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Comparison of Methods for Preparation of Municipal Compost for Analysis of Metals by Atomic Absorption Spectrophotometry

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Four digestion methods were examined for determination of cobalt, nickel, chromium, cadmium, lead, copper, zinc, manganese, iron, potassium, sodium, calcium, and magnesium in municipal compost (refuse/sludge) samples by atomic absorption spectrophotometry. The four methods examined were: (1) dry ashing followed by digestion with aqua regia, (2) digestion with aqua regia, (3) digestion with nitric acid, and (4) digestion with nitric acid followed by treatment of the residual by sulfuric acid and dry ashing. Based on results concerning observed metal concentrations, precision, and recovery of digested standard solutions, dry ashing was found to be an inefficient digestion method, while the other three methods were comparable. Digestion with aqua regia may have a small advantage compared to digestion with nitric acid and digestion with nitric acid followed by dry ashing.

Milling of the compost samples prior to digestion improved the precision for the alkali- and the earth-alkali metals but increased the chromium content of the compost because of wear on the milling equipment.

KEY WORDS: Municipal compost, sample digestion, sample homogenization, metal determination, atomic absorption spectrophotometry.

INTRODUCTION

Characterization of municipal compost (a mixture of refuse and sewage sludge) in terms of heavy metal content is of major importance when compost is disposed of on land intended for agricultural production. The use of atomic absorption spectrophotometry for analytical determination of the metals is predominating in the investigations reported in the literature. But several different methods are used for treatment of municipal compost samples prior to the analytical determination. The treatment involves a possible homogenization or milling and a digestion of the samples. Homogenization or milling of the samples may allow the use

of subsamples for the digestion. The digestion methods basically involve either dry ashing, aqua regia, nitric acid, or sequential use of two or more acid or oxidising agents, but many variants exist due to variations in specified concentrations, temperature, pressure, and time. A recent interlaboratory comparison on metals in a finely ground compost sample¹ has revealed high over-all variations in measured metal concentrations, which to some extent may be due to the use of different digestion methods at different laboratories.

The question on milling of the compost sample prior to digestion is closely related to the substantial inhomogeneity of the compost, while the question on digestion of the sample prior to metal analysis is partly analogous to the question on analysis of metals in sewage sludge. The latter question has been investigated extensively by several authors (e.g. confer Christensen *et al.*²), but no recommendable digestion method has yet been agreed upon. Methods useful for digestion of sewage sludge may, on the other hand, not necessarily show useful for digestion of municipal compost, which contains metals in fractions of plastics, printed matter, magazines, and discarded metallic products.

The aim of this article is to evaluate a few potential methods for digestion of municipal compost samples prior to metal determination. Furthermore, the effect of milling of the samples prior to digestion is investigated.

LITERATURE

A few evaluations of digestion methods for compost samples have been reported in the literature, partly by means of statistical examination of results from an interlaboratory comparison, and partly by means of parallel digestions of several identical samples by different digestion methods at a single laboratory.

Muntau and Leschber state in their summary¹ of a recent European interlaboratory comparison involving 39 laboratories, that aqua regia is suitable for digestion of municipal compost samples and sewage sludge samples. However, statistical tests (approximative *t*-test) of the observed average compost metal concentrations after exclusion of extreme observations support no preference of aqua regia to nitric acid or dry ashing.

Rosopulo and Scholl³ compared the digestion of compost by a dry ashing and a wet ashing method with respect to Pb, Cd, Cr, Ni, Cu, Zn, and Mn. The wet ashing (a mixture of sulphuric, nitric, and perchloric acid) was considered to be a better method than the dry ashing (450°C, followed by hydrochloric acid and redissolution in nitric acid) for all

elements but Pb. The coefficients of variation were of the order of 3–15%. Grabner *et al.*⁴ compared dry ashing (500°C, dissolution in nitric acid), aqua regia (25% HNO_3 + 75% HCl), and wet ashing by nitric + perchloric acid with respect to Cr, Cu, Pb and Fe, and found that dry ashing resulted in much lower concentrations than the other methods. An extensive investigation (13 metals) of the wet ashing by nitric + perchloric acid, which they apparently preferred, showed that the amount of acids added to the samples and the control of the digestion temperature were major factors for obtaining good precision. Andersson⁵ found that treatment with sulphuric acid and dry ashing of the residuals from nitric acid extraction of compost increased the observed metal concentrations of Cd (28%), Cr (25%), Mn (22%), Ni (20%), Co (9%), Zn (6%), but decreased the concentrations of Cu (–22%) and Pb (–13%).

