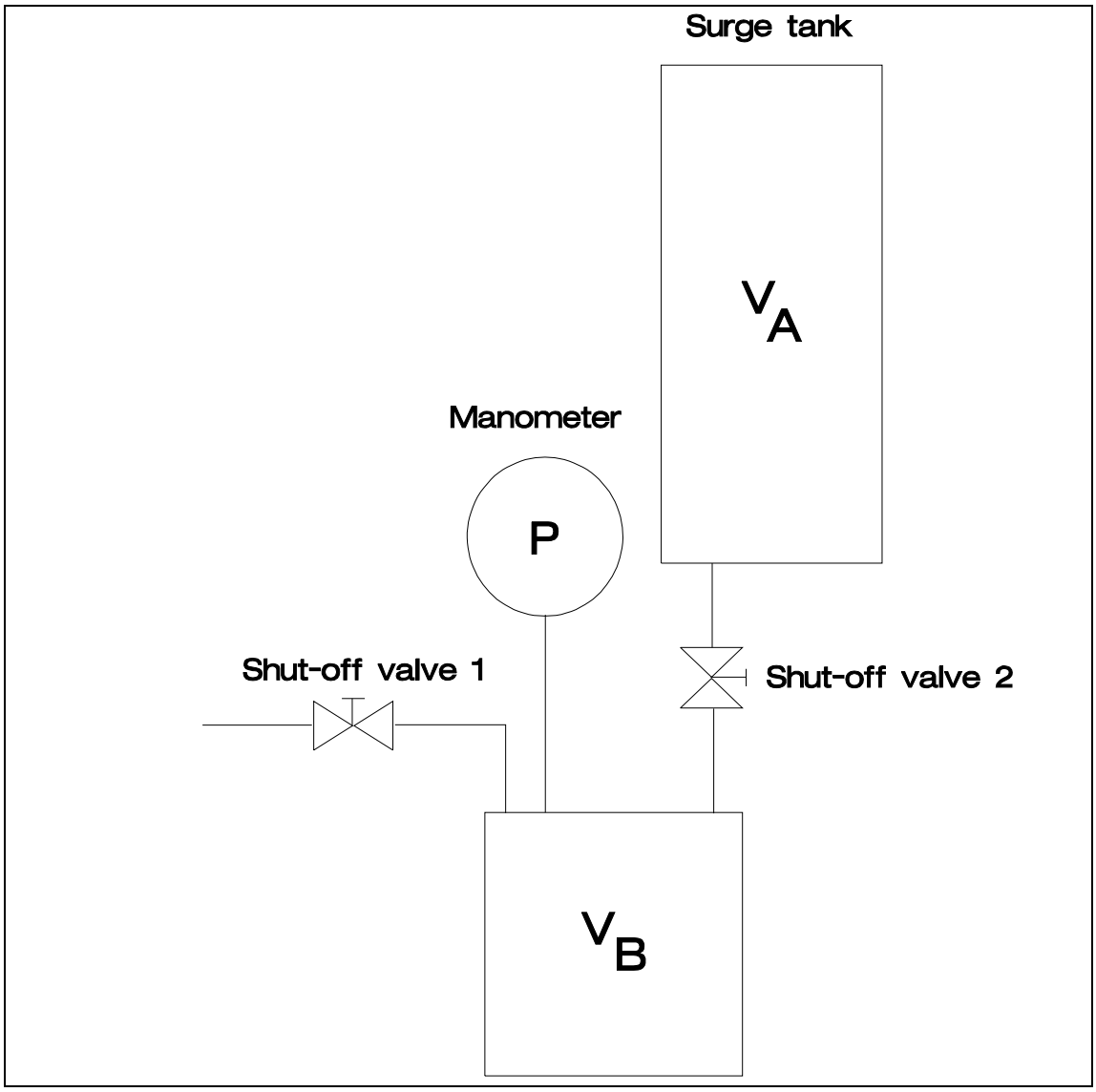
The sample should be filled into the pressure tank with as little disturbance as possible.

3 Materials

- Pressure tank with pressure display (e.g. manometer)
- Two shut-off valves
- Surge tank

4 Carrying out the testing

Open shut-off valve 2 to the surge tank. The fresh sample is filled in the pressure tank (V_B) (full). Shut-off valve 2 to the surge tank (V_A) is closed. The pressure tank is filled with 2 bar of compressed air through shut-off valve 1. Shut-off valve 1 is closed. The pressure is read (P_1). Shut-off valve 2 to the surge tank is opened. The second pressure value is read (P_2).



Illus.1: Measurement of the air void volume according to the pressure change method

5 Calculation and evaluation of the results

The relation

$$p \cdot V = \text{const.}$$

delivers, at a constant temperature with

$$V_p = P_2 \cdot V_A / P_1 - P_2$$

the air void volume V_p. The proportion of the air void volume is calculated with

$$\square_K = (V_p / V_B) \cdot 100$$

The result should be given accurate to 0.1%.

V_p	:	Air void volume [l]
V_A	:	Volume of the surge tank [l]
V_B	:	Volume of the pressure tank [l]
P_1	:	Pressure before opening shut-off valve 2 [Pa]
P_2	:	Pressure after opening shut-off valve 2 [Pa]
$\square_K$	:	Porosity of the material [%]

6 Remarks

If the volumes of the pressure tank and the surge tank deviate a lot from each other, special attention is to be directed to a constant temperature. I.e. if $V_A << V_B$, even a light heating of V_A can cause a substantial measurement error.

Determination of the water capacity

1 Preliminary remark

By water capacity of soil, the water amount is meant that a soil sample can absorb up to full capillary saturation.

2 Sample preparation

A naturally moist sample is sieved to < 10 mm.

3 Materials

- Glass cylinder, height 120 mm, diameter inside 35.7 mm, with a close-meshed plastic net bottom
- Filter paper
- Watch glass
- Beaker 1 l, high form
- Scales

4 Carrying out the testing

The sieve bottom of the glass cylinder is covered up with moistened filter paper. Following this, the entire cylinder is weighed (m_0). The naturally moist sample material, < 10 mm, is filled into the cylinder with light shaking and weighed anew (m_e). The glass cylinder is then placed into the beaker. Following this, tap water is slowly added up to a height appropriate for the substrate, so the material can soak itself full with water from the bottom.

If the substrate is well moistened up to the surface, as much water is added again until the substrate is overdammed by approx. 1 cm. This coating is allowed to stand for 24 h.

After this, the cylinder is taken out of the water, dried from the outside and placed on a water-saturated cellulose base covered with a watch glass. After 2 h, the glass cylinder is weighed back in (m_{moist}), then drained again and finally weighed back in anew.

This is repeated until no serious weight change can be determined any longer. Simultaneously with this determination, the water content of the fresh sample used has to be determined (WC).

5 Calculation of the results

Max. Water Capacity WK_{max} given in [% DS]:

$$Wk_{max} = (E_{moist} - E_{dr}) / E_{dr} \times 100\%$$

Mass of the dry sample: $E_{dr} = (m_e - m_0) \times (1 - WC/100)$

Mass of the wet sample: $E_{moist} = (m_{moist} - m_0)$

WC: Water content of the fresh sample (naturally moist) in [%FS]

m_0: Mass cylinder + wet filter paper

m_e: Mass cylinder + weighed-in sample

m_{moist}: Mass cylinder + wet sample

6 Literature

Laboratory method of the Münster Advanced Technical College, Laboratory for waste economy, Housing development water resources policy and environmental chemistry, 1993

Determination of organic contaminants

1 Polychlorinated dibenzodioxin and polychlorinated dibenzofurane(AbfKlärV - Sewage Sludge Decree - of April 15, 1992)

1.1 Preliminary remark

The following determination procedure is to be used for the PCDD and PCDF compounds selected for the determination stipulated for precautionary reasons.

It represents an investigation concept and is arranged in such a way that it integrates the necessary and possible elements of an analytical method; when it is followed and applied in laboratories experienced in trace analysis and when the measures for quality assurance and control for the realization of the AbfKlärV are regularly carried out, sufficiently dependable results are obtained.

Short description: The dried and ground sample is treated with ^{13}C-tagged PCDD and PCDF standards and extracted with toluene. The standards added and the PCDD/PCDF compounds possibly contained in the sample are freed from the interfering attendant material to a great extent, undone through capillary gas chromatography and subsequently determined with a mass spectrometer according to the MID (Multiple Ion Detection) technique, in the process of which the quantification step takes place after the isotope dilution method.

1.2 Sample preparation

The individual steps of the multi-stage sample preparation can be completely different at the qualified and experienced investigation departments. This is permissible, because the comparability, with the quality assurance and control accompanying the investigation, of the results obtained at the various investigation departments is ensured. There is an example for a procedure (1) set down in the following that is proven and used in many investigation laboratories (Official note: **Variations that make do without the dangerous working material benzene are to be given preference in the procedure described here, in so far as the attendant material interfering with the PCDD/PCDF analysis is sufficiently separated out and the comparability of the results is ensured.)**:

50 g (in individual cases more) of the dried and ground sample are treated with the following ^{13}C-tagged PCDD and PCDF: 5 ng each of 2,3,7,8-TetraCDD, 2,3,7,8,-TetraCDF, 1,2,3,7,8-PentaCDD, 1,2,3,7,8-PentaCDF, 1,2,3,6,7,8-HexaCDD and 1,2,3,6,7,8-HexaCDF, as well as 10 ng each of 1,2,3,4,6,7,8-HeptaCDD, 1,2,3,4,6,7,8-HeptaCDF, OctaCDD and OctaCDF.

The sample is subsequently extracted in a Soxhlet apparatus for 20 h with toluene. The toluene extract is concentrated to approx. 25 ml. In some cases, in which the extract can only be concentrated to around 40 ml, benzene is used to fill up to 200 ml. The values given in the following in parentheses refer to the samples that are absorbed in 200 ml benzene. 50 g (or 75 g as the case may be) of aluminum oxide are filled into a chromatography column (60 x 4 cm) and provided with a layer of 50 g of sodium sulfate.

The extract is applied to the column and eluted with 300 ml (or 400 ml) of benzene and 300 ml (or 500 ml) of n-hexane/dichloromethane (98:2).

The eluates are thrown out. Following this, the PCDD/PCDF fraction is eluted with 300 ml n-hexane/ dichloromethane (1.1). After a solution agent change in n-hexane, the samples are chromatographed on a "mixed" column of silica gel (2 g), silica gel/NaOH (5 g), silica gel (2 g), silica gel/H_2SO_4 (10 g), silica gel (2 g) and silica gel/$AgNO_3$ (5 g). Elution is done with 300 ml n-hexane. The eluate is concentrated to approx. 5 ml and subsequently chromatographed on a column (30 x 2.5) filled with BioBeads S-X3, with cyclohexane/ethyl acetate (1:1) as the elution agent. The fraction from 100-160 ml contains the PCDD/PCDF. It is concentrated to a few millimeters, transferred to a 3 ml sample glass, the solvent is blown off in the nitrogen stream and the "residual" is absorbed with approx. 50 µl of toluene. After the wall of the sample glass is carefully rinsed with the solvent, 5 ng of $^{13}C_6$-1,2,3,4-TetraCDD are added and the volume of the sample solution is reduced to app. 20µl.

