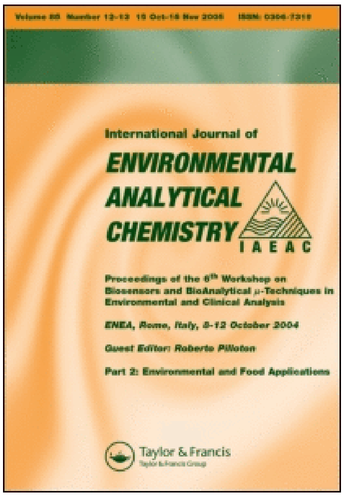

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Characterization of Compost with Respect to its Content of Heavy Metals. Part I: Sample Digestion and ICP-AES Analysis

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CHARACTERIZATION OF COMPOST WITH RESPECT TO ITS CONTENT OF HEAVY METALS.
Part I: Sample Digestion and ICP-AES Analysis

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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. An unambiguous analytical procedure must be available to enable supervision of the observance of the legal regulations on maximum tolerable content of heavy metals. The present study deals with the element determination stage, including the digestion of a test portion and the element determination in the test solution. Aqua regia digestion was examined using conventional as well as microwave heating. It is shown that the performance of both procedures is similar with respect to accuracy and precision. Microwave heating was preferred because that procedure is less time-consuming. Simultaneous determination of the elements Cr, Cu, Ni, Pb and Zn by ICP-AES was feasible. However, due to the occurrence of severe spectral interferences, Cd had to be determined separately.

KEY WORDS: Compost, heavy metals, digestion, ICP-AES.

INTRODUCTION

In recent years the Dutch policy on management of household waste has been increasingly directed towards recycling. As about one half of the household waste collected consists of kitchen left overs, yard waste, and animal dung, composting might be an important step in the direction of recycling. However, there is a growing concern on the quality of compost, especially with regard to its content of heavy metals. Therefore a decree by the Dutch Government is in preparation in which values will be given for maximum tolerable levels of heavy metals in compost[1,2] (see Table 1). To make such requirements operational, a total analytical procedure must be available. In addition, the accuracy and precision of the recommended procedure must be under experimental control.

A total analytical procedure includes sampling, sample preparation and analysis. The variance (s^2_{total}) of the eventual analytical result can be divided into contributions associated with the individual steps that form part of the total analytical

Table 1 Provisional values ($\mu g\, g^{-1}$ dry matter) for Dutch tolerable levels of heavy metals in compost

Element	*Short-term*	*Long term*
Cd	3	2
Cr	300	200
Cu	500	300
Ni	60	50
Pb	600	200
Zn	1300	900

procedure. Diagram 1 lists the various steps involved (nomenclature according to Ref. 3) and the components of variance, which are defined as:

s^2_{sampl}: total variance associated with sampling;
s^2_{incr}: variance associated with withdrawal of increments from the lot;
s^2_{subd}: variance associated with subdivision of laboratory sample;
s^2_{anal}: total variance associated with analysis of test portions;
s^2_{hetr}: variance associated with rest heterogeneity after sample preparation;
s^2_{det}: variance associated with element determination in a homogeneous test sample;
s^2_{dig}: variance associated with digestion of test portions;
s^2_{ICP}: variance associated with ICP measurement in test solutions.

In three successive papers various aspects of the total analytical procedure for determining heavy metals in compost will be treated. In the present paper the analysis stage will be discussed, comprising digestion of test portions and the determination of heavy metals in the corresponding test solutions by inductively coupled plasma—atomic emission spectroscopy (ICP-AES). The reason to start with the analysis stage is that data on the imprecision of sampling and sample preparation can be established only if the precision of the analysis of test portions is known. In order to ensure that the results have general validity within the scope of the aim intended, analysis has been studied for a variety of types of composts as well as for a sewage sludge amended soil.