As indicated by the above summarized investigations, no firm basis exists for selection of a proper method for digestion of municipal compost prior to metal analysis by atomic absorption spectrophotometry.

No information has been found in the literature on the effect of homogenization or milling of the compost prior to digestion.

EXPERIMENTAL

The investigation reported in this article involved four digestion methods: (1) dry ashing, (2) aqua regia, (3) nitric acid, and (4) nitric acid + dry ashing. The digestions were accomplished on a compost sample and on standards. Furthermore, the effect of milling the compost prior to digestion was investigated in the case of digestion method (4): nitric acid + dry ashing. The investigated metals were: Co, Ni, Cr, Cd, Pb, Cu, Zn, Mn, Fe, K, Na, Ca and Mg.

Digestion Methods

(1) Dry ashing: In a quartz crucible compost was ashed at 450°C for 1 hour. The crucible was transferred to a hot plate (100°C), 10 ml of aqua regia (25% HNO_3 + 75% HCl) was added, and the crucible was covered with a watch glass. After 30 minutes another 10 ml aqua regia was added. After another 60 minutes the watch glass was removed, and the sample evaporated to a low volume. The residual was dissolved in 1.4 N HNO_3 and filtered. Dilution to volume (200 ml) with 1.4 N HNO_3 . The low ashing temperature should limit the loss of Cd, and extraction of the residuals with aqua regia should recover Cu better than extraction with nitric acid.⁴

(2) Aqua regia: In an Erlenmeyer flask compost was repeatedly treated at near boiling with 10 ml of aqua regia (25% HNO_3 + 75% HCl), until the organic matter was mineralized. During the digestion the Erlenmeyer flask

was covered with a watch glass. The sample was evaporated to near dryness, redissolved in 1.4 N HNO_3 and filtered. Dilution to volume (200 ml) with 1.4 N HNO_3 . The method is modified after Delfino and Enderson.⁶

(3) Nitric acid:⁵ In an Erlenmeyer flask (supplied with a watch glass) compost was treated at 100°C with 10 ml of conc. HNO_3 per g of sample. The digestion continued until brown nitrous-oxide fumes ceased, but at least for 5 hours. Approximately 8 ml of deionized, distilled water was added per g of sample, the sample was filtered and diluted to volume (200 ml) with 1.4 N HNO_3 .

(4) Nitric acid + dry ashing:⁵ After treatment of the sample as described in method (3), the filter paper and residuals were transferred to a quartz crucible. 10 ml $4\text{ N H}_2\text{SO}_4$ was added and the crucible kept at 130°C overnight. This was followed by ashing at $450\text{--}500^\circ\text{C}$ for 45 minutes. After cooling, 15 ml 4.7 N HNO_3 was added, the crucible covered with a watch glass and heated for 45 minutes at near boiling. After filtering, the sample was diluted to volume (200 ml) with 1.4 N HNO_3 .

Analytical Procedures

Flameless atomic absorption spectrophotometry (Perkin-Elmer 370, HGA 76, deuterium background corrector) was used for determination of Co, Ni, and Cr. Flame atomic absorption spectrophotometry (Perkin-Elmer 300S) was used for determination of Cd, Pb, Cu, Zn, Mn, Fe, K, Na, Ca and Mg. The specific instrumental conditions are found in Table I and II.

Samples, Standards, etc.

The compost investigated originated from two full scale plants receiving municipal refuse and sewage sludge. The compost had passed magnetic separation equipment and coarse sieves at the plants, so only minor pieces of metals and plastics were visible in the compost. The compost was dried at 105°C and thoroughly mixed before sampling. All digestions involving compost were accomplished in triplicate. Samples with no pretreatment in the laboratory in terms of milling contained 25 g of compost, while samples of milled compost contained 10 g of compost. The milling was accomplished on a micro hammermill (Culatti, Italy) with a 2 mm sieve. Prior to subsampling from the milled compost, the compost was wetted with deionised, distilled water and mixed thoroughly. The comparison of the digestion methods was accomplished on milled compost.