1.3 Materials

All of the devices coming into contact with the sample and it solutions/extracts have to be free of PCDD and PCDF within the scope of the verification limit of the procedure. All chemicals have to have a degree of purity that the mass-spectroscopic determination of PCDD and PCDF allows within the scope of the verification limit of the procedure. This is to be checked and guaranteed by regular blind-value examinations.

1. Usual laboratory devices
2. Gas chromatograph for capillary chromatography
3. Mass spectrometer with evaluation unit
4. Gas chromatographic separation columns
   - polar column, e.g. SP 2331 or SP 2330, 60 m
   - non-polar column, e.g. DB-5, 25 m
5. Separation columns/packing materials for multi-stage column chromatography
6. Calibration substances

For the quantification to be carried out according to the isotope dilution method, a solution of ^{13}C-tagged PCDD and PCDF standards is used that contains one PCDD or PCDF isomer each per homologous group.

1.4 Carrying out the testing

The identification and quantification of the 17 PCDD/PCDF compounds to be used for the TCDD toxic equivalent calculation takes place with capillary gas chromatography and mass spectrometric detection. The VDI Guideline 3499 (2) is to be applied during the execution of this step.

1.5 Calculation and evaluation of the results

The results are formed as the arithmetic mean value from two separate determinations (extractions). In the process, the mass concentrations of the 17 PCDD/PCDF compounds to be used for the TCDD toxic equivalent calculation are individually stated in ng/kg dry mass, rounded off to 1 ng/kg. The respective mass concentrations are multiplied with the following factors and the products added for the calculation of the sum of the 2,3,7,8-TCDD toxic equivalents (TE).

Toxic equivalents according to the BImSchG Decree (I-TE)

2,3,7,8-TCDD	= 1	2,3,7,8-TCDF	= 0.1
1,2,3,7,8-PeCDD	= 0.5	1,2,3,7,8-PeCDF	= 0.05
		2,3,4,7,8-PeCDF	= 0.5
1,2,3,6,7,8-HxCDD	= 0.1	1,2,3,6,7,8-HxCDF	= 0.1
1,2,3,4,7,8-HxCDD	= 0.1	1,2,3,4,7,8-HxCDF	= 0.1
1,2,3,,7,8,9-HxCDD	= 0.1	1,2,3,7,8,9-HxCDF	= 0.1
		2,3,4,6,7,8-HxCDF	= 0.1
1,2,3,4,6,7,8-HpCDD	= 0.01	1,2,3,4,6,7,8-HpCDF	= 0.01
		1,2,3,4,7,8,9-HpCDF	= 0.01
OCDD	= 0.001	OCDF	= 0.001

The so-called international toxic equivalents (I-TE values) are generally used for the calculation of the "toxic equivalents". The BGA values are likewise calculated and stated for a general comparability:

Toxic equivalents according to the BGA

2,3,7,8-TCDD	= 1	2,3,7,8-TCDF	= 0.1
1,2,3,7,8-PeCDD	= 0.1	1,2,3,7,8-PeCDF	= 0.1
		2,3,4,7,8-PeCDF	= 0.1
1,2,3,6,7,8-HxCDD	= 0.1	1,2,3,6,7,8-HxCDF	= 0.1
1,2,3,4,7,8-HxCDD	= 0.1	1,2,3,4,7,8-HxCDF	= 0.1
1,2,3,7,8,9-HxCDD	= 0.1	1,2,3,7,8,9-HxCDF	= 0.1
		2,3,4,6,7,8-HxCDF	= 0.1
1,2,3,4,6,7,8-HpCDD	= 0.01	1,2,3,4,6,7,8-HpCDF	= 0.01
		1,2,3,4,7,8,9-HpCDF	= 0.01
Sum TCDD	= 0.01	Sum TCDF	= 0.01
Sum PeCDD	= 0.01	Sum PeCDF	= 0.01
Sum HxCDD	= 0.01	Sum HxCDF	= 0.01
Sum HpCDD	= 0.001	Sum HpCDF	= 0.001
OCDD	= 0.001	OCDF	= 0.001

1.6 Remarks

Quality assurance and quality control

- The magnitude and reproducibility of the recovery rate (RR) of the ^{13}C-tagged PCDD and PCDF standards for the selected separation steps are to be checked regularly; for OCDD/OCDF, the RR has to be > 40%, for all other compounds at > 70%.
- The efficiency of the measurement system (GC/MS) is to be checked and calibrated by regular measurements (e.g. maintaining inspection cards).

1.7 Literature

(1) Hagenmaier, H Investigations of selected soils and plants for dioxin and furane. Research Report UBA, No. 107010100, Tübingen, 1988

(2) VDI (Publ) VDI 3499, Sheet 1, Measurement of PCDD and PCDF in purified and raw gas from furnaces with the dilution method. Determination in the filter dust, boiler ash and in slag. Draft March, 1990

(3) Anonymous Sewage Sludge Decree (AbfKlärV), Federal Legislation Gazette I, P. 912, April 15, 1992

2 Polycyclical aromatic hydrocarbons PAH

2.1 Preliminary remark

The procedure described here is suitable for the determination of the 6 PAH (fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene) in accordance with the drinking water decree in biowaste composts, as well as the starting material in mass concentrations > 10 ng/g DS (verification limit).

The expected range of the individual substances is 50 - 5000 ng/g DS.

2.2 Sample preparation

The sample material is extracted in the ultrasound bath with an ethyl acetate/cyclohexane mix. The extract is pre-clarified by solid phase extraction on silica gel and still-existing interfering attendant material is separated using gel chromatography on a Bio-Beads S-X3 phase.

The determination of the PAH takes place with the help of high-performance fluid chromatography with an UV and fluorescence detector.

2.3 Materials and reagents

Devices:

- Ultrasound device
- Centrifuge
- Solid phase extraction unit
- Rotary evaporator
- Gel chromatography column
- High-performance fluid chromatograph with gradient elution, as well as UV and fluorescence detectors
- Separating column, suitable for the determination of PAH (RP C-18 phase).

Reagents:

- Ethyl acetate for analysis
- Cyclohexane for residual analysis
- Acetonitrile gradient grade
- Water ultra pure
- Silica gel one-time separating columns (3 ml)
- BioBeads S-X3
- PAH standard solutions

2.4 Carrying out the testing

1 g of sample material is extracted 3 times with 10 ml ethyl acetate-cyclohexane 1:1 (v/v) each time for 15 min. in the ultrasound bath and centrifuged for 10 min. with a rotary speed of 4000/min.

The combined extraction solutions are concentrated and pre-clarified through a mini-silica gel column. The subsequent gel chromatographic isolation takes place on a Bio-Beads S-X3 column (250 mm length, 10 mm diameter) with a mixture of ethyl acetate/cyclohexane 1:1.

The eluate of the solid phase extraction, concentrated to approx. 1 ml, is given to the chromatography column and eluted with a flow rate of 2 ml/min with a slight nitrogen overpressure. The singling from 20 ml contains the strongly colored impurities, while the PAH are to be found in the main fraction between 20 - 45 ml.

The main fraction is concentrated to approx. 1 ml, treated with 2 ml methanol and 0.5 ml acetonitrile, and concentrated to 0.5 ml. This solution is diluted to 1 ml with acetonitrile and a determination can be made with the help of the HPLC.

If the mostly yellow-colored solution still contains undissolved components, they should be separated with a spray filter.

HPLC determination:

Mini-bore separating column: Nucleosil 5 C18-PAH (250/1/4"/2)
Injection volume: 10 µl
Elution: acetonitrile/water mixture
A = acetonitrile/water (50/50), B = acetonitrile
0 - 7 min. 88% A, 12% B, flow 0.2 ml/min., isocratic
7 - 8 min. 65% A, 35% B, flow 0.3 ml/min., linear gradient
8 - 25 min. 0% A, 100% B, flow 0.3 ml/min., linear gradient
25 - 59 min. 0% A, 100% B, flow 0.3 ml/min., isocratic
59 - 60 min. 88% A, 12% B, flow 0.2 ml/min., linear gradient
60 - 80 min. 88% A, 12% B, flow 0.2 ml/min., isocratic
Detection: UV (254 nm), fluorescence (Ex:260 nm, Em: 410 nm)

2.5 Evaluation

The calibration with an external standard takes place with a 6-component standard solution.

Component	Retention time [min.]	Recovery [%]
Fluoranthene	25.30	93
Benzo(b)fluoranthene	32.00	96
Benzo(k)fluoranthene	34.00	95
Benzo(a)pyrene	35.10	76
Benzo(ghi)perylene	39.50	94
Indeno(1,2,3-cd)pyrene	41.70	96

3 Polychlorinated biphenyls (PCB) and organochlorine pesticides

3.1 Preliminary remark

The method serves to determine 6 selected polychlorinated biphenyls (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153 and PCB-180 according to Ballshmiter) and the selected pesticides HCB, alpha, beta, gamma HCH, heptachlor, heptachlor epoxy resin, aldrin, dieldrin, endrin and DDT/DDD/DDE and isomers.

The sample purification using solid-phase extraction, as well as the gas chromatographic determination take place following the methods DIN 51527, Section 1 and DIN 38407, Section 2.

3.2 Sample preparation

The sample material is extracted in the Soxhlet with hexane and subsequently purified using solid-phase extraction on the column combination benzene sulfonic acid/silica gel. The separation of the individual substance groups takes place through a step-wise elution with hexane and toluene/hexane mixtures of various compositions.

3.3 Materials and reagents

Devices:

- Soxhlet apparatus
- Rotary evaporator
- Solid phase extraction unit

Reagents

- n-hexane for residual analysis
- Benzene sulfonic acid one-time separating column
- Silica gel one-time separating column
- Toluene for analysis
- PCB standard
- Pesticide standard

3.4 Carrying out the testing

10 g of compost sample are extracted with 200 ml hexane for 8 h in the Soxhlet. Following this, rinse the apparatus 3 times with 10 ml hexane each time and combine with the extract. The sample, concentrated almost up to dryness, is absorbed with 0.5 ml n-hexane and deposited on the frit of a dry benzene sulfonic acid separating column, that is placed on a 3 ml silica gel separating column using an adapter. The sample is brought to the packing of the upper column by the application of a slight underpressure and eluted twice with 1 ml n-hexane each time to the lower column. Following this, remove the benzene sulfonic acid column and transfer the sample into a receiver by eluting the silica gel column three times with 0.5 ml hexane.

This eluate (1st fraction) contains the PCB, as well as several organochlorine pesticides.

Further organochlorine pesticides can be isolated in a second fraction by a step-wise elution of the silica gel column with hexane/toluene mixtures.

3 ml m-hexane/toluene (95:5)
6 ml m-hexane/toluene (65:35)

One obtains a third fraction by eluting the separated benzene sulfonic acid separating column with 3 ml n-hexane/toluene (95:5).

The three fractions contain the following pesticides and PCB:

	Fraction			Recovery
	1	2	3	[%]
PCB 028	X	-	-	97
PCB 052	X	-	-	93
PCB 101	X	-	-	77
PCB 153	X	-	-	71
PCB 138	X	-	-	74
PCB 180	X	-	-	79
α-HCH	-	X	-	90
Hexachlorobenzene	X	-	-	59
β-HCH	-	-	X	87
Lindane	-	X	-	96
Heptachlor	X	-	-	94
Aldrin	X	-	-	95
Heptachlor epoxy resin	-	X	X	108
o,p'-DDE	X	-	-	113
p,p'-DDE	X	-	-	109
Dieldrin	-	-	X	105
o,p'-DDD	-	X	-	102
Endrin	-	-	-	0
p,p'-DDD	-	X	-	112
o,p'-DDT	X	-	-	109
p,p'-DDE	X	X	-	110

Endrin cannot be verified with this method.