Instrumental Method of Determination

ICP-AES was the instrumental method of choice as this method allows rapid simultaneous multi-element determination. The method provides an extended linear dynamic range and is suitable for the determination of a large number of elements. Since the composition of the inorganic matrix of compost varies, correction for matrix effects may be required.[4,5]

Digestion

Several evaluations of digestion procedures for compost have been reported in the

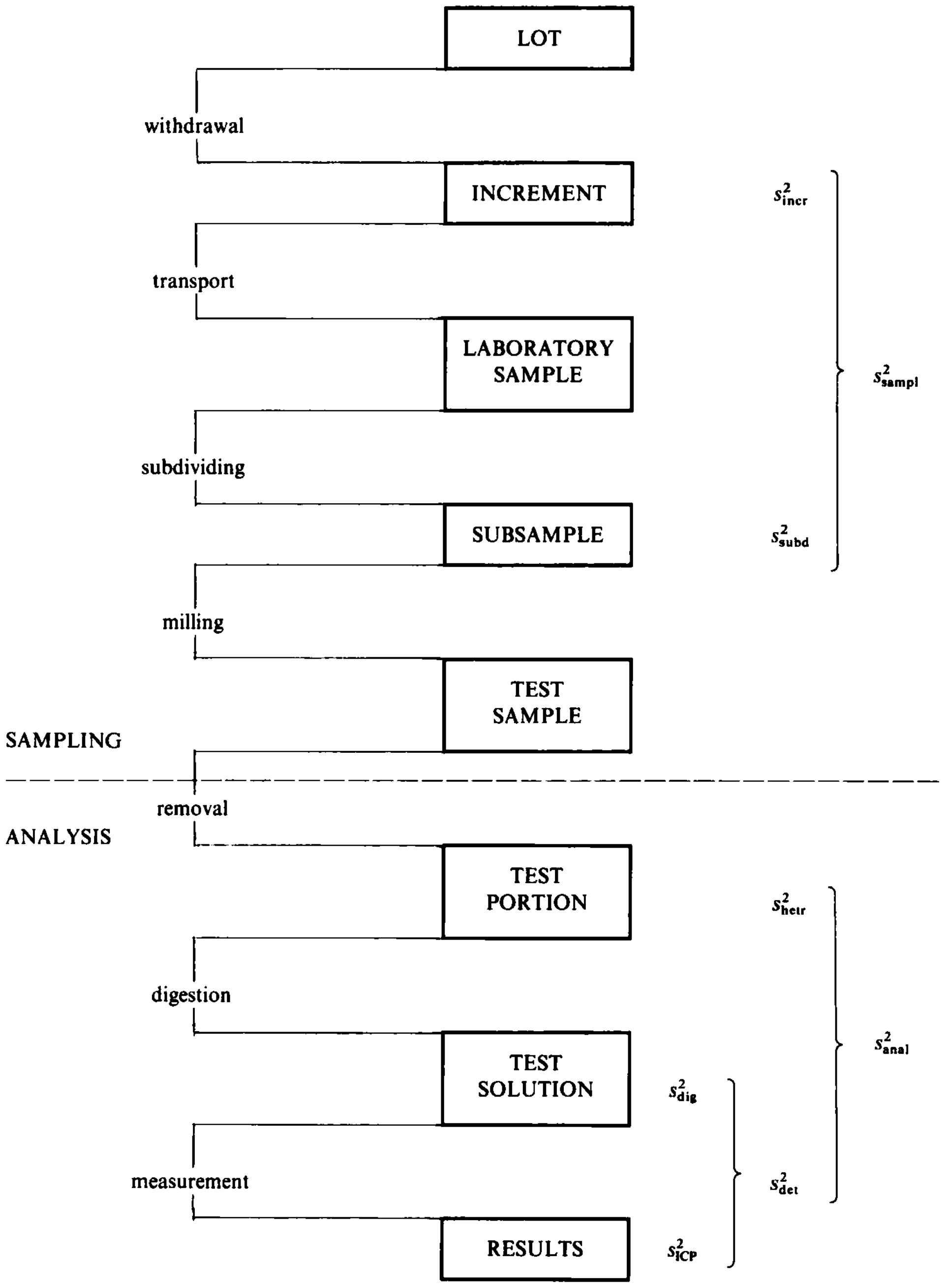

Diagram 1 TOTAL ANALYTICAL PROCEDURE

Table 2 Heavy metals in CW1 for aqua regia digestion, according to Ref. 10

Element	*Content* ($\mu g\,g^{-1}$)	*Standard deviation* ($\mu g\,g^{-1}$)
Cd	6.6	1.8
Cr	177	56
Cu	705	183
Ni	253	42
Pb	1609	108
Zn	1816	238

literature.[6-11] In general, authors agree that wet digestion is preferable to dry ashing.[6-9]. However, no common opinion exists with regard to the nature of the acids to be used. Muntau[10] as well as Cottenie[11] state that aqua regia should be preferred in standard procedures. Christensen[6] compared digestion with HNO_3 and with aqua regia. This author concludes that aqua regia yields the most satisfactory results. From results of preliminary investigations performed in the present study it was concluded that digestion with aqua regia and with HNO_3 results in comparable recoveries of trace metals but that the repeatability is better in the case of aqua regia.[12] Therefore, aqua regia was used as the digesting agent.

Digestion by conventional as well as by microwave heating was examined. Microwave heating is a very fast method that has successfully been used for the digestion for a variety of materials[13-15] and has therefore been examined for the digestion of compost.

To keep random error due to rest heterogeneity of the test sample to a minimum, the precision of the analysis stage was studied using next to homogeneous reference materials. As a consequence only approximate values of s^2_{dig} will be obtained.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade (Merck, Darmstadt, FRG).

Types of Materials Analyzed

The following materials were considered.

Composted garbage CW1, supplied by the E.C. Joint Research Centre Ispra (Ispra, Italy). CW1 is a compost which has been analyzed in an extensive interlaboratory study. The relative standard deviation due to inhomogeneity is less than 2% for the elements considered in the present study.[10,16] Table 2 lists the content of heavy metals and the corresponding standard deviations found for digestion of CW1 with aqua regia.[10]

Table 3 Heavy metals in RM No. 143, according to Ref. 17

Element	*Certified value*		*Soluble in aqua regia*	
	Content ($\mu g g^{-1}$)	*s.d.* ($\mu g g^{-1}$)	*Content* ($\mu g g^{-1}$)	*s.d.* ($\mu g g^{-1}$)
Cd	31.4	2.2	31.5	2.0
Cr			208	20
Cu	236.5	14.7	236	13
Ni	99.5	9.2	92.7	4.7
Pb	1333	65	1317	55
Zn	1272	53	1301	60

Sewage sludge amended soil RM No. 143, a reference material supplied by the E.C. Bureau of Reference (BCR, Brussels, Belgium). The relative standard deviation due to inhomogeneity is less than 3.3% for the elements considered in the present study.[17] Table 3 lists certified values for content of heavy metal and corresponding standard deviation (s.d.) for RM No. 143 as well as values reported in the same study obtained after digestion with aqua regia.[17]

Compost Wijster, a compost produced from the compostable fraction of household waste obtained after sieving and magnetic removal of iron objects.

Compost Soest-Baarn, a compost produced from mixed household waste by the DANO-process.[18]

Compost Nuenen, a compost produced from vegetable, fruit and garden waste from households, separated at the source in the community of Nuenen (the Netherlands).

Compost Amsterdam, a compost produced from vegetable, fruit and garden waste from households, separated at the source in the outskirts of the city of Amsterdam (the Netherlands).

All materials were used studying possible background enhancement in ICP-AES. The materials CW1 and RM No. 143 were used in assessing accuracy and precision of the digestion procedure.

Instrumentation

A Philips Compact AVM702 (1100 W, 2450 ± 50 Hz) microwave oven was used. The ICP-AES equipment was a Jarrell-Ash Division AtomScan 2000 (sequential ICP-system) and a Jarrell-Ash model 975 Plasma AtomComp (simultaneous ICP-system). For experimental conditions, see Ref. 4. Table 4 presents the wavelengths of the analysis lines used. The spectral lines were selected in such a way that spectral interferences from Fe lines are avoided.