A mixed standard solution containing all 13 metals investigated was made up as a 1 N HNO_3 solution from industrial metal standards. This

TABLE I
Analytical operation conditions for flameless-AAS

Element	Line (nm)	Slit (nm)	Ashing ^a (°C)/sec	Atomizing ^{b,c} (°C)/sec	Standards mg/l
Co ^d	240.7	0.2	900/15	2500/5	0.05–0.25
Ni ^d	232.0	0.2	800/10	2500/4	0.05–0.25
Cr	357.9	0.7	1000/10	2500/4	0.01–0.05

^aIn the HGA cycle, all samples were dried at 175°C for 2 sec.

^bIn the HGA cycle, the argon flow was stopped during atomizing.

^cAtomizing was followed by 2500°C for 2 sec with argon flow.

^dExtracted by 2% DDDC in xylene before injections.

TABLE II
Analytical operation conditions for flame-AAS

Element	Line (nm)	Slit (nm)	Flame	Standards ^a (mg/l)
Cd	228.8	2	air/C ₂ H ₂	0.05–0.75
Pb	283.3	0.7	air/C ₂ H ₂	5–40
Cu	324.7	2	air/C ₂ H ₂	1–25
Zn	213.9	0.7	air/C ₂ H ₂	0.3–3
Mn	279.5	0.2	air/C ₂ H ₂	0.5–3
Fe	248.3	0.2	air/C ₂ H ₂	1–25
K ^b	766.5	0.7	air/C ₂ H ₂	0.5–5
Na ^c	588.6	0.7	air/C ₂ H ₂	0.1–2
Cd ^d	422.7	0.7	N ₂ O/C ₂ H ₂	1–15 ^b
Mg ^d	285.2	0.7	N ₂ O/C ₂ H ₂	0.5–15 ^b

^aStandards were adjusted to proper HNO₃ concentration.

^b0.2% Na was added to samples and standards.

^c0.2% K was added to samples and standards.

^d0.6% La and 0.1% Na were added to samples and standards.

mixed standard solution was added to blind reference digestions, which were accomplished in duplicate.

All plastic and glass ware used was soaked overnight in 3 N HNO₃ and thoroughly rinsed in deionised, distilled water.

If not stated otherwise, all reagents were of analytical grade.

RESULTS

The results of the triplicate digestions of milled compost are shown in Table III in terms of average observed metal concentrations and in Table

IV in terms of coefficients of variation expressed relative to the observed averages. In Table III, the observations marked with A are significantly higher than the observations (for the same element) marked with B, which furthermore are higher than the ones marked with C. An approximate *t*-test and a 90% significance level have been applied. It is seen that no single digestion method always yielded the highest metal concentrations, and hence that none of the investigated digestion methods was the most efficient for all elements. Defining an efficiency of the individual digestion method by expressing the observed metal concentration relative to the highest concentration found for a specific element by the four digestion methods helps generalizing the results. In Table V the elements are grouped in heavy metals, manganese/iron, and alkali/earth-alkali metals with and without potassium, and the average digestion efficiencies are calculated for these groups. Method (2): aqua regia and method (4): HNO₃ + dry ashing showed the best over-all (13 elements) efficiencies of 95%, while method (1): dry ashing showed the lowest over-all efficiency of 84%. Aqua regia showed for no elements efficiencies lower than 88%, which may make this digestion method more suitable than method (4): HNO₃ + dry ashing, which in two cases showed lower efficiencies: 77% for Co and 86% for Ni. Method (3): HNO₃ resulted in low concentrations for Co, Ni, Cd and Fe.

TABLE III

Observed metal concentrations in municipal compost by four sample digestion methods (average of 3 replicates of 10 g of milled compost)

Element	(1) Dry ashing μg/g		(2) Aqua regia μg/g		(3) HNO ₃ μg/g		(4) HNO ₃ + ashing μg/g	
Co	4.35	A	4.75	A	3.4	C	3.65	B
Ni	70	A	76		59	B	65	A
Cr	245	B	335	A	340	A	380	A
Cd	4.5	C	5.7	A	5.3	B	6.2	A
Pb	535	C	600	B	680	A	690	A
Cu	250	B	315	A	305	A	310	A
Zn	1710		1735		1730		1740	
Mn	700	B	765	B	845	A	845	A
Fe	8090	A	8450	A	7100	B	7660	
K	2790	C	4550	B	4790	AB	4970	A
Na	4375	A	4180		3920	B	4110	
Ca	21150	B	21100	B	24150	A	24200	A
Mg	1885	C	2040	AB	1935	B	2010	A

A, B, C: Observations marked with A are significantly higher than the observations (for the same element) marked with B, which furthermore are higher than the ones marked with C. An approximate *t*-test and a 90% significance level have been applied.