The calibration of the method takes place with an external standard.

The calibration of the chromatographic determination with an internal standard takes place with PCB 209.

Determination methods:

The determination methods mentioned are to be understood as examples; in individual cases, the methods are to be adapted to the equipment in the laboratory.

GC/ECD method for PCB

Sample feed:	splitless
Injector temperature:	280°C
Detector temperature:	300°C
Separating column:	SE-54 (L = 50 m / ID = 0.32 mm / df = 0.35 µm)
Carrier gas:	Nitrogen
Temperature schedule:	1 min. at 80°C
	25°C/min to 180°C
	10°C/min to 210°C
	5°C/min to 290°C
	10 min. at 290°C

GC/ECD method for pesticides and PCB

Sample feed:	splitless
Injector temperature:	280°C
Detector temperature:	325°C
Separating column:	CP-SIL (L = 50 m / ID = 0.25 mm / df = 0.25 µm)
Carrier gas:	Nitrogen
Temperature schedule:	1 min. at 45°C
	25°C/min to 195°C
	10°C/min to 205°C
	1°C/min to 230°C
	15°C/min to 305°C
	12 min. at 305°C

3.5 Literature

DIN 51 527, Section 1, Determination of polychlorinated biphenyls (PCB). Beuth Verlag, Berlin (1987)

DIN 38 407, Section 2 (draft), German uniform proc. for water, waste water and slurry investigation; Jointly ascertainable material groups (Group F); Gas chromatographic determination of halogen-organic compounds not easily volatilized (F2). Beuth Verlag, Berlin (1991).

4 Phenoxyalkane carboxylic acid herbicide 2,4-D and 2,4,5-T

4.1 Preliminary remark

The procedure described here is suitable for the determination of the herbicide 2,4-dichlorphenoxy ethanoic acid (2,4-D) and 2,4,5-trichlorphenoxy ethanoic acid (2,4,5-T) in biological waste composts, as well as in the starting materials in mass concentrations > 5 ng/g DS.

The expected range of the individual substances is 10 - 100 ng/g DS. Reference substances for the gas chromatographic determination are the methyl esters of the acids.

The enrichment in an RP-C18 phase, as well as obtaining the derivatives takes place following the draft of the method DIN 38407, Section 14 of 1990 on water, waste water and slurry investigations.

4.2 Sample preparation

The extraction of 10 g of sample material takes place with a watery methanol solution (2% H_2O) in the ultrasound bath. Following this, the contaminants are enriched in an inversion phase (octadecyl) of a watery agent at pH 2 and eluted with methanol. After the esterification with methanol and conc. sulfuric acid, the methyl ester derivatives are extracted with n-hexane and, if necessary, repurified through silica gel.

4.3 Materials and reagents

Devices:

- Various glass devices
- Ultrasound bath
- Filtration unit
- Solid phase extraction unit
- Rotary evaporator

Reagents:

- Methanol for analysis
- HCl solution (pH 2)
- Toluene for analysis
- Octadecyl one-time separating column
- Hexane for residual analysis
- Sulfuric acid conc.
- Sodium sulfate
- Sodium hydrogen carbonate
- Silica gel one-time separating column (3 ml)
- Standard solutions of the chlorphenoxy ethanoic acids and their methyl esters

4.4 Carrying out the testing

10 g of sample material is extracted 3 times each with 30 ml watery methanol solution (2% H_2O) in the ultrasound bath for 10 min. and subsequently filtered. For the complete isolation of the phenoxyalkane carboxylic acid in octadecyl phases, the extract is concentrated almost to dryness and the residual solution is diluted with diluted HCl (pH 2) to approx. 100 ml and sucked through the conditioned octadecyl column. Rewash the column with 10 ml of water and suck dry for approx. 5 min. After this, wash 2 times with 1 ml of hexane and lastly suck up completely. Elute the phenoxyalkane carboxylic acids subsequently twice with 1 ml of methanol each time.

For the esterification of the carboxylic acids, dilute the eluate to 4.5 ml with methanol and add approx. 0.5 ml conc. sulfuric acid drop by drop. Allow the solution to react in a closed flask with frequent twirling around for 10 min. Following this, add 50 ml of Na_2SO_4 solution (5%) and extract the methyl esters with n-hexane. Wash the organic phase with 50 ml $NaHCO_3$ solution (4%), dry through a little Na_2SO_4, and concentrate to a defined volume.

If a repurification is necessary, one brings the sample to a 3 ml silica gel column (conditioned with hexane) and elutes with toluene-hexane mixture 70:30. Concentrate the eluate almost to dryness, blow dry with nitrogen and absorb the residual into 1 ml of hexane.

The calibration of the gas chromatographic determination method with an external standard takes place with methyl ester reference solutions. The calibration of the overall procedure with an external standard takes place with the free acids.

GC/ECD determination method

Sample feed:	splitless
Injector temperature:	300°C
Detector temperature:	300°C
Separating column:	CP-SIL 8 CB (L = 50 m / ID = 0.25 mm / df = 0.25 µm)
Carrier gas:	Nitrogen
Temperature schedule:	Starting temperature 130°C
	1st rate 1°C/min to 185°C
	2nd rate 10°C/min to 300°C

4.5 Remarks

Column conditioning:

Give a column filling, one after the other, of hexane, methanol, as well as water acidified to pH 2, to a 3 ml octadecyl column (500 mg) and suck through under vacuum, avoid dry running in the process.

4.5 Literature

DIN 38 407, Section 2 (draft), German uniform proc. for water, waste water and slurry investigation; Jointly ascertainable material groups (Group F); Determination of phenoxyalkane carboxylic acid using, and mass spectrometric detection according to, solid-fluid extraction and obtaining derivatives (F14). Beuth Verlag, Berlin (1991).

Determination of the total carbon content

Depending on the type of task, the course of analysis leads, starting with the determination of the inorganic TIC (total inorganic carbon), through the determination of the total carbon content TC (total carbon) to the calculation of the organically-bound carbon TOC (total organic carbon).

The following determinations can be cited:

- COULOMETRIC DETERMINATION
- DETERMINATION USING ELEMENTARY ANALYSIS

1 Coulometric determination

1.1 Preliminary remark

The determination method permits the analysis of more than 50 mg of sample material (50 - 1000 mg weigh-in).

1.2 Sample preparation

Drying the unscreened fresh sample (original sample) at 105°C.
Grinding of at least 30 g of dry substance with a suitable grinder to < 250 µm.

1.3 Materials

- Precision analytical scales
- Vitreous fused silica combustion boat for the weigh-in of the sample
- Combustion furnace or coulomat
  Combustion device with integrated post-combustion
  Carbon dioxide analyzer
- Combustion temperature in the vitreous fused silica tube: 950°C

1.4 Carrying out the testing

The sample is burned at approx. 950°C in the tube furnace in the oxygen stream, the gas mixture that arises is dried and the CO_2 is coulometrically titrated after quantitative absorption in the alkaline barium perchlorate solution.

The weigh-in is approx. 50 mg.

1.5 Calculation and evaluation of the results

The amount of CO_2 formed is determined through the pH value change. This measurement supplies the total carbon content TC.

Description: Total carbon content TC in [%DS]

1.6 Remarks

Approx. 3-5 g of dried sample are treated with a strong acid (approx. 10 ml HCl_{conc}) in a closed reaction vessel for the determination of the inorganic carbon content (TIC).
The carbon dioxide stripped from the carbonates in this way is fed to the analyzer

and quantitatively absorbed in the barium perchlorate solution and coulometrically titrated.

The content of TC and TIC determined in this way serve in the calculation of the TOC:

$$TOC = TC - TIC$$

2 Determination using elementary analysis

2.1 Preliminary remark

The determination of the C_{tot} content using elementary analysis is a workable alternative for the simplification and streamlining of the analyses of a sample to be carried out (also see analysis of the N_{tot} content). On top of this is also the significant health aspect and the low use of chemicals that represent contamination of the environment.

2.2 Sample preparation

Drying the unscreened fresh sample at 105°C.
Grinding of at least 30 g of dry substance with a suitable grinder to < 250 µm.

2.3 Materials

Elementary analyzer
Carrier gas: Helium
Gas chromatograph with a thermal conductivity detector (TCD)

2.4 Carrying out the testing

10 - 80 mg of the sample, dried and ground fine, are oxidized at approx. 1000°C in an oxygen pulse while hermetically sealed. The gas is separated with gas chromatography and measured with a TCD.

2.5 Calculation and evaluation of the results

The determination supplies the TC content.
Description: Total carbon content TC in [%DS]

2.6 Literature

Various methods for the determination of organic, inorganic and total carbon content (TOC, TIC, TC) in selected solid waste templates; Kraschon G., C.U. Schmidt, A. M. Bahadir; Garbage and Waste 3/93

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Results of a parallel interlaboratory test 1993

1 Introduction

In the spring of 1993 the **Bundesgütegemeinschaft Kompost e.V.** (FCQAO) assigned the waste management faculty of the University of Essen the task of organising and executing a parallel interlaboratory test to review the quality of work of the laboratories approved for compost analysis.

One of the chief functions of the Federal Compost Quality Assurance Organisation is, as the name implies, the quality assurance of composts. Assessment and control of the compost quality is carried out at regular intervals for those compost producers who have joined up to form a quality assurance organisation and who are subject to a common quality system. The investigations necessary within the framework of external monitoring are conducted by independent laboratories. If the specified quality criteria are met, the **Bundesgütegemeinschaft Kompost e.V**. awards a "RAL compost quality sign". Fundamental for the functioning of such an external monitoring and quality assurance system is, besides the selection of suitable test parameters, standardized and reproducible test procedures. In addition, a uniformly high level of quality of work of the executing laboratories must be assured. Only then are the test results from different laboratories comparable, i.e. the composts originating from different producers can be subjected to comparative assessment. Standardized execution of the required analysis and hence reproducibility of the results was hitherto lacking. To be able to satisfactorily fulfill the quality assurance mandate it was consequently necessary to define standardized analytical procedures and to check the quality of work of the laboratories in a parallel interlaboratory test using these binding procedures.

2 Objectives of the parallel interlaboratory test

Based on the task of assuring the quality of composts already described and the problems mentioned, the following concrete objectives were to be achieved with the execution of the parallel interlaboratory test:

- Preparation of a binding set of procedures ("methods book") for the analysis of all parameters relevant to external monitoring.
- Reviewing and assessing the quality of work of the participating laboratories, recommendation of particularly suitable laboratories and exclusion of unsuitable laboratories with a view to assuring competent external monitoring of the quality of composts.
- Evaluation of the defined test procedures with respect to workability, determination of critical methods and stating causes of difficulties which might arise in the execution phase.
- Determination of statistical quantities for the variance bands of the individual methods when uniform and homogenous sample material is analysed by different laboratories.
- The pilot character of the parallel interlaboratory test as previously no such extensive analysis had been carried out for all specified parameters. The results serve as a basis for the execution of further parallel interlaboratory tests which are necessary within the framework of quality assurance.

3 Planning and preparation

To be able to achieve the targets set, it was necessary to distibute a large quantity of a "real compost sample" to the participating laboratories. In contrast to water analysis where the production of synthetic samples is in no way problematic, in the case of "real samples" the "true values" of the individual test parameters in the test material are unknown. Therefore, according to DIN 38 402 (Part 41), only the respective non-outlier total mean values can serve as "conventionally correct values".

Determination of the "conventionally correct values" by reference laboratories with an ensuing comparison with the results of all other participating laboratories was not possible as to date there are no recognized reference laboratories.

The laboratories were directed to test 4 increments each in a series of repeat analyses to enable a differentiation between the individual components which were contributory factors to the total variation of the results. In particular, the **sampling error** (proportion of the total variation on account of different contents in the different samples) was to be distinguishable from the **laboratory error** (proportion of the total variation on account of systematic laboratory effects).

The analyses were to be carried out using the procedures set out in the "methods book" compiled by the **Bundesgütegemeinschaft Kompost e.V**. A copy of the "methods book" specially modified to the requirements of the parallel interlaboratory test was sent to all participating laboratories in advance. The respective sample preparation was specified for all parameters to be analysed. Figure 1 shows the sample preparation procedure. 20 litres of of fresh compost per increment proved sufficient to be able to carry out all analyses with the required number of repetitions.

A finely sieved fresh compost was selected as suitable sample material. For the assessment of the quality of analysis of the biological parameters, especially the self-heating test for determination of the rotting degree, it was necessary to use an "active" and not yet fully rotted test substrate. By using fine-grained material (< 10 mm) a very good homogenization of the population was attained; further, the sample quantities to be dispatched were kept low and the laboratories were spared the task of the time-consuming sieving to < 10 mm. Four samples (increments from the homogenized population) were randomly dispatched to the 100 registered laboratories. To this end, the laboratories were allocated consecutive numbers (L001 - L100) and randomly assigned 4 numbers from consecutive sample numbers (P001 - P400) with the aid of a randomization device. Laboratory L001 received, for example, the samples P021, P104, P223 and P241. The labour-intensive randomized distribution of the increments to the participating laboratories was necessary to rule out systematic sampling effects and to create the pre-conditions for a subsequent variance-analytical evaluation of the data.

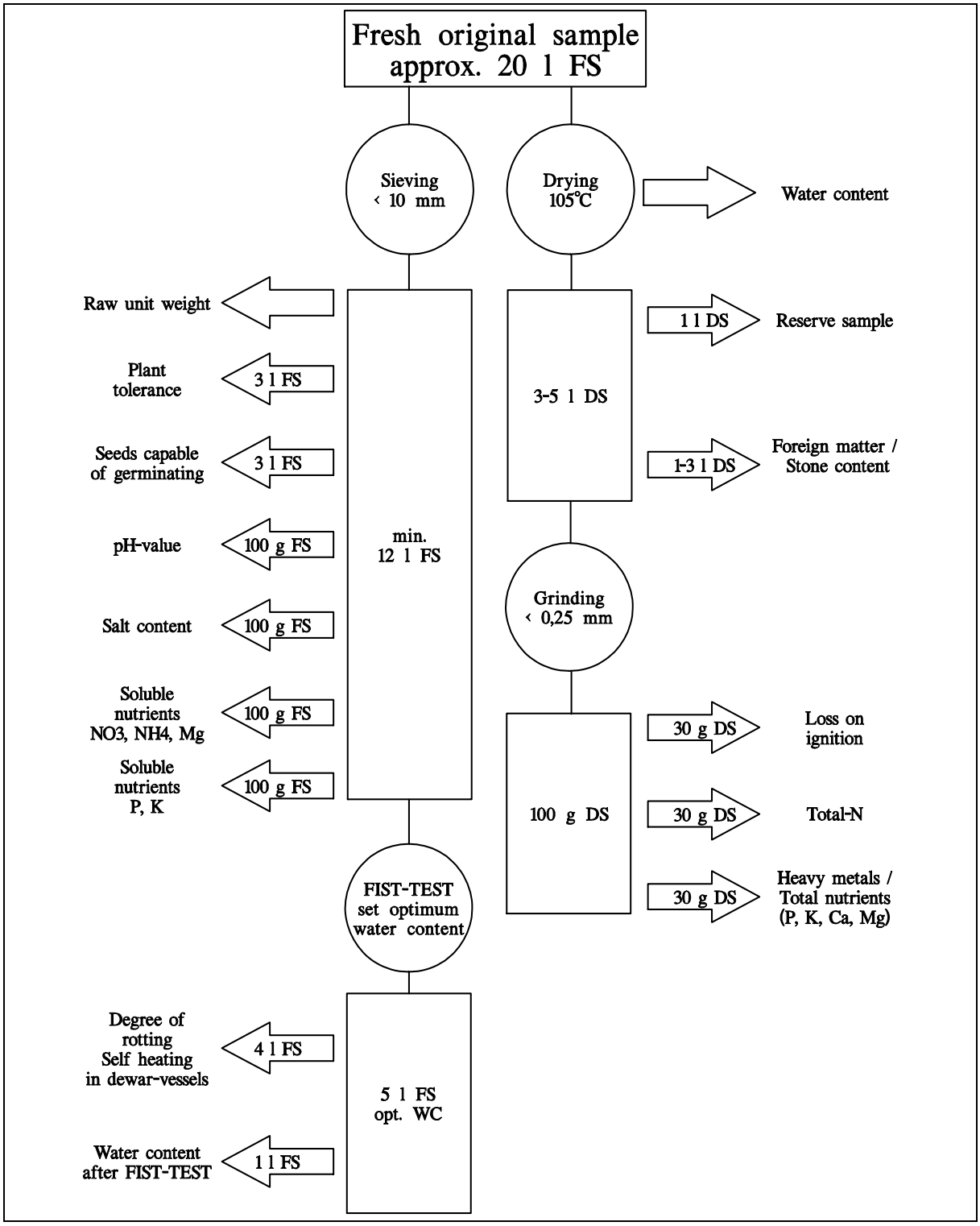

Figure 1: Sample preparation procedure diagram

4 Sampling procedure

In order to satisfy the requirements stated under point 3, a finely sieved (< 10 mm) fresh compost from biowaste and green waste after 6 weeks intensive rotting was selected as test substrate. The suitability of the material was tested in advance in preliminary tests at the University of Essen.

The first step to homogenize the sample was carried out in situ at the producers by taking as homogenous a batch as possible from the rotting process followed by sieving of the material to < 10 mm. In a second step, the entire sieved batch (approx. 10 m^3) was mixed a number of times with a wheel loader.

Sampling and sample dispatch was effected by taking 400 increments of 20 l from the 10 m^3 population. The increments were packed in polyethylene bags and provided with the numbers P001 - P400. Each laboratory received 4 increments in line with the previously prepared allocation plan. Dispatch was by courier who guaranteed delivery within 24 hours. Delivery of the samples went very smoothly; only in 6 cases was the delivery delayed by a day and only 3 laboratories received samples with damaged packaging.

5 Evaluation

The laboratories had a total of 6 weeks to conduct the tests and to give notification of the results. Standardized forms were used on which all results from the repeat analyses and the mean values of the individual samples (increments) were to be documented.

5.1 Statistical quantities

The essential descriptive statistical quantities are listed below along with the abbreviations used:

MW_{Lab}: Laboratory mean over all 4 increments

$Stdabw_{Lab}$: Laboratory standard deviation

$Varkoef_{Lab}$: Laboratory variation coefficient

MW_{ges} (Ø): Total mean or mean of the laboratory means

Stdabw(MW_{Lab}):(σ) Standard deviation of the laboratory means

Varkoef (MW_{Lab}): Variation coefficient of the laboratory means

25% percentile[1)]: 25% percentile of the laboratory means

Median[1)]: Median of the laboratory means

75% percentile[1)]: 75% percentile of the laboratory means

MIN(MW_{Lab}): Minimum of laboratory means

MAX(MW_{Lab}): Maximum of laboratory means

$Anzahl_{Lab}$: Number of labs who carried out the analysis

MW($Stdabw_{Lab}$)[2)]: Mean of the laboratory standard deviations

MW($Varkoef_{Lab}$)[2)]: Mean of the laboratory variation coefficients

[1)] only calculated for the data sets subjected to outlier correction

[2)] only calculated for the complete data sets

Median and percentiles were only calculated for the outlier-corrected data sets. These quantities are insensitive to extreme deviations (outliers) so that an additional calculation for the complete data sets was dispensed with.

The means of the laboratory standard deviations and the laboratory variation coefficients were calculated for the complete data sets in order to be able to demonstrate that, even if the outliers are taken into account, the variations between the sample repetitions in the laboratory are appreciably lower than the variations between the outlier-corrected laboratory means. This makes possible a first simple assessment of the significance of **sampling effect** and **laboratory effect** and it becomes apparent that the variations in the results are not attributable to non-homogenous increments but rather arise as a result of varying levels of working quality of the laboratories.

5.2 Determination of outliers and error analysis

Determination of outliers in the individual analyses was carried out according to DIN 38 402 (Part 42) using the Grubbs test with the difference that only type 2 outliers were eliminated. Type 2 outliers are minimum or maximum laboratory means $\mathbf{MW}_{Lab}$ which significantly deviate from the total mean $\mathbf{MW}_{ges}$ under consideration of the standard deviation of the laboratory means **Stdabw($\mathbf{MW}_{Lab}$)** (α = 10%, bilateral). The associated test quantity $\mathbf{PG}_{(n)}$ is

$$PG_{(n)} = \frac{|MW_{Lab}^{*} - MW_{ges}|}{Stdabw(MW_{Lab})}$$

given by the following equation:

The calculated test quantity is compared with the corresponding Grubbs tabular value. The tabular values are dependent on the number **n** of the laboratory means entered in the calculation. If the tabular value is exceeded, the corresponding laboratory mean $\mathbf{MW}_{Lab}$ is eliminated as an outlier and the calculation repeated with **n-1** values. This procedure is repeated until no more outliers are established. For all determined outliers of the laboratory means it was additionally tested whether the deviation had occurred solely on account of an extreme increment value. Laboratory means which were identified merely due to such extreme deviations of an individual sample (increment) were indeed eliminated for the ensuing statistical calculations but the result was not judged to be an error analysis in the subsequent laboratory assessment. This instance only occurred in the determination of the heavy metal contents of lead (1x), copper (6x) and zinc (1x), in other words, it was an extremely rare occurrence.

The total mean $\mathbf{MW}_{ges}$ and the standard deviation of the laboratory means were calculated again from the outlier-corrected data sets and additionally all results which deviated from the mean by more than the double standard deviation were classed as error analyses.

In this case too results from laboratories where the deviation arose solely due to a single sample outlier were not classed as error analyses. This instance was observed only twice, namely in the determination of the contents of lead (1x) and mercury (1x).

6 Criteria for laboratory assessment

The total number of determined error analyses, i.e. outlier analyses and unpermissible deviations from the total mean after outlier correction formed the basis for laboratory assessment which was carried out by the quality assurance committee of the Federal Compost Quality Assurance Organisation. Depending on the number of error analyses, the laboratories were classified into 4 different categories (I-IV). Table 1 gives an overview of the classification criteria.

The assessment of the laboratories was based on three independent criteria. The first criterion was the total number of error analyses across the whole parameter spectrum (without NO_3-N and plant tolerance EEO_{abs}, $25\%_{abs}$, $50\%_{abs}$, $50\%_{rel}$ (EE0= standard soil). Laboratories with a total of more than 5 error analyses are in future excluded from external monitoring duties.

Table 1: Criteria for laboratory classification into different categories

Laboratory assessment citeria		
Category	**Assessment**	**Criteria**
I	Recommended	No error analyses
II	Approved	Error analysis total max. 5 Error analysis per group max. 3 Error analysis heavy metals max. 1
II	Approved subject to restrictions	Exceeding max permissible number only due to error analysis on Cr/Ni Error analysis heavy metals (>1) max.2
IV	Excluded	Exceeding the max. permissible number of error analyses

As a second criterion the individual parameters were divided into two groups (A and B) according to their importance and differently weighted. Table 2 shows the the classification of the parameters in groups A and B. The weighting is determined by the different number of parameters in the groups and the specification that (for both groups) more than 3 error analyses leads to exclusion of the laboratory concerned. The parameter nitrate content was not utilized for the laboratory assessment as this analysis is associated with considerable methodological difficulties, especially in the case of low NO_3 contents. Moreover the results sent in had not been precisely determined in many instances but rather indicated as "<" values or as "not detectable" which made the statistical evaluation more difficult. In the case of the parameter plant tolerance only the results of the relative yields of the 25% compost mixture were used for laboratory assessment.

The results of the pH determination were only evaluated with limitations since the simple calculation of the statistical quantities mean and standard deviation is not correct. For determining the outlier laboratories the pH values were converted into the concentrations of the H^+ ions; further assessment was dispensed with.

The third criterion was the maximum possible number of error analyses in the determination of the heavy metal contents. A maximum of one error analysis was allowed for the unrestricted approval (category II), more than two error analyses resulted in exclusion. Closer investigation of the error analyses with the heavy metals revealed a frequent joint exceeding of the values for chromium and nickel. This joint exceeding was recorded in a total of 8 laboratories. Proceeding from the assumption that these high values were attributable to the use of an unsuitable mill, these laboratories were granted a quasi Cr/Ni bonus and the joint upper deviations were only rated singly. Laboratories with a Cr/Ni bonus and laboratories with more than one error analysis with the heavy metals (max. 2) were approved subject to restrictions and classified into category III.

If a laboratory managed to fulfill all three criteria it is approved as an analytical laboratory for future external monitoring (category II).

Laboratories which displayed no error analysis across the complete parameter spectrum are specially recommended by the Federal Compost Quality Assurance Organisation (category I).

Table 2: Classification of the parameters into groups for laboratory assessment

Laboratory assessment parameter grouping			
	Group A	**Group B**	**No Assessment**
1	Foreign matter	Germinable seeds	Plant tolerance in standard soil EE0 $_{abs}$
2	Plant tolerance 25% $_{rel}$	Stone content	Plant toler. 25% $_{abs}$
3	Rotting degree(T_{max})	Water content	Plant toler. 50% $_{abs}$
4	Loss on ignition	Salt content	Plant toler. 50% $_{rel}$
5	Lead	(pH value)	NO_3-N $_{soluble}$
6	Cadmium	Bulk density	
7	Chromium	NH_4-N $_{soluble}$	
8	Copper	Mg $_{soluble}$	
9	Nickel	P_2O_5 $_{soluble}$	
10	Mercury	K_2O $_{soluble}$	
11	Zinc		
12	N $_{total}$		
13	P_2O_5 $_{total}$		
14	K_2O $_{total}$		
15	CaO $_{total}$		
16	MgO $_{total}$		

7 Results

7.1 Statistical evaluation

Tables 3 and 4 show the total number of error analyses, mean and median, range (min.-max.), standard deviation and percentile margin (25% - 75%) for the outlier-corrected data sets.

Table 3:Number of error analyses, positional and dispersion values for group A after outlier correction

Group A						
Parameter	Error analyses	Total mean	Med.	Standard deviation	Range (Min-Max)	Percentiles (25%-75%)
For. mat.[%]	10	0,24	0,22	0,11	0,03 - 0,56	0,18 - 0,28
PT 25%$_{rel}$[%]	8	105,6	100,7	16,57	69,3-155,9	94,7 - 114,9
T_{max} [☜C]	13	50,1	52,5	8,94	23,7 - 67,5	46,2 - 55,9
GV [% DS]	6	44,9	45,4	3,29	35,1 - 52,0	43,1 - 46,8
Heavy metals [mg/kg DS]						
Pb	8 (10)	59,0	58,4	11,94	24,9 - 96,3	53,1 - 63,0
Cd	12	0,56	0,55	0,18	0,02 - 1,06	0,45 - 0,64
Cr	14	26,6	23,6	0,10	11,1 - 57,0	20,3 - 28,1
Cu	8 (14)	65,1	64,0	9,60	42,7 - 94,7	60,0 - 70,1
Ni	13	16,8	16,2	3,41	7,3 - 25,6	14,5 - 19,0
Hg	15 (16)	0,16	0,16	0,06	0,06 - 0,33	0,13 - 0,18
Zn	9 (10)	214	212	27,63	151 - 299	197 - 226
Total nutrients [% DS]						
N	8	1,78	1,76	0,14	1,51 - 2,18	1,69 - 1,84
P_2O_5	13	1,08	1,00	0,17	0,58 - 1,54	0,98 - 1,18
K_2O	15	1,09	1,09	0,12	0,78 - 1,43	1,02 - 1,16
CaO	9	4,38	4,50	0,79	2,09 - 6,61	4,05 - 4,88
MgO	12	0,65	0,65	0,08	0,42 - 0,87	0,60 - 0,69

Table 4:Number of error analyses, positional and dispersion values for the parameters of group B and the non-evaluated parameters after outlier correction

Group B and non-evaluated parameters						
Parameter	Error anal.	Total mean	Median	Standard deviation	Range (Min-Max)	Percentiles (25%-75%)
Germ. seeds [No./l FS]	16	0,09	0	0,15	0,00 - 0,52	0,00 - 0,17
Stone Content [%DS]	5	0,66	0,66	0,25	0,16 - 1,39	0,50 - 0,84
Water content [%FS]	8	27,4	27,5	0,8	24,9 - 29,1	27,1 - 28,0
Salt [g KCl/l FS]	8	7,2	7,2	0,99	4,8 - 10,1	6,7 - 7,9
pH value	2	7,8	7,8	0,19	7,4 - 8,3	7,7 - 7,9
Bulk density [g/l FS]	5	558	559	17,84	514 - 608	546 - 570
Soluble nutrients [mg/l FS]						
NO_3-N	11	10	5,1	10,97	0,1 - 43,5	1,2 - 18,3
NH_4-N	12	164	166	49,95	16 - 272	143 - 192
Mg	15	209	207	32,58	126 - 309	190 - 223
P_2O_5	12	827	807	256,1	67 - 1577	687 - 987
K_2O	12	3537	3493	826,1	951 - 6125	3218 - 3794
Plant tolerance PT (not evaluated) (EE0 = Standard soil)						
PT EE0 $_{abs}$ [g]	4	8,2	7,4	2,9	2,5 - 15,7	6,0 - 10,2
PT 25% $_{abs}$ [g]	7	8,5	7,8	2,62	2,3 - 16,7	6,6 - 9,7
PT 50% $_{abs}$ [g]	6	7,4	7,1	2,53	1,9 - 15,3	5,7 - 8,8
PT 50% $_{rel}$ [%]	6	91,3	88,7	18,63	54,3 - 150,1	80,1 - 99,5

Tables 5 and 6 give a comparison between the the mean values of the laboratory standard deviations **MW(Stdabw$_{Lab}$)** and the laboratory variation coefficients **MW(Varkoef$_{Lab}$)** and the standard deviations **Stdabw(MW$_{Lab}$)** and variation coefficients **Varkoef(MW$_{Lab}$)** of the laboratory mean values.

Table 5: Comparison of the means of the laboratory standard deviations and laboratory variation coefficients (including outlier laboratories) with the standard deviations and variation coefficients of the the laboratory mean values for parameters of group A

Group A				
Parameter	MW ($Stdabw_{Lab}$)	MW ($Varkoef_{Lab}$)	Stdabw (MW_{Lab})	Varkoef (MW_{Lab})
Foreign matter	0,07	0,3	0,11 (0,25)	0,44 (0,91)
PT 25%$_{rel}$	6,91	0,07	16,57 (18,83)	0,16 (0,18)
Rotting degree (T_{max})	2,33	0,05	8,94 (8,94)	0,18 (0,18)
Loss on ignition	1,38	0,03	3,29 (3,53)	0,07 (0,08)
Heavy metals				
Pb	6,96	0,1	11,94 (15,60)	0,20 (0,26)
Cd	0,1	0,1	0,18 (0,88)	0,33 (1,24)
Cr	3,76	0,08	10,10 (39,81)	0,38 (1,10)
Cu	17,82	0,17	9,60 (28,80)	0,15 (0,40)
Ni	2,12	0,07	3,41 (21,99)	0,20 (1,01)
Hg	0,08	0,19	0,06 (0,45)	0,34 (1,73)
Zn	42,15	0,1	27,63 (271,67)	0,13 (1,12)
Total nutrients				
N	0,07	0,04	0,14 (0,29)	0,08 (0,17)
P_2O_5	0,11	0,09	0,17 (1,09)	0,16 (0,94)
K_2O	0,04	0,03	0,12 (0,71)	0,11 (0,58)
CaO	0,2	0,04	0,79 (0,98)	0,18 (0,22)
MgO	0,04	0,04	0,08 (0,66)	0,13 (0,89)

Table 6: Comparison of the means of the laboratory standard deviations and laboratory variation coefficients (including outlier laboratories) with the standard deviations and variation coefficients of the laboratory mean values for parameters of group B and non-evaluated parameters

Group B and non-evaluated parameters				
Parameter	MW ($Stdabw_{Lab}$)	MW ($Varkoef_{Lab}$)	Stdabw (MW_{Lab})	Varkoef (MW_{Lab})
Germ. seeds	0,28	0,49	0,15 (1,27)	1,65 (3,13)
Stone content	0,2	0,33	0,25 (0,28)	0,37 (0,41)
Water content	0,5	0,02	0,80 (1,64)	0,03 (0,06)
Salt content	0,25	0,04	0,99 (1,69)	0,14 (0,24)
pH-value	0,09	0,01	0,19 (0,20)	0,02 (0,03)
Bulk density	7,06	0,01	17,84 (21,26)	0,03 (0,04)
Soluble nutrients				
NO_3-N	2,38	0,2	10,97 (34,42)	1,10 (1,81)
NH_4-N	24,5	0,14	49,95 (174,00)	0,30 (0,92)
Mg	10,5	0,04	32,58 (154,18)	0,16 (0,66)
P_2O_5	42,4	0,05	256,1 (831,6)	0,31 (0,86)
K_2O	138,7	0,05	826,1 (1171,7)	0,23 (0,32)
Plant tolerance PT (not evaluated) (EE0 = Standard soil)				
PT EE0 $_{abs}$	0,49	0,07	2,90 (3,13)	0,35 (0,37)
PT 25% $_{abs}$	0,55	0,07	2,62 (3,14)	0,31 (0,36)
PT 50% $_{abs}$	0,55	0,08	2,53 (2,72)	0,34 (0,36)
PT 50% $_{rel}$	7,1	0,08	18,63 (19,94)	0,20 (0,22)

In the calculation of the means of the laboratory standard deviations and laboratory variation coefficients the complete data sets (including outlier laboratories) were taken into account. The values of the standard deviations and variation coefficients of the laboratory means were calculated for the outlier-adjusted data sets and for the complete data sets (values in brackets). The effect of outlier correction is clearly manifested in the decrease in the values of standard deviation and variation coefficient.

Even after outlier correction the variations of the results between the laboratories are significantly greater than within the laboratory. For the majority of parameters the variations between the laboratories are two to five times higher than the mean variation within the laboratories (ratio of **Varkoef(**$\mathbf{MW_{Lab}}$**)** to **MW(**$\mathbf{Varkoef_{Lab}}$**)**). The only exception is the parameter copper content. Here the mean laboratory variation coefficient of 0.17 is slightly higher than the variation coefficient of the outlier-corrected laboratory means with 0.15. This is to be explained by the fact that, in the case of copper as the only parameter, several laboratories exhibited strong variations between the sample repetitions (a total of 6 laboratory outliers as a result of only one sample outlier). This effect is carried over into the calculation of the mean laboratory variation coefficients whereas it is eliminated in the calculation of the variation coefficients of the outlier-free laboratory mean values (prior to outlier correction **Varkoef(**$\mathbf{MW_{Lab}}$) is appreciably higher with 0.40).

Comparison of the means of the laboratory variation coefficients with the variation coefficients of the laboratory means is more suitable (on account of the standardization) for this simple evaluation than comparison of the standard deviations or variances which would have to be applied in the case of a systematic variance-analytical evaluation. Even this simple evaluation clearly shows that systematic differences between the analytical results of the different laboratories do exist and indeed for all parameters investigated (including copper). Even after outlier correction of the data sets, substantial variations between the laboratory results can be observed.

As the comparison of the variation coefficients indicates, these variations do not arise on account of different contents in the individual sample repetitions but are the unambiguous result of the different level of working quality of the laboratories taking part in the parallel interlaboratory test.

7.2 Comparison of parameters

Using the variation coefficients of the laboratory means **Varkoef(MW_{Lab})** the investigated parameters can also be compared with each other. The variation coefficients normalise the standard deviations to the respective mean **(Varkoef(MW_{Lab}) = Stdabw(MW_{Lab}) / MW_{ges})**, thereby giving the simple standard deviation as a percental deviation from the mean.

Table 7 divides the tested parameters into three groups. Group 1 contains the parameters with low variations Varkoef(MW_{Lab}) < 10%, group 2 the parameters with medium variations 10% ≤ Varkoef(MW_{Lab}) < 20% and group 3 the parameters with strong variations Varkoef(MW_{Lab}) ≥ 20%.

Besides the parameters water content, loss on ignition and pH value which are relatively easy to analyse, group 1 also contains the total nitrogen content and the bulk density. With the pH value, however, the above-mentioned limitations (see point 6) must be taken into consideration because the actual variations become blurred with logarithmic values. The strikingly low variations for the parameter bulk density were not predicatable in advance; it has become evident, however, that this simple method of density determination yields highly reproducible results, at least with fine-grained compost (< 10 mm).

Parameters displaying medium variations are the relative plant tolerance with 25% compost admixing, the rotting degree, the heavy metal contents of copper and zinc, the salt content as well as the remaining total nutrient contents and the soluble magnesium content.

Table 7:Classification of the parameters according to the level of analysis variations

Parameter classification according to analysis variations		
Group 1 Varkoef(MW_{Lab}) < 0,1	Group 2 0,1 ≤ Varkoef(MW_{Lab}) < 0,2	Group 3 Varkoef(MW_{Lab}) ≥ 0,2
Water content	Plant tolerance 25%$_{rel}$	Germinable seeds
Loss on ignition	Rotting degree (T_{max})	Foreign matter
pH value	Copper	Stone content
Bulk density	Zinc	Lead
Total-N	Salt content	Cadmium
	Total-P_2O_5	Chromium
	Total-K_2O	Nickel
	Total-CaO	Mercury
	Total-MgO	Nitrate
	Magnesium$_{sol}$	Ammonium
		Phosphorous$_{sol}$
		Potassium$_{sol}$
		Plant tolerance EE0$_{abs}$
		Plant tolerance 25%$_{abs}$
		Plant tolerance 50%$_{abs}$
		Plant tolerance 50%$_{rel}$

Although the relative plant tolerance with 25% compost admixing was able to be classified into group 2, if the absolute results of the plant tolerance test are considered, it can be seen that there are significant differences between the laboratories using this method ((Varkoef(MW_{Lab}) of the absolute results > 0.3). With the standardized reference substrate EEO these variations indeed turn out to be the largest! The differences between minimum and maximum of the outlier-free laboratory means of the absolute yields (see table 4) range from approx. 2 g to approx. 15 g and 16 g respectively. Even with the exclusion of those laboratories which deviate from the total mean by more than the double standard deviation (Stdabw(MW_{Lab}), there still remains a possible maximum range of at least 10 g. The lower variations with the relative yields are the purely mathematical consequence of the division by the results of the EEO variant. So even if the variations are lower for the relative yields decisive for compost assessment, the results of the plant tolerance tests nevertheless show that numerous laboratories were actually not in a position to conduct this analytical procedure correctly. To obtain reproducible analytical results in future there is still a need for substantive corrective action.

The same applies for the parameter rotting degree. It is true that the variation coefficient of the laboratory means of 0.18 is still just about in the middle variation band but with the calculated statistical quantities this parameter cannot be satisfactorily evaluated as the self-heating capability of the compost material can in principle not be overrated (except in the case of defective thermometers or read-off errors). The total mean as a measure of the "conventionally correct value" for this parameter and the standard deviation as a measure of the permissible deviation are therefore unsuitable. The exclusion criterion of 40^{o} C was extremely generously selected for the investigated fresh compost; the result was only classed as error analysis in the case of 13 laboratories. If an exclusion limit of 50^{o} C had been chosen, error analyses would have been identified in no less than 32 laboratories. Expressed in terms of rotting degrees the 40^{o} C limit means that rotting degree III result was still tolerated as correct although the fresh compost used exhibited maximum rotting degree II. It can therefore be concluded that the determination of the rotting degree is still absolutely inadequate in many laboratories.

A notable statistical effect is that if more stringent evaluation criteria were to be applied with a 50^{o} C limit for error analysis, the total mean value would have been the exclusion criterion!

In view of the significance of this parameter, more care must be exercised in its determination; in particular, attention must be paid to correct adjustment of the water content by means of the "fist test" and to regulations governing sample storage which are presumably the main reasons for the frequent overrating of the rotting degree. Among the parameters exhibiting strong variations are, besides the germinable seeds, the foreign matter and stone content, the majority of the heavy metals, the soluble nutrient contents as well as the absolute results of the plant tolerance tests and the relative plant tolerance with 50% compost admixing.

With the exceptions of copper and zinc all heavy metals display standard deviations of the laboratory means of at least 20% from the total mean (see table 5, Varkoef(MW_{Lab})). In the laboratory assessment, only laboratory means deviating from the the total mean by more than the double standard deviation were categorised as error analysis. This means a very large possible variation band in the heavy metal analysis of composts, alone due to laboratory effects. Table 8 gives an overview of the possible variation bands for the determination of heavy metals if a compost sample had just contained the corresponding limit values as actually correct values. In the parallel interlaboratory test all results with values inside the variation bands (last column of table 8) would still have been assessed as correct analyses! In the light of this, corresponding tolerance ranges should be taken into account when defining heavy metal limit values in composts or when evaluating routine analyses.

When determining very small substance concentrations, a tendency towards an increase in the normalized analysis variations is to be expected. This correlation, which is clearly discernible with the heavy metals (the variation coefficients of the laboratory means of Cd and Hg are appreciably higher than those of the other heavy metals with the exception of chromium) holds true in particular when limit values are pushed to the analytical determination limit.

Notice must also be taken of this correlation when discussing limit values for organic harmful substances in composts; reliable data on the quality of analysis must however still be collected.

Table 8: Tolerance ranges for heavy metal standard values under consideration of the determined variations and permissible double standard deviation from the total mean

Limit values for heavy metal contents and tolerance ranges				
Heavy metal	Limit value$_{30\%\ OS}$ [mg /kg DS]	Varkoef(MW_{Lab})	Permissible deviation [mg /kg DS]	Tolerance range [mg /kg DS]
Lead	150	0,20	✂ 60	90 - 210
Cadmium	1,5	0,33	✂ 0,99	0,51 - 2,49
Chromium	100	0,38	✂ 76	24 - 176
Copper	100	0,15	✂ 30	70 - 130
Nickel	50	0,20	✂ 20	30 - 70
Mercury	1,0	0,34	✂ 0,68	0,32 - 1,68
Zinc	400	0,13	✂ 104	296 - 504

Strong variations between the laboratory means are also recorded for the soluble nutrient contents. The significance of these variations is less dramatic as these parameters are not relevant for awarding the quality sign. When using composts for horticultural purposes it should be kept in mind that the analytical results may display variations of this magnitude.

If the classification criteria stated in table 7 are applied to the mean laboratory variation coefficients MW($Varkoef_{Lab}$), it emerges that only the parameters germinable seeds, foreign matter, stone content and nitrate display strong variations (see tables 5 and 6). This is primarily a consequence of the low content levels of these parameters.

In the determination of germinable seeds this is compounded by the fact that the analysis takes the form of a count as a result of which the variations at low values stand out more strongly. Due to the natural colouring of the extracts, the determination of the nitrate content of composts can lead to analytical difficulties with resultant variations. The extremely high variation coefficient of the laboratory means Varkoef(MW_{Lab}) = 1.10 for nitrate is nevertheless a clear indicator that many laboratories did not conduct this analysis thoroughly enough.

The mean values of the laboratory variation coefficients for the heavy metals lead, cadmium, copper, mercury and zinc as well as for ammonium display medium variations, whereby only copper, mercury and ammonium clearly exceed the 10% limit. In the case of copper the before-mentioned sample outliers lead to the increased variations whereas in the case of mercury it is the very low contents in the samples. All other parameters show low laboratory variation coefficients < 0.1 which makes clear that well homogenized sample material was used for the four increments and that the deviations between the laboratories were significantly higher than within the individual laboratories.

A further possibility of comparing the quality of analysis for the different parameters is given on the basis of the number of error analyses. Tables 9 and 10 give a more precise break-down of the number of error analyses for the two parameter groups A and B. In addition to the differentiation into statistically significant outliers according to the Grubbs test and error analyses resulting from more than double deviation from the total mean, the deviations are also broken down into upwards (+) and downwards (-) deviations. The figures in brackets indicate the total number of error analyses when the values are taken into account whose deviations arose merely on account of one sample outlier (see point 5.2). The second column of tables 9 and 10 gives the number of laboratories who carried out the respective analysis; the low number of only 78 laboratories for the nitrate content is because of the frequently inadequate and non-evaluatable results ("<" or not detectable) with this parameter. The total number of error analyses differentiated into upwards (+) and downwards (-) deviations make up the last two columns (the sum of all error analyses has already been given in tables 3 and 4).

Table 9:Number and kind of error analyses with the parameters of group A

Group A							
Parameter	Number lab.	Outliers according to Grubbs		$\boxtimes MW_{Lab} - MW_{ges} \boxtimes > 2 * \sigma$		Total error analysis	
		+	-	+	-	+	-
Foreign matter	94	4	0	6	0	10	0
PT 25%$_{rel}$	91	2	0	5	1	7	1
Rotting degree	91	-	-	-	-	13	-
Loss on ignition	95	1	0	2	3	3	3
Heavy metals							
Pb	95	1 (2)	1	3 (4)	3	4 (6)	4
Cd	95	6	0	4	2	10	2
Cr	95	8	0	6	0	14	0
Cu	95	3 (9)	0	4	1	7 (13)	1
Ni	95	9	0	3	1	12	1
Hg	94	10	0	5 (6)	0	15 (16)	0
Zn	95	2 (3)	1	4	2	6 (7)	3
Total nutrients							
N	95	2	3	3	0	5	3
P_2O_5	95	4	5	2	2	6	7
K_2O	95	7	2	2	4	9	6
CaO	95	3	0	1	5	4	5
MgO	95	4	1	2	5	6	6

Table 10: Number and kind of error analyses with parameters of group B and the non-evaluated parameters

Group B and non-evaluated parameters							
Parameter	No. lab.	Outliers according to Grubbs		$\boxtimes MW_{Lab} - MW_{total} \boxtimes > 2 * \sigma$		Total error analysis	
		+	-	+	-	+	-
Germinable seeds	91	10	0	6	0	16	0
Stone content	94	1	0	3	1	4	1
Water content	95	1	2	1	4	2	6
Salt content	95	1	4	1	2	2	6
pH value	95	0	2	-	-	0	2
Bulk density	95	1	0	3	1	4	1
Soluble nutrients							
NO_3-N	78	8	0	3	0	11	0
NH_4-N	94	3	0	3	6	6	6
Mg	95	6	1	5	3	11	4
P_2O_5	95	4	0	4	4	8	4
K_2O	95	4	1	4	3	8	4
Plant tolerance PT (not evaluated) (EE0 = Standard soil)							
PT EE0 $_{abs}$	91	1	0	3	0	4	0
PT 25 % $_{abs}$	91	2	0	4	1	6	1
PT 50 % $_{abs}$	91	1	0	4	1	5	1
PT 50 % $_{rel}$	91	1	0	5	0	6	0

Ten or more error analyses are attributed to the parameters foreign matter, germinable seeds, rotting degree, the heavy metals cadmium, chromium, nickel and mercury, the total nutrient contents phosphorous, potassium and magnesium as well as all soluble nutrient contents. According to table 7 all these parameters display medium to strong variations of the analytical results and must as such be rated extremely critically.

No simple correlation, however, exists between the number of error analyses with one parameter and the extent of analysis variations, since, with parameters with large analysis variations, only correspondingly greater deviations will result in assessment as error analysis. This becomes evident, for example, when looking at the abolute yields of the plant tolerance tests which all exhibit very strong variations (Varkoef(MW_{Lab}) > 0.3) but which registered only few error analyses (4 - 7) (see tables 4 and 6).

With the majority of parameters, more upwards (+) than downwards (-) deviations were established. Only the parameters water content, salt content and the total nutrients phosphorous and calcium recorded more lower than upper deviations. The ratio was balanced with the parameters loss on ignition, lead content, total MgO and ammonium content.

There is hence a general tendency to overrate the values of the majority of parameters in instances of error analysis. This is particularly clearly manifested with parameters whose contents are at an extremely low level such as germinable seeds, foreign matter, stone content, nitrate content as well as the heavy metals cadmium and mercury. But the contents of all the other heavy metals (excluding lead) are much more frequently overrated than underrated. This likewise applies for the results of the plant tolerance tests (absolute and relative yields), for the soluble nutrient contents with the exception of ammonium and for the parameter bulk density.

In the case of the parameter rotting degree underrating is impossible on principle. However, it should be noted here that overrating of the rotting degree means that the maximum temperature in the self-heating test was underrated.

7.3 The effect of applying more stringent criteria to error analysis using the example of heavy metals

Application of the double standard deviation of laboratory means from the total mean as a criterion for error analyses with the outlier-corrected data sets is an arbitrary process and has no statistical inspection status as is the case, for example, with the elimination of extreme values (outliers) using the Grubbs test. In principle, the proportion of error analyses to be sorted out is prescribed, whereby the criterion was selected very generously at the cost of the permissible variations. Given a normal distribution of the data sets this criterion leads to the elimination of approx. 5% of the results as error analysis. The level of the respective standard deviation therefore has no effect on the proportion of error analysis but it does have an effect on the width of the permissible variation band. The elimination criterion in the parallel interlaboratory test results in large permissible variation bands for many parameters. The following exposition focuses on the effects of more stringent elimination criteria on the proportion of error analyses and the permissible variation bands using the example of the heavy metal contents.

Table 11 shows the number and percental proportions of error analyses for heavy metals when applying different elimination criteria.

According to the assessment criteria defined in the parallel interlaboratory test (2 σ), the permissible deviation from the total mean (for the heavy metal contents) is between 26% for zinc and 76% for chromium (see table 8). The proportion of error analysis is around 5 - 8%. Even if more stringent assessment criteria were to be applied by allowing only a maximum single deviation (1 σ) from the mean, deviations of minimum 13% for zinc up to maximum 38% for chromium would still be possible in heavy metal analysis. Such a limitation of the maximum permissible deviation would have meant that (given a normal distribution of the analytical results) approx. 32% of the results would have been eliminated as error analysis. The actual proportion of error analyses would have been marginally smaller by virtue of the non-exact normal distribution of the data (table 11, column 3).

Table 11: Number of error analyses with the heavy metal contents under consideration of different elimination criteria (percental proportions in brackets)

Heavy metal error analysis with different elimination criteria				
Heavy metal	Elimination criteria			
	2 σ	1 σ	Dev. 10%	2*MW($Varkoef_{Lab}$)
Lead	7 (7,6)	23 (25,0)	42 (45,7)	24 (26,1)
Cadmium	6 (6,7)	27 (30,3)	61 (68,5)	39 (43,8)
Chromium	6 (6,9)	20 (23,0)	63 (72,4)	52 (59,8)
Copper	5 (5,8)	24 (27,9)	34 (39,5)	4 (4,7)
Nickel	4 (4,7)	24 (27,9)	54 (62,8)	42 (48,8)
Mercury	6 (7,1)	23 (27,4)	56 (66,7)	17 (20,2)
Zinc	6 (6,6)	25 (27,5)	32 (35,2)	12 (13,2)

If the position of the middle 50% of the laboratory means is taken as a criterion for the maximum permissible deviations and the percentile margins are related to the respective median (see table 3), the resultant variation or tolerance bands are at least 7% for zinc up to maximum 17% for cadmium. The proportion of error analyses is specified with this procedure too with the result that 50% of all results (therefore not listed in table 11) are always eliminated as error analysis.

A fundamentally different criterion for error analysis could entail defining deviation bands from the very start, for instance 10% difference as permissible deviation from the respective total mean. On account of the different dispersion of the results, such an approach would lead to different proportions of error analyses for the different parameters. The strict definition of the permissible deviations as a 10% difference from the respective mean would have meant that between 35.2% (zinc) and 72.4% (chromium) of the results would have been eliminated as error analyses (table 11, column 4).

The advantage of this procedure is without doubt that tolerable deviations can be defined beforehand, independently of the respective dispersion of the results. On the other hand variations of the analytical results are not only dependent on systematic laboratory effects but are also subject to methodological influences.

One possibility of taking these influences into consideration while still achieving more stringent assessment criteria and consequently narrower variation bands is to define the criteria for the permissible deviations utilizing the mean laboratory variation coefficient MW($Varkoef_{Lab}$). If the double mean laboratory variation coefficients are taken as a measure of the permissible percental deviation from the total mean, the variation bands would be significantly narrower for all heavy metals with the exception of copper (see 7.1, table 5). The proportion of error analyses would then naturally be correspondingly higher. The big advantage of this procedure is that the methodological variations are taken into consideration without the proportion of error analyses being specified beforehand. If the special case of copper is ignored, the proportion of error analyses is between 13.2% for zinc and 59.8% for chromium.

When evaluating analytical results, tolerance bands should definitely be taken into consideration in dependence of the selected elimination criterion and the strictness of the selected criterion.

8 Laboratory assessment

A key objective of the parallel interlaboratory test was the exclusion of laboratories which were not adequately qualified for the analysis of compost. On exceeding the maximum permissible number of error analyses a laboratory is no longer approved for external monotoring of composts. In addition, the laboratories were classified into different categories according to the quality of their work.

Table 12: Classification of the laboratories into quality categories

Laboratory assessment: Classification into quality categories					
Category	**I**	**II**	**III**	**IV**	**Total**
No. of Laboratories	17	52	12	14	95
Proportion in %	17,9	54,7	12,6	14,7	100

It can be seen from table 12 that approx. 15% of the participating laboratories were allocated to category IV and consequently lose their approval to function as an analysis laboratory for the Federal Compost Quality Assurance Organisation. This high proportion makes clear just how necessary it was to conduct this parallel interlaboratory test to be able to assure a high-grade quality assurance of composts.

Three laboratories were excluded because they failed to conduct analyses without giving reasons. In the case of the other category IV laboratories a tendency to a concentration of error analyses with the heavy metals, the total nutrient contents and the soluble nutrients can be observed. However, this concentration is not particularly clear in its interpretation; many of the excluded laboratories displayed error analyses over almost the entire parameter spectrum. Over half the laboratories (approx. 55%) satisfied the criteria specified by the Federal Compost Quality Organisation without limitations. The relatively generous exclusion criteria specified for this parallel interlaboratory test (max. 5 error analyses in total or 3 per group) means that there is an urgent requirement for improving the quality of analysis of the majority of the category II laboratories. This applies particularly for the laboratories grouped into category III. A maximum of two permissible error analyses with the heavy metals along with the single assessment of a joint upper deviation from the limits with chromium and nickel (Cr/Ni bonus) can only be justified under the aspect that the laboratories concerned bring about immediate improvements in the quality of their work (by the next parallel interlaboratory test at the latest).

These laboratories have been expressly warned of the necessity of improvements in their qualitative analysis by the Federal Compost Quality Assurance Organisation. If the stricter assessment criteria had been applied as originally foreseen, the category III laboratories would have been excluded so that more than a quarter (27.3%) of the participating laboratories would have been judged unsuitable for qualitatively satisfactory compost analysis.

It is pleasing that 18% of the participating laboratories recorded no error analysis whatsoever with the result that these laboratories were specially recommended for compost analysis as external monitors. Adequate analysis capacities are therefore available for a high standard of compost analysis and hence a high-grade quality assurance.

9 Separate statistical evaluation of the category I laboratories

Tables 13 and 14 show the descriptive statistical quantities for the specially recommended category I laboratories. The comparison with the values for the complete (outlier-corrected) data sets in tables 3 and 4 illustrates how the positional and dispersion values change if restricted to the specially recommended laboratories. The values in brackets in the "Range" columns of tables 13 and 14 indicate the respective bands for the complete, outlier-adjusted data sets.

Restricting the focus to the category I laboratories only brings about insignificant changes to the positional values mean and median compared to the complete (outlier-adjusted) data sets. With the majority of parameters the deviations amount to less than 10% related to the values of the complete data sets. The mean or median only change by more than 10% in the case of the parameters germinable seeds, nitrate content and relative plant tolerance PT 50%$_{rel}$.

Table 13: Statistical quantities for the parameters of group A under sole consideration of the category I laboratories

Group A						
Parameter	No. Labs.	MW_{ges}	Median	Standard deviation	Range	Percentiles (25%-75%)
For. matter [%]	17	0,24	0,24	0,07	0,25 (0,53)	0,18 - 0,28
PT 25%$_{rel}$[%]	17	98,3	97,7	8,51	35,2 (86,6)	93,2 - 100,7
RG (T_{max}) [☜C]	17	52,2	53,9	4,43	13,9 (43,8)	46,2 - 55,9
GV [% DS]	17	45,2	45,3	1,76	7,2 (16,9)	43,6 - 46,4
Heavy metals [mg/kg DS]						
Pb	17	59,1	58,2	10	45,5 (71,4)	53,3 - 61,5
Cd	17	0,52	0,55	0,14	0,52 (1,04)	0,39 - 0,63
Cr	17	24	21,6	8,24	28,3 (45,9)	18,8 - 25,1
Cu	16	61,5	63	6,49	25,0 (52)	56,5 - 65,2
Ni	17	16,6	15,4	3,3	9,9 (18,3)	13,7 - 19,1
Hg	17	0,14	0,14	0,03	0,11 (0,27)	0,12 - 0,16
Zn	16	207	203	21,7	82 (148)	193 - 225
Total nutrients [% DS]						
N	17	1,77	1,8	0,1	0,34 (0,62)	1,67 - 1,83
P_2O_5	17	1,14	1,15	0,11	0,47 (0,96)	1,07 - 1,20
K_2O	17	1,09	1,07	0,08	0,31 (0,65)	1,04 - 1,13
CaO	17	4,46	4,41	0,53	2,22 (4,52)	4,22 - 4,82
MgO	17	0,63	0,64	0,04	0,16 (0,45)	0,61 - 0,68

The range (difference between minimum and maximum laboratory mean) of the analytical results of the individual parameters narrows appreciably if only the category I laboratories are considered.

Table 14: Statistical quantities for the parameters of group B and the non-evaluated parameters under sole consideration of the category I laboratories

Group B and non-evaluated parameters						
Parameter	No. Lab.	MW $_{total}$	Median	Standard Deviation	Range	Percentiles (25%-75%)
G. s. [No./l FS]	17	0,03	0	0,07	0,25 (0,52)	0,00 - 0,00
Stone c. [%DS]	17	0,58	0,56	0,19	0,72 (1,23)	0,46 - 0,72
Water c. [%FS]	17	27,7	27,8	0,55	2,1 (4,2)	27,4 - 28,2
Salt [g KCl/l FS]	17	7,2	7,1	0,67	2,3 (5,3)	6,7 - 7,6
pH value	17	7,9	7,9	0,19	0,6 (0,8)	7,7 - 8,0
Bulk d. [g/l FS]	17	556	558	16,7	57 (95)	543 - 569
Soluble nutrients [mg/l FS]						
NO_3-N	13	4,9	4,7	6,59	25,2 (43,4)	0,3 - 5,9
NH_4-N	17	159	164	27,23	113 (143)	147 - 175
Mg	17	206	205	22,48	88 (183)	193 - 219
P_2O_5	17	792	753	169,1	549 (1509)	643 - 960
K_2O	17	3612	3526	407,7	1280(5173)	3219-3965
Plant tolerance PT (not evaluated) (EE0 = Standard soil)						
PT EE0 $_{abs}$ [g]	16	9,1	7,8	3,28	10,4 (13,2)	6,5 - 12,2
PT 25% $_{abs}$ [g]	16	8,9	7,3	3,31	10,3 (14,4)	6,5 - 12,5
PT 50% $_{abs}$ [g]	16	7,4	6,2	3,13	9,4 (13,4)	4,6 - 10,8
PT 50% $_{rel}$ [%]	17	80,1	83	12,67	45,9 (95,8)	75,9 - 88,0

When comparing with the values of the complete, outlier-corrected data sets (values in brackets) it must be borne in mind that their calculation is still based on maximums and minimums which were generally eliminated as error analyses on account of more than double the standard deviation from the total mean.

The standard deviations also substantially decrease with most of the parameters (in part up to 50%). The absolute yields of the plant tolerance tests represent a notable exception; here the standard deviations actually increase (!) if only the category I laboratories are considered. This can be explained in mathematical terms by the overcompensation of the overall narrower range widths of the results due to the lower number of laboratories entered in the calculation and due to the significantly higher percentile margins. This peculiarity shows that a decrease in dispersion due to restriction to the category I laboratories does not take place automatically (as a pure computing effect).

The changes in the standard deviations and variation coefficients with the heavy metals are relatively slight. A comparison of tables 3 and 13 reveals that the standard deviation only falls off sharply in the case of mercury (0.03 instead of 0.06). Table 15 shows a comparison between the variation coefficients of the heavy metal contents of the complete, outlier-adjusted data sets with the variation coefficients obtained when only evaluating the category I laboratories. Analogous to table 8 tolerance bands are likewise calculated for the determination of heavy metal contents under exclusive consideration of the analysis variations of the category I laboratories. Related to the values of the complete data sets the variation coefficients of all heavy metal contents decrease by more than 10% with the exception of nickel. The variation coefficient of nickel remains constant, in the case of copper and mercury the variation coefficients drop sharply by 26.6% and 38.2% respectively.

Tab. 15: Comparison of the variation coefficients of the heavy metal contents of the complete data sets with the category I laboratories and tolerance ranges for heavy metal standard values under consideration of the variations determined for the category I laboratories.

Comparison of the variation coefficients and tolerance ranges for heavy metal limit values				
Heavy metal	Varkoef(MW_{Lab}) compl. DS	Vark.(MW_{Lab}) Catagory I	Permissible deviation [mg/kg DS]	Tolerance range [mg /kg DS]
Lead	0,20	0,17	✂ 51	99 - 201
Cadmium	0,33	0,27	✂ 0,81	0,69 - 2,31
Chromium	0,38	0,34	✂ 68	32 - 168
Copper	0,15	0,11	✂ 22	78 - 122
Nickel	0,20	0,20	✂ 20	30 - 70
Mercury	0,34	0,21	✂ 0,42	0,58 - 1,42
Zinc	0,13	0,11	✂ 88	312 - 488

The last column of table 15 shows calculated tolerance bands for a compost sample (based on the analysis variations of the category I laboratories) which would have just contained the limit values of the corresponding heavy metals. As with the calculation of the variation bands in table 8, the calculation was based on the double standard deviation from the total mean as maximum permissible deviation. The reduced standard deviations and variation coefficients result in a corresponding narrowing of the tolerance bands. However, even when considering the analysis variations of the category I laboratories in isolation, large variation bands are still possible with the heavy metals.

10 Summary

Essential preconditions for a workable quality assurance system have been created with the compilation of a binding "methods book" for the analysis of composts and the execution of the parallel interlaboratory test in 1993.

A total of 95 laboratories took part in the 1993 parallel interlaboratory test who analysed a total of 31 parameters from four randomly allocated increments from an homogenous population. The majority of parameters were determined by multiple repetition analysis. The essential calculated statistical positional and dispersion values for the outlier-adjusted data sets (laboratory mean values) were the total mean, median, standard deviation, variation coefficient, range and percentiles.

The excellent homogenity of the samples and the avoidance of systematic sampling effects on the analytical results by random allocation of the increments to the participating laboratories is demonstrated by comparing the means of the laboratory variation coefficients MW($Varkoef_{Lab}$) with the variation coefficients of the laboratory means Varkoef(MW_{Lab}) for the respective parameters. The mean values of the laboratory variation coefficients as an average measure of the dispersion between the individual increments are substantially lower for all investigated parameters (two to five-fold) than the variation coefficients of the laboratory means which represent a measure of the variations of the results between the participating laboratories.

Outliers were eliminated from the complete data sets of the individual analytical results using the Grubbs test as per DIN 38 402 (Part 42) and classed as error analysis in the laboratory assessment. According to DIN 38 402 (Part 41) the outlier-free total mean values MW_{ges} were taken as a measure of the "conventionally correct values". Further, (on the basis of the outlier-corrected data sets) all laboratory mean values were classed as error analyses which deviated from the total mean MW_{ges} by more than the double standard deviation Stdabw(MW_{Lab}).

Using this procedure, about half the investigated parameters exhibited an error analysis proportion of 5 - 10%; a proportion in excess of 10% was established for the other half.

Even after outlier-adjustment of the data sets and limiting the admissible variation of the results to the double standard deviation of the laboratory means, the majority of parameters still show considerable variations between the laboratories.

With over 50% of the investigated parameters the assessment criteria of the parallel interlaboratory test permit variations in excess of 40% related to the outlier-free total mean. This appears to be particularly relevant when defining limit values for individual parameters. In the case of the heavy metal permissible variations from the respective total mean were between 26% for zinc and 76% for chromium due to the variations between the laboratories. A restriction of the permissible deviation from the total mean using the double mean laboratory variation coefficients would take the purely methodological influences better into consideration and would lead to significantly narrower variation bands. Variations which arise on account of different laboratory analytical procedures are quantifiable and should be taken into account when defining limit values or evaluating routine analyses by applying associated tolerance bands.

The laboratory assessment was based on the number of error analyses established in the individual laboratories. The decisive criterion was the total number of established error analyses (max. 5). The investigated parameters were additionally weighted in two different groups (A and B), whereby each group was only allowed a maximum of 3 error analyses. Moreover, a special evaluation of the heavy metal analysis was carried out. The laboratories were classified into four different quality categories (I-IV). Almost 18% of the participating laboratories recorded zero error analyses (category I, specially recommended by the Federal Compost Quality Assurance Organisation), 55% satisfied the set requirements without limitations, approx. 13% were approved subject to restrictions and 15% were excluded by the Association from acting as external quality monitors.

The sole calculation of the statistical quantities for the category I laboratories and the comparison with the complete (outlier-adjusted) data sets shows only slight changes to the positional values total mean and median. The range widths of the values clearly narrow when only considering the category I laboratories and the standard deviations and variation coefficients fall off sharply in part. It must be mentioned, however, that especially in the case of the heavy metals, there are still appreciable variations of the results even when considering the category I laboratories in isolation.

A fundamental objective of the 1993 parallel interlaboratory test has been achieved with the classification of the participating laboratories, in particular the exclusion of unsuitable laboratories on account of inadequate analysis quality and, on the other hand, the recommendation of especially suitable laboratories.

The experience gained during the first ever execution of such an extensive parallel interlaboratory test will facilitate the organisation and evaluation of further parallel tests. It would be desirable to reduce the number of parameters to be investigated on account of the work burden on the participating laboratories and the volume of data which has to be evaluated. Nevertheless, the results of the parallel interlaboratory tests show that virtually all the parameters were relevant for laboratory assessment and that only the relatively simple analyses, namely water content, loss on ignition, pH value, bulk density and total nitrogen content displayed slight analysis variations.

The thoroughness with which the sampling procedure and sample distribution were carried out should also be assured for further parallel interlaboratory tests; the number of sample repetitions must also not be reduced so as to enable a useful and meaningful statistical evaluation of the results.

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