Digestion Procedures

i) Aqua regia, conventional heating In a roundbottom flask, 1.5 g of compost were

Table 4 Analysis lines used

Element	*Species*[a]	*Wavelength* (*nm*)
Cd	I	228.803
Cr	II	267.716
Cu	I	324.754
Ni	I	341.476
Pb	II	220.353
Zn	I	213.856

[a] I: atom; II: ion.

heated with 30 ml of aqua regia (25% conc. HNO_3 + 75% conc. HCl) under reflux conditions for 2.5 h. After cooling the mixture was filtered over a Millipore filter (1.2 μm). The filtrate was made up to 100 ml.

ii) Aqua regia, microwave heating In an Erlenmeyer flask, 30 ml of aqua regia were added to 1.5 g of compost. The flask was placed in the glass-lined microwave oven and heated for 15 min under suction. After cooling the mixture was filtered over a Millipore filter (1.2 μm). The filtrate was made up to 100 ml.

Analysis of Variance

In order to distinguish in s^2_{det} contributions resulting from the digestion, s^2_{dig}, and the ICP-AES measurements, s^2_{ICP}, the following experimental set-up was chosen. For a test sample, eight test portions were digested and each test solution was analyzed in quadruplicate by ICP-AES. Thus, eight groups of four test results were obtained to which oneway analysis of variance was applied, providing values for s^2_{det}, s^2_{dig} and s^2_{ICP}.

Homogeneity of variance was checked using Cochran's *c*-test and Barlett-Box *F*-test.

RESULTS AND DISCUSSION

ICP-AES: Background Enhancement

The elements Al, Ca, Fe and Mg are major constituents of mineralized compost. These elements inevitably lead to enhancement of the spectral background. Preliminary investigations showed that the relative contribution of the background enhancement to the gross line intensity ranged from a few per cent up to 20% for the various materials considered. So, corrections for background have to be made.

The procedure for background correction will be illustrated for "Amsterdam" and "Wijster" compost. These materials are typical for compost gained from source-separated and mechanically separated garbage and represent future Dutch compost materials.

Figure 1 shows spectra in the vicinity of the analysis lines (cf. Table 4) obtained with test solutions resulting from aqua-regia-digested "Amsterdam" compost.