TABLE IV

Relative coefficients of variation (C.V., %) for observed metal concentrations in municipal compost by four sample digestion methods (3 replicates of 10 g of milled compost). Averages of observed concentrations are found in Table III

Element	(1) Dry ashing C.V., %	(2) Aqua regia C.V., %	(3) HNO ₃ C.V., %	(4) HNO ₃ + ashing C.V., %
Co	13.0 ^a	8.5	1.3	0.9
Ni	6.8	24.1 ^a	2.8	4.6
Cr	10.9 ^a	7.1	14.3 ^a	11.3 ^a
Cd	9.8	4.3	5.8	9.1
Pb	7.3	7.5	8.5	8.4
Cu	9.1	5.4	5.7	5.6
Zn	14.1 ^a	6.8	5.8	5.7
Mn	2.9	7.7	1.2	1.2
Fe	3.7	7.9	8.7	7.3
K	3.9	6.9	3.3	3.6
Na	5.0	7.3	9.2	8.6
Ca	4.2	6.6	0.8	0.7
Mg	2.0	5.3	1.3	2.2

^aCoefficients of variation are considered to be unsatisfactorily high. No statistical considerations attempted, since estimates are based on only 3 replicate samples.

TABLE V

Average digestion efficiencies^a of four compost sample digestion methods for groups of investigated elements

Digestion efficiency ^a (average)	(1) Dry ashing %	(2) Aqua regia %	(3) HNO ₃ %	(4) HNO ₃ + ashing %
Co, Ni, Cr, Cd, Pb, Cu, Zn	82.2	95.3	88.4	94.4
Mn, Fe	89.3	95.3	92.0	95.4
K, Na, Ca, Mg	84.0	93.6	95.2	98.1
Na, Ca, Mg	93.2	92.9	94.8	97.5
All 13 elements	83.8	94.7	91.1	95.7

^aDigestion efficiency is calculated for a specific element as observed metal concentration divided by the largest metal concentration observed for the four methods investigated. Basic data from Table III.

The coefficients of variation as shown in Table IV were for methods (2), (3) and (4) in general of the same order of magnitude: 2–9%, while method (1): dry ashing for several metals seemed to be less precise. The extremely high uncertainty for Ni for aqua regia digestion may be due to an error and may explain the low efficiencies for methods (3) and (4) in the case of Ni.

The recoveries of known amounts of metals added to blind reference digestions are shown in Table VI. Recoveries within 90–110% are considered acceptable. No statistical test can reasonably be used to identify the recoveries deviating from 100%, since only duplicate digestions were accomplished. The results are blurred by significant uncertainty, in particular for Cr. The low recovery of Cd for method (1): dry ashing is consistent with the low Cd concentration found in the compost for this digestion method. This latter fact may disqualify dry ashing digestion of compost, since Cd most likely is the element of most environmental concern when compost is disposed of on land.

The results of the investigation of the effect of milling the compost samples prior to digestion is presented in Table VII in terms of average metal concentrations and coefficients of variation with and without milling

TABLE VI
Recovery (%) of a mixed metal standard added to blind reference digestion (average of duplicates)

Element	(1) Dry ashing %	(2) Aqua regia %	(3) HNO ₃ %	(4) HNO ₃ + ashing %
Co	102.3	105.8	96.3	96.8
Ni	^a	^a	^a	^a
Cr	139.5 ^b	122.5 ^b	96.0	96.0
Cd	80.7 ^b	91.7	100.6	100.6
Pb	101.3	101.8	101.4	101.4
Cu	97.8	98.9	94.5	94.5
Zn	97.1	98.4	105.6	105.7
Mn	100.3	96.7	104.3	104.3
Fe	102.6	99.4	94.0	94.0
K	97.4	98.0	97.5	97.5
Na	104.0	103.5	89.9 ^b	90.1
Ca	97.4	97.8	109.6	109.6
Mg	104.0	105.9	99.2	99.2

^aUncertainty about the absolute recovery. Aqua regia showed about 20% higher recovery than the other methods.

^bThe recovery is worse than 90–110% of the added metal.

(3 different compost samples each with 3 replicates) and in Table VIII in terms of observed ratios of concentrations of milled samples to concentrations of untreated samples. Furthermore Table VIII shows the average coefficients of variation for milled and untreated samples. From Table VII it is seen that for only Cr consistent and significant differences between milled and untreated samples were found. The milled samples showed more than twice the Cr content of the untreated samples. This is

TABLE VII

Observed metal concentrations in municipal compost with and without milling of samples prior to digestion (method 4). The metal concentrations are averages of 3 replicates. Milled samples contained 10 g of compost and samples with no treatment contained 25 g of compost

Element	Treatment ^a	Sample 1		Sample 2		Sample 3	
		Average µg/g	C.V. %	Average µg/g	C.V. %	Average µg/g	C.V. %
Co	M	2.7	8	2.9	18	3.6	20
	NT	2.8	11	3.2	1	4.5 ^b	16
Ni	M	53 ^b	3	114 ^b	15	59	24
	NT	44	11	84	17	64	33
Cr	M	175 ^b	35	245 ^b	3	115 ^b	12
	NT	85	10	67	3	65	12
Cd	M	10.0	54	11.0 ^b	19	8.5	13
	NT	6.5	58	5.5	7	11.0 ^b	9
Pb	M	530	7	560 ^b	3	740	1
	NT	600	24	440	18	820 ^b	2
Cu	M	160	7	840	110	1450	95
	NT	235	67	1995	49	1290	62
Zn	M	1620	15	1350	22	1540	9
	NT	1470	4	1170	3	1680	11
Mn	M	690	2	440	13	550	9
	NT	760 ^b	10	350 ^b	4	500	5
Fe	M	8600	13	14400	22	14800	9
	NT	9400	10	11300	9	14100	7
K	M	4610	3	3320	3	3250	2
	NT	4540	6	3080	13	3150	11
Na	M	3770 ^b	4	2800 ^b	6	3520	1
	NT	3490	7	2120	12	3600	16
Ca	M	22000	8	23200	6	28800	11
	NT	23500	23	24100	15	28300	11
Mg	M	770	6	1170	14	1400	8
	NT	700	43	1190	24	1500	22

^aTreatment prior to digestion: M=milling, NT=no treatment.

^bObservations marked with b are significantly higher than the corresponding observation with opposite treatment. An approximative t-test and a 90% significance level have been applied.

TABLE VIII

Comparison of metal concentrations in municipal compost determined with and without milling of samples prior to digestion (method 4). Basic data from Table VII.

Element	Ratio of "Milled" to "No Treatment"					Coefficients of variation (%)	
	sample 1	sample 2	sample 3	\bar{X}	C.V.	"Milled"	"No Treatment"
Co	0.97	0.92	0.79	0.89	0.09	15.3	9.4
Ni	1.20	1.36	0.94	1.17	0.22	13.9	20.1
Cr	2.07	3.69	1.79	2.52	1.03	16.6	8.1
Cd	1.57	2.00	0.79	1.45	0.61	28.5	24.6
Pb	0.87	1.27	0.90	1.02	0.22	3.5	14.7
Cu	0.69	0.42	1.12	0.74	0.36	70.3	59.2
Zn	1.11	1.16	0.91	1.06	0.13	15.3	6.1
Mn	0.90	1.28	1.11	1.10	0.19	8.0	6.2
Fe	0.91	1.27	1.05	1.08	0.18	14.7	13.6
K	1.02	1.08	1.03	1.04	0.03	2.7	10.1
Na	1.08	1.32	0.98	1.13	0.18	3.6	11.6
Ca	0.93	0.96	1.02	0.97	0.04	8.5	16.2
Mg	1.10	0.99	0.93	1.01	0.09	9.0	29.7

probably due to wear on the hammers of the micro mill. The observed effect may be specific for the type of micro mill used in this investigation, but points the attention to the problem of affecting the metal content of the compost samples when milling is applied as a treatment method prior to digestion. Table VIII shows that milling of the samples consistently improved the precision of the determination of only the alkali and earth-alkali metals. Milling of compost samples prior to metal analysis is thus not recommendable when focus is on the heavy metal content. It should be noted that the untreated samples contained 25 g of compost and the milled samples only 10 g of compost.

CONCLUSION

Comparison of four methods for digestion of compost samples prior to determination of Co, Ni, Cr, Cd, Pb, Cu, Zn, Mn, Fe, K, Na, Ca and Mg by atