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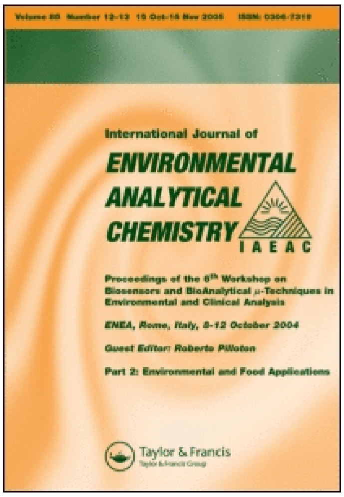

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Characterization of Compost with Respect to its Content of Heavy Metals. Part II: Sample Preparation

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CHARACTERIZATION OF COMPOST WITH RESPECT TO ITS CONTENT OF HEAVY METALS.

Part II: Sample Preparation

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This paper forms part of a study aimed at the development of a procedure for the determination of heavy metals in compost. The present paper deals with the sample preparation stage, including subdividing laboratory samples and reduction of the particle size.

The effect of particle size reduction on the random error due to the analysis of test portions was examined. It was found that milling for 20 min in a quartz planet ball mill yields sufficiently homogeneous test samples. As the milling capacity of this device is too small, prior to milling subdivision of the laboratory sample is required. Subdivision before drying is recommended for practical reasons.

KEY WORDS: Compost, heavy metals, particle size reduction, subdivision.

INTRODUCTION

General

A Decree is in preparation in which the Dutch Government will specify values for maximum tolerable levels of heavy metals in compost. For the implementation of the Decree analytical procedures have to be developed. In a previous paper[1] a diagram of the total analytical procedure for the determination of heavy metals in compost has been presented. In the same paper the precision and accuracy of the determination of heavy metals in a test sample, including digestion and instrumental element analysis, have been discussed. The present paper deals with the sample preparation stage, which leads from the laboratory sample towards the test sample and which includes subdivision and reduction of the particle size (milling).

Reduction of Particle Size

The purpose of particle size reduction is to obtain a homogeneous test sample. The degree of inhomogeneity of the test sample becomes manifest when determining the content of heavy metals in a series of test portions taken from a test sample. The variance of the analytical results can be expressed as:

$$s^2_{anal} = s^2_{det} + s^2_{hetr} \qquad (1)$$

where s^2_{anal} is the total variance associated with analysis of test portions, s^2_{det} is the variance associated with element determination in a homogeneous test sample, and s^2_{hetr} is the variance associated with rest heterogeneity after sample preparation.

Values for s^2_{det} have been presented in an earlier study in which the standard deviation associated with element determination for two near homogeneous materials, viz. RM No. 143 (a sludge amended soil) and CW1 (composted garbage), was examined. It was found that the relative standard deviation, RSD_{det}, in both materials for the elements considered is between 2 and 5% (test portion: 1.5 g).[1] The particle size of both materials is less than 0.09 mm.[2,3]

The objective of the present study is to establish a sample preparation procedure which leads to a homogeneity of the test sample such, that s^2_{hetr} is not a dominant factor in s^2_{anal}. Besides, particle size reduction should be performed with minimal time and cost. From the foregoing, it is obvious that there is no use in striving for RSD_{anal} to be less than 5%.

Lorber and Kümmlee[4,5] found that the relative standard deviation associated with the analysis of garbage compost test samples—with a content of heavy metals ranging from 3 mg/kg d.m. for Cd to 1200 mg/kg d.m. for Zn—depended on the particle size. For test samples consisting of particles smaller than 1 mm, RSD_{anal} for the majority of heavy metals ranged between 5 and 15%, whereas RSD_{anal} in the case of test samples with an upper particle size limit of 0.25 mm was in general smaller than 10%. These observations indicate that in order to obtain the grade of homogeneity aimed at—i.e. RSD_{anal} to approach 5%—reduction to particle sizes smaller than 0.25 mm has to be performed.

In the present study investigations are described resulting in a proposal for particle size reduction, based on a compromise between the milling effort and the attained homogeneity of the test sample.

Subdivision

Prior to milling, sample preparation may require subdivision of the laboratory sample. This is necessary when the capacity of the milling device is not sufficiently large. Subdivision generates an additional contribution to the random error. This contribution, expressed as s_{subd}, has also been estimated. When subdivision is a necessary step, a decision has to be made whether drying is done before or after subdivision. As this may influence s_{subd} as well, both options have been examined.

EXPERIMENTAL

Reagents

Nitric acid (65%), analytical grade (Merck, Darmstadt, FRG). Hydrochloric acid (37%), analytical grade (Merck, Darmstadt, FRG).

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Types of Composts Analyzed

The following types of composts were examined: Compost Wijster, Compost Nuenen, and Compost Purmerend. For a description of these materials, see Reference 1.

The composts were used as such, i.e. the obviously non-compostable components were not discarded.

Determination of Heavy Metals

The determination of heavy metals in compost was performed according to the procedure described in Reference 1.

Instrumentation

Subdivision equipment Riffle splitter; ten slits, width 30 mm.

Milling equipment Quartz planet ball mill Pulverisette 5, Fritsch GmbH, FRG; volume beaker 250 ml, diameter ball 30 mm, four balls per beaker. Cross beater mill 200 AN, Peppink, The Netherlands; capacity 1000 ml; 1.0 and 2.0 mm sieves. Throughput for compost was within 2 min for both sieves.

Sieving equipment Vibrating sieve apparatus Analysette 3, Fritsch GmbH, FRG; 0.25 and 0.125 mm sieves.

Reduction of Particle Size

Two devices have been used for the reduction of the particle size: a cross beater mill and a quartz planet ball mill. The cross beater mill has the advantage of a large capacity and a short milling time. The material is in continuous contact with the fast turning cross beater and is simultaneously forced to pass the selected sieve, retaining particles the size of which is not further reduced under the milling conditions employed. The size reduction depends upon the sieve used. Size reduction for compost is limited to 1 mm. The use of a finer sieve leads to blockage.

In a quartz planet ball mill no separation between coarse and fine particles occurs: the compost is milled in a closed beaker. The milling capacity is less than for the cross beater mill. However, à more drastic size reduction can be achieved. The extent of the reduction depends on the milling time used. For compost this dependency was established in the present study.

Dried compost samples were milled in such a way that four size classes were obtained which, according to preliminary experiments, have an increasing grade of fineness (see Table 1). Classes I and II were obtained with the cross beater mill using 2 mm and 1 mm sieves, respectively. Classes III and IV resulted from milling by the quartz planet ball mill employing milling times of 20 min and 60 min, respectively. The extent of particle size reduction when using the planet ball mill

Table 1 Size classes used for establishing effect of particle size reduction on the homogeneity of test samples

Size class	*Preparation method*
I	Cross beater mill; 2 mm sieve
II	Cross beater mill; 1 mm sieve
III	Planet ball mill; 20 min
IV	Planet ball mill; 60 min

was determined by sieving. For the cross beater mill less than 1% did not pass the sieve. To obtain a representative test sample, in both cases the material that had passed the sieve and the material retained by the sieve were mixed prior to analysis.

Subdivision and Drying

Subdivision of laboratory samples "as delivered" as well as subdivision of dried laboratory samples has been performed, using a riffle splitter. Replicate laboratory samples of 1 kg taken from a lot of *Purmerend* as well as from a lot of *Wijster* compost were considered. Subdivision was performed in such a way, that eight subsamples were obtained. Subsequently all subsamples were milled for 20 min using a quartz planet ball mill. Finally, replicate test samples were analyzed. Analysis of variance was performed to distinguish RSD_{subd} from RSD_{anal}.

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RESULTS AND DISCUSSION

Reduction of Particle Size

In a preliminary study the possibility of particle size reduction with a quartz planet ball mill was studied. The investigations started with size reduction to 0.25 mm. Figure 1 depicts the dependency of the weight percentage of the material with a particle size smaller than 0.25 mm on the milling time for *Nuenen* and *Wijster* compost. The curves show that a reduction of the particle size to less than 0.25 mm for over 95% for the *Nuenen* compost is reached after 10 min of milling and for the *Wijster* compost after 20 min.

To obtain more detailed information, the extent of particle size reduction was established by sieving through 0.25 mm and 0.125 mm sieves for milling times of 20 and 60 min. The results are presented in Table 2. The results show that a notably further reduction can be achieved by milling for 60 min instead of for 20 min.

From the results obtained so far it can be concluded that size reduction of compost to less than 0.25 mm is easily feasible for over 95% of the material using a quartz planet ball mill. Size reduction to 0.125 mm demands more effort and may not be feasible for all types of compost.

To establish optimal size reduction, s^2_{anal} was determined for all size classes given

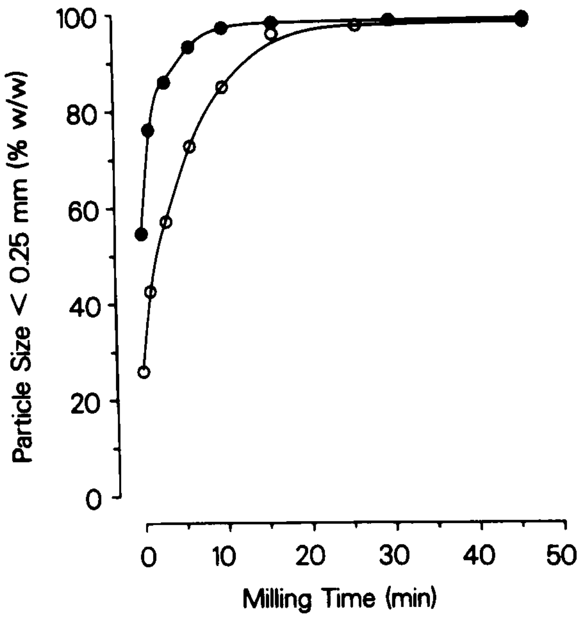

Figure 1 Dependency of the weight percentage of material with a particle size smaller than 0.25 mm on the milling time for *Nuenen* compost (●) and *Wijster* compost (○).

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Table 2 Particle size reduction using a quartz planet ball mill

Compost:	*Wijster*		*Nuenen*	
Sieve size:	*0.25 mm*	*0.125 mm*	*0.25 mm*	*0.125 mm*
Milling time (min)	*Through sieve (%)*			
20	95.3	59.7	97.2	57.7
60	99.4	86.2	99.8	96.3

in Table 1. From the test samples of each class eight test portions were withdrawn and analyzed. The results, in terms of RSD_{anal}, are presented in Table 3. Evaluation of the milling procedures was performed using the F-test ($\alpha = 0.05$), taking size class IV as the reference. For size classes I and II in the majority of cases the error is significantly larger as compared to size class IV. For size class III, RSD_{anal} significantly differs in two out of five cases for *Wijster* compost and in one out of five cases for *Nuenen* compost.

Formal values for the relative standard deviation due to heterogeneity, RSD_{hetr}, can be calculated in the following way. Equation 1 written in terms of RSD reads:

$$RSD^2_{anal} = RSD^2_{det} + RSD^2_{hetr}. \tag{1a}$$

Values for RSD_{anal} follow from Table 3. For RSD_{det} a value of 5% is taken. As a

Table 3 Relative standard deviation associated with analysis of test portions (RSD_{anal}) for various milling procedures[a]

Compost:	*Wijster*				*Nuenen*			
Size class:	*I*	*II*	*III*	*IV*	*I*	*II*	*III*	*IV*
Element				RSD_{anal} (%)				
Cr	12.2	10.2	5.2	7.8	*16.0*	*5.9*	*4.5*	1.2
Cu	*26.4*	*10.7*	3.6	4.4	*10.9*	*9.2*	2.4	3.9
Ni	*9.5*	*11.1*	*7.4*	3.7	6.3	7.1	6.3	4.9
Pb	*12.8*	4.9	5.3	2.9	11.0	*36.6*	6.1	10.6
Zn	*6.6*	*7.7*	*4.0*	1.9	*8.8*	*11.3*	5.3	2.8

[a]Italic type: Value significantly greater than for size class IV (F-test; $\alpha = 0.05$).

Table 4 Relative standard deviation associated with rest heterogeneity (RSD_{hetr}) for various milling procedures

Compost:	*Wijster*				*Nuenen*			
Size class:	*I*	*II*	*III*	*IV*	*I*	*II*	*III*	*IV*
Element				RSD_{hetr} (%)				
Cr	11.3	8.9	1.4	6.0	15.2	3.1	0	0
Cu	25.9	9.5	0	0	9.7	7.7	0	0
Ni	8.1	9.9	5.5	0	3.8	5.0	3.8	0
Pb	11.8	0	1.8	0	9.8	36.3	3.5	9.4
Zn	4.3	5.9	0	0	7.2	10.1	1.8	0

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matter of fact this will lead to negative calculated values for RSD^2_{hetr} in a number of cases, especially when the heterogeneity contributes only negligibly to RSD_{anal}. In these cases RSD_{hetr} has been formally assigned the value 0. The results for RSD_{hetr} are given in Table 4, while in Figures 2 and 3 the dependency of RSD_{hetr} on the particle size is depicted graphically.

The results show that for the size classes I and II a substantial contribution of RSD_{hetr} to RSD_{anal} is observed. Size classes III and IV are generally sufficiently homogeneous. Therefore it is concluded that milling for 20 min in a quartz planet ball mill leads to sufficiently homogeneous test samples.

In an additional experiment RSD_{hetr} has been determined for the material of size class IV which passes the 0.125 mm sieve, discarding the coarse particles. The results are given in Table 5. It can be seen that this material is still more homogeneous. However, this alternative has to be rejected because discarding the coarse material may lead to non-representative test samples, as is illustrated for *Wijster* compost in Table 6. The content of Cr, Cu and Ni for this compost in the coarse fraction is notably higher than in the fine fraction.

Subdivision

From the foregoing it is clear that only particle size reduction in the planet ball

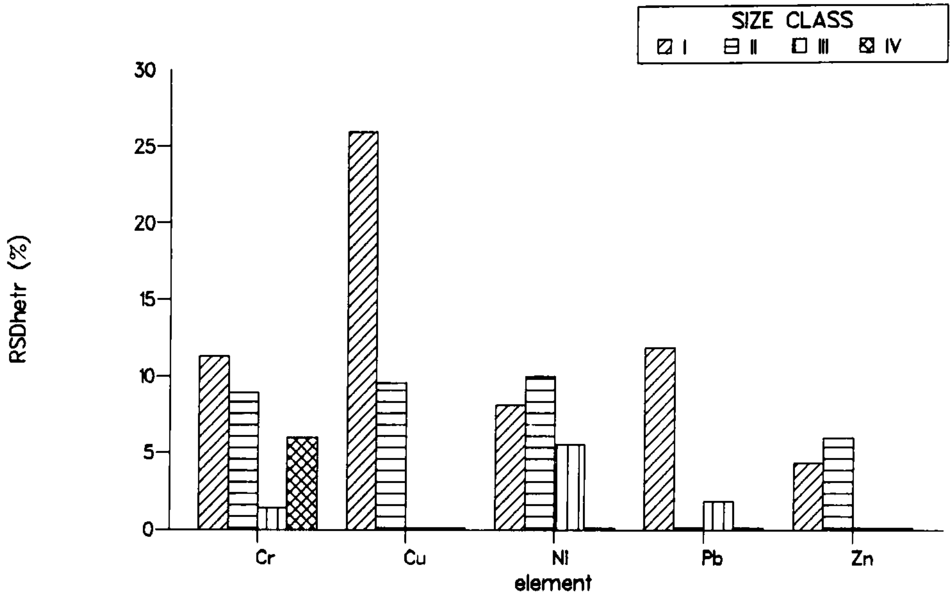

Figure 2 Dependence of RSD_{hetr} on particle size for *Wijster* compost.

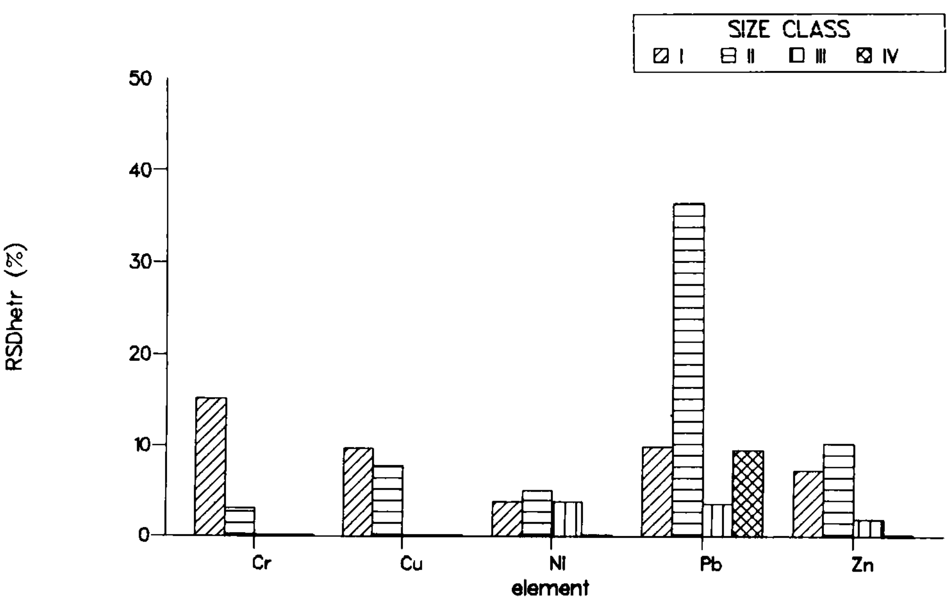

Figure 3 Dependency of RSD_{hetr} on particle size for *Nuenen* compost.

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Table 5 Relative standard deviation associated with analysis of test portions (RSD_{anal}) and with rest heterogeneity (RSD_{hetr}) for particle size less than 0.125 mm

Element	*Compost*			
	Wijster		*Nuenen*	
	RSD_{anal} (%)	RSD_{hetr} (%)	RSD_{anal} (%)	RSD_{hetr} (%)
Cr	2.5	0	3.3	0
Cu	3.8	0	1.7	0
Ni	2.6	0	5.0	0
Pb	1.6	0	6.9	4.8
Zn	1.0	0	3.7	0

Table 6 The content of heavy metals in the fine fraction and in the coarse fraction for *Wijster* compost (mg/kg d.m.)

Element	*Particle size*	
	<0.125 mm	*0.125–0.25 mm*
Cr	28	45
Cu	180	240
Ni	25	36
Pb	360	380
Zn	480	510

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mill yields test samples of such homogeneity that s^2_{hetr} is not a dominant factor in s^2_{anal}. Due to the limited capacity of the planet ball mill, subdivision of the laboratory sample seems to be a necessary step in the total analytical procedure. However, as mentioned earlier, subdivision generates an extra contribution to the error in the final analytical results. It may turn out that this contribution is so large that the conclusions arrived at so far for the particle size reduction procedure will have to be reconsidered as no sample subdivision is needed when the cross beater mill is used.

The random error associated with subdivision was examined for replicate laboratory samples taken from a lot of *Wijster* as well as from a lot of *Purmerend* compost. At the same time the effect of drying before and after subdivision was studied.

Since the results, in terms of RSD_{subd}, show large variations in replicate experiments, only the range in which the values occur are mentioned (see Table 7). The results do not show substantial differences between subdivision before or after drying. For both procedures the majority of RSD_{subd} values are below 10% and over half of the values are below 5%. Thus, from the point of view of random error, there is no reason to discriminate between the procedures. However,

Table 7 Ranges of the relative standard deviation associated with subdivision of laboratory samples before and after drying

Compost lot	*RSD_{subd}*				
	<5%	*5–10%*	*10–15%*	*15–25%*	*>25%*
Drying before subdivision					
Wijster	Cr, Pb, Zn	—	—	—	Cu
Purmerend	Cu, Zn	Cr	—	Pb	—
Purmerend	Cr, Zn	Pb	Cu	—	—
Drying after subdivision					
Wijster	Zn	Pb, Cr	Cu	—	—
Wijster	Cr, Pb, Zn	—	Cu	—	—
Purmerend	Cu	Cr, Pb, Zn	—	—	—
Purmerend	Cr, Cu, Pb, Zn	—	—	—	—

subdivision before drying has the practical advantage that less material has to be dried.

An indication for RSD_{subd} based on the arithmetic mean over all results is, that it will range from 5 to 8%. It can be concluded that compost laboratory samples are so inhomogeneous that the subdivision step, necessary when applying to the planet ball mill, results in a random error of at least the same magnitude as for analysis of test portions obtained by the cross beater mill. As the use of the cross beater mill does not require subdivision, this way of particle size reduction may be even preferable. However, to arrive at conclusions regarding this aspect, a larger number of subdivision experiments has to be performed. Therefore, a large-scale experiment has been set up in order to establish the subdivision error in combination with the examination of the error associated with the withdrawal of increments from a lot. Five different lots of compost were examined. From each lot 12 laboratory samples were withdrawn and subsequently subdivided and analyzed. The results will be presented in a future paper which includes the comparison of various individual sampling schemes on the basis of the precision of the final analytical data.

CONCLUSIONS

Particle size reduction of the laboratory sample is a necessary step to attain sufficient homogeneity of the test sample, i.e. to ensure that the random error associated with the heterogeneity of the test sample, s^2_{hetr}, is not a dominant factor in s^2_{anal}. It appears that milling in a planet ball mill during 20 min is sufficient to attain the degree of homogeneity aimed at, but the relatively small capacity of the planet ball mill requires subdivision of the laboratory sample. Subdivision generates an additional random error, s^2_{subd}. Preliminary results indicate that s^2_{subd} constitutes a non-negligible contribution to the total error. This may lead to a reconsideration of the conclusion regarding the preference of the planet ball mill

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over the cross beater mill. In order to enable an unambiguous assessment of individual sampling schemes additional information on s^2_{subd} is a prerequisite.

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References

1. J. W. A. Lustenhouwer *et al.*, *Intern. J. Env. Anal. Chem.*, in press.
2. BCR Information No. 143 (Commission of the European Communities, Luxembourg, 1983).
3. H. Muntau, EC Joint Research Centre, Ispra, personal communication.
4. K. E. Lorber and G. Kümmlee. In: *Kompostierung von Abfälle 2* (EF-Verlag, Berlin, 1985), pp. 495–526.
5. K. E. Lorber. In: *Kompostierung und Brennstoffgewinnung* (EF-Verlag, Berlin, 1983), pp. 747–773.

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