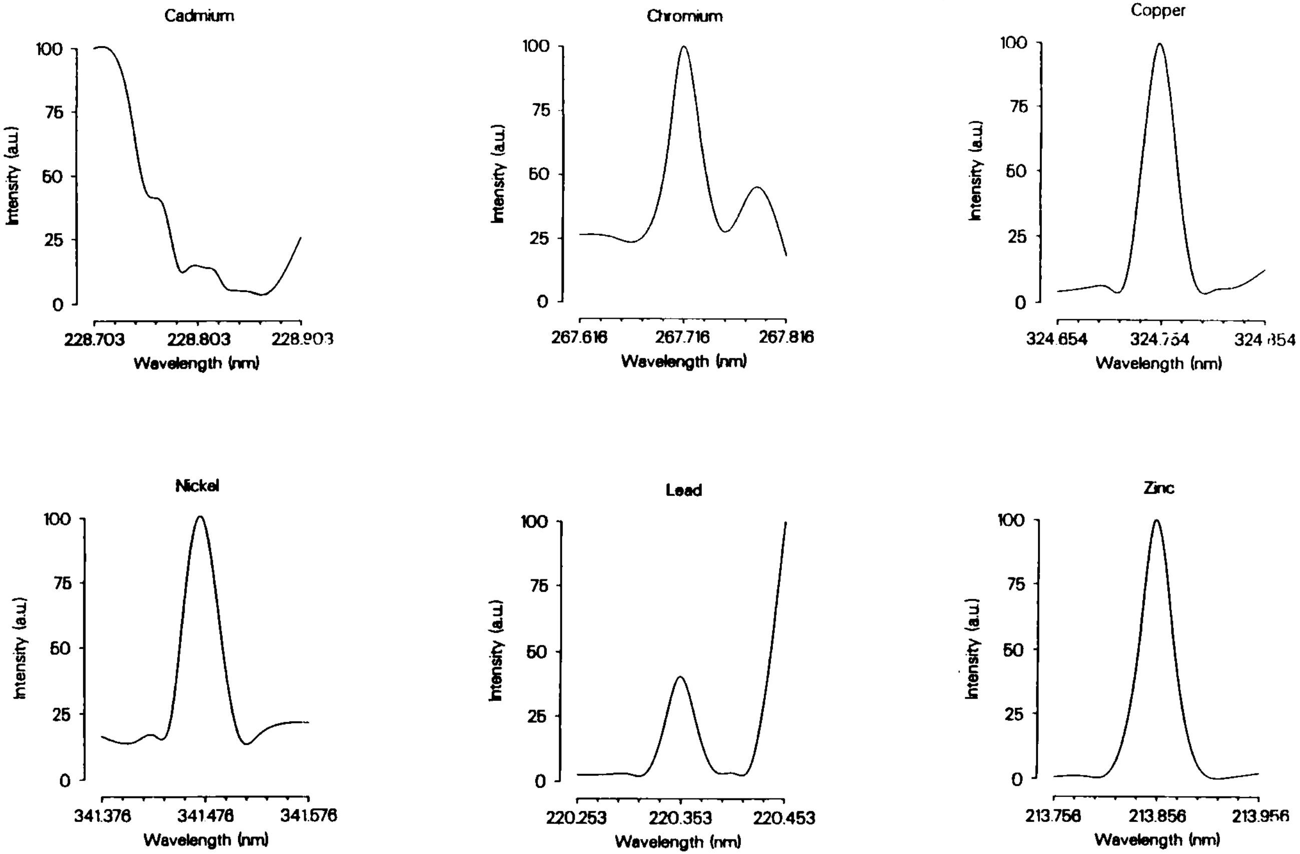

Figure 1 First-order spectra of the test solution of "Amsterdam" compost in the vicinity of the analysis line.

Similar spectra for "Wijster" compost are shown in Figure 2. From the spectra it becomes apparent that for all but the analysis line of Cd suitable wavelength positions for background correction are located at a distance of about 0.07 nm lower than the wavelength of the analysis line. This means that for all trace metals but cadmium, the background can be measured simultaneously.

The determination of cadmium was also examined by making use of the sequential ICP system. This instrument permits the application of a higher-order spectrum, resulting in a better spectral resolution. Figure 3 shows spectra for test solutions resulting from aqua regia digestion of "Amsterdam" and "Wijster" compost in the vicinity of the Cd analysis line applying second order measurements. The spectra show that the Cd analysis line in the second order is sufficiently separated from the Fe lines and that suitable background correction is feasible at a position 0.03 nm higher than the wavelength of the analysis line.

The findings about background correction stated above were confirmed by ICP measurements of test solutions of the other types of compost mentioned in the experimental section.

Digestion Procedure

In Table 5 the results of conventional and microwave heating for digestion of CW1 are presented; Table 6 does so for RM No. 143. The results of the multiplicate digestions are presented in terms of the average metal content found ($\mu g\,g^{-1}$ dry matter) and the standard deviations associated with digestion of test samples (s_{dig}), ICP measurement (s_{ICP}) and element determination of a homogeneous test sample (s_{det}). Comparison of the digestion methods used is made in terms of accuracy and precision.

Accuracy was assessed by checking whether the 95% confidence interval for the reference materials overlap with the 95% confidence interval for the experimental values of the present study. An overview is given in Table 7 for CW1 and in Table 8 for RM No. 143.

For CW1 95% confidence intervals overlap in all cases. For RM No. 143 this is so for all elements except lead (conventional heating). From these results it can be concluded that both methods show a similar performance in terms of accuracy. As a result of an interlaboratory imprecision component, the standard deviations reported by the suppliers of CW1 and RM No. 143, are considerably larger than the corresponding values observed in this study.

Precision of digestion was assessed by comparison of s_{det} values reported in Tables 5 and 6, using the F-test. The results are presented in Tables 9 and 10 for CW1 and RM No. 143, respectively. For both materials it can be concluded that the precision of the two digestion procedures is similar.

From Tables 5 and 6 it can also be seen that s_{dig} is notably larger than s_{ICP}. As a consequence, it is pointless to consider the use of more precise methods of determination.

As stated before, values for s_{dig} and s_{det} obtained in this study are approximations because the assumption that the reference materials are homogeneous is, strictly spoken, not fully true. From the Tables 9 and 10 it can be seen that the

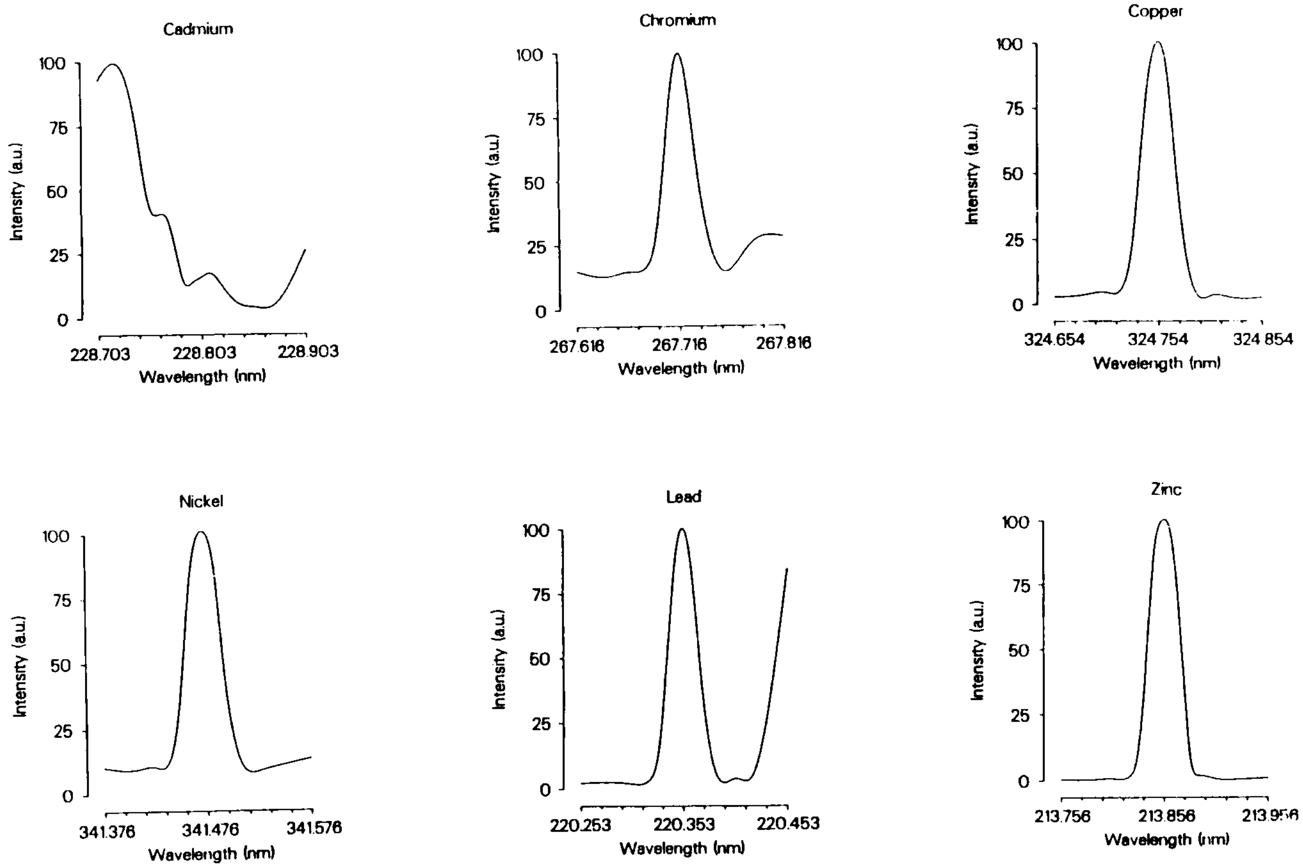

Figure 2 First-order spectra of the test solution of "Wijster" compost in the vicinity of the analysis line.

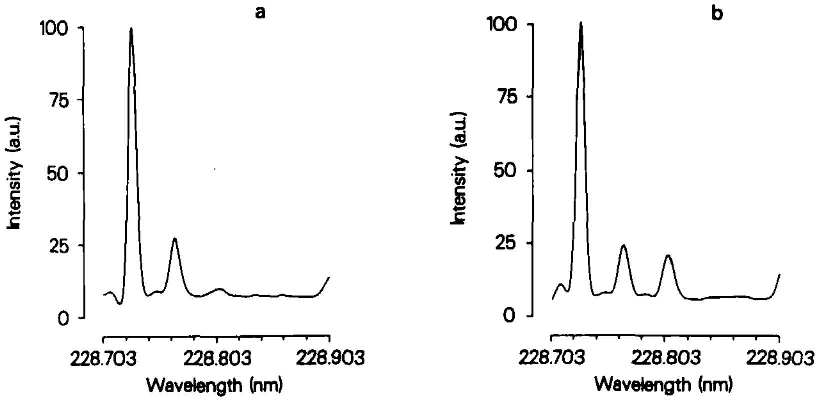

Figure 3 Second-order spectra of the test solution of (a) "Amsterdam" and (b) "Wijster" compost in the vicinity of the analysis line of Cd.

Table 5 Results of element determination for CW1 by conventional heating and by microwave heating ($\mu g\, g^{-1}$ d.m.)

		Conventional heating			
Element	*n*	*Average*	s_{dig}	s_{ICP}	s_{det}
Cd	8	4.6	0.07	0.13	0.15
Cr	8	179	5.8	2.8	6.5
Cu	8	570	20.8	5.2	21.5
Ni	8	237	5.0	3.5	6.1
Pb	8	1410	49.6	9.2	50.4
Zn	8	1640	75.4	13.8	76.6

		Microwave heating			
Element	*n*	*Average*	s_{dig}	s_{ICP}	s_{det}
Cd	8	4.6	0.22	0.15	0.27
Cr	7[a]	168	4.6	3.3	5.7
Cu	8	600	14.1	5.1	15.0
Ni	8	238	4.2	3.8	5.7
Pb	8	1420	62.4	22.0	66.2
Zn	8	1580	77.1	13.7	78.3

[a] One outlier (determined with Dixon's test) omitted.

approximate values for RSD_{det}—actually representing the composite error due to inhomogeneity, digestion and ICP measurement—in general range from 3–5%. Reported *RSD* values due to inhomogeneity of the reference materials are 2 and 3.3% for CW1 and RM 143, respectively. From these observations it can be concluded that inhomogeneity of the reference materials is not a dominant factor in RSD_{det}. Therefore, it seems reasonable to assume that the RSD_{det} values obtained in the study of the reference materials set a minimum for RSD_{anal} values to be expected for homogeneous compost materials. This assumption was used in

Table 6 Results of element determination for RM No. 143 by conventional heating and by microwave heating ($\mu g\,g^{-1}$ d.m.)

		Conventional heating			
Element	*n*	*Average*	s_{dig}	s_{ICP}	s_{det}
Cd	8	27.5	0.37	0.42	0.56
Cr	8	167	6.1	3.9	7.2
Cu	7[a]	226	12.0	4.2	12.8
Ni	8	102	3.7	3.4	5.0
Pb	8	1040	45.9	20.8	50.4
Zn	8	1190	20.4	16.5	26.2

		Microwave heating			
Element	*n*	*Average*	s_{dig}	s_{ICP}	s_{det}
Cd	8	27.9	0.95	0.39	1.0
Cr	8	163	4.5	2.2	5.0
Cu	8	224	6.6	2.8	7.1
Ni	8	95	5.6	3.4	6.5
Pb	8	1170	31.6	12.5	34.0
Zn	7[a]	1230	23.7	10.0	25.7

[a] One outlier (determined with Dixon's test) omitted.

Table 7 Accuracy check for digestion procedures (sample, CW1; $\mu g\,g^{-1}$ d.m.)[a]

Element	*Reference values (soluble in aqua regia)*		*Observed values*			
			Conventional heating		*Microwave heating*	
	$M-2S$	$M+2S$	$m-2sm$	$m+2s$	$m-2s$	$m+2s$
Cd	3.0	10.2	4.3	4.9	4.0	5.1
Cr	65	289	166	192	157	179
Cu	339	1070	527	613	570	630
Ni	169	337	225	249	226	250
Pb	1390	1830	1310	1510	1290	1550
Zn	1340	2290	1490	1790	1420	1740

[a] *M*: reported mean; *S*: reported standard deviation; *m*: observed mean; *s*: observed standard deviation (s_{det}).

a study of sample preparation of compost, the results of which will be published in a future paper.

CONCLUSIONS

Aqua regia digestion using conventional or microwave heating show similar performance in terms of accuracy and precision. It can therefore be concluded that

Table 8 Accuracy check for digestion procedures (sample, RM No. 143; $\mu g\,g^{-1}$ d.m.)[a]

Element	*Reference values (soluble in aqua regia)*		*Observed values*			
			Conventional heating		*Microwave heating*	
	$M-2S$	$M-2S$	$m-2s$	$m+2s$	$m-2s$	$m+2s$
Cd	28	36	26	29	26	30
Cr	168	248	153	181	153	173
Cu	210	262	200	252	210	238
Ni	83	102	98	108	83	108
Pb	1210	1430	940	1140	1100	1240
Zn	1180	1420	1140	1240	1180	1280

[a] *M*: reported mean; *S*: reported standard deviation; *m*: observed mean; *s*: observed standard deviation (s_{det}).

Table 9 Comparison of precision of digestion procedures (sample, CW1)

Element	*Digestion method*		F^a
	Conventional (RSD_{det}, %)	*Microwave* (RSD_{det}, %)	
Cd	3.2	5.9	3.22
Cr	3.6	3.4	1.30
Cu	3.8	2.5	2.05
Ni	2.6	2.4	1.14
Pb	3.6	4.7	1.73
Zn	4.7	5.0	1.04

[a] No significant values ($\alpha = 0.05$) observed.

Table 10 Comparison of precision of digestion procedures (sample, RM No. 143)

Element	*Digestion method*		F^a
	Conventional (RSD_{det}, %)	*Microwave* (RSD_{det}, %)	
Cd	2.0	3.7	3.42
Cr	4.3	3.1	2.08
Cu	5.7	3.2	3.25
Ni	4.8	6.8	1.71
Pb	4.8	2.8	2.93
Zn	2.2	2.1	1.04

[a] No significant values ($\alpha = 0.05$) observed.

Table 11 Content of heavy metals in various Dutch composts ($\mu g\,g^{-1}$ d.m.)

Element	*Compost*			
	Soest-Baarn	*Wijster*	*Nuenen*	*Amsterdam*
Cd	2.3	1.5	0.3	0.9
Cr	25.2	24.4	9.7	15.2
Cu	154	207	13.8	32.3
Ni	23.9	35.8	4.2	13.3
Pb	323	387	22.2	122
Zn	465	541	85.4	177

microwave heating is a useful method for wet aqua regia digestion of compost. The advantage of being notably less time-consuming compared to conventional heating makes microwave heating the preferable method.

Rapid determination of elements in the compost test solution by ICP-AES is feasible. The resolving power of spectrometers most frequently used in ICP-AES permits the simultaneous determination of the elements Cr, Cu, Ni, Pb and Zn using the instrument in the first spectral order. However, due to spectral interferences by iron lines, Cd determination requires second-order spectral measurements.

ICP-AES is sufficiently precise, as the dominant part in the standard deviation associated with element determination is caused by the digestion step.

The recommended method—viz. microwave digestion in an aqua regia medium followed by ICP measurement—was applied to determine the heavy metal content of some Dutch composts (see Table 11). The results show that compost with a low content of heavy metals can be obtained by means of separation at the source of compostables. Only then the lead content in compost can meet the long-term tolerable levels (see Table 1). It can also be concluded that the heavy metal content in CW1 is so high that this reference material does not seem to be representative for composts that will be produced in the future in the Netherlands.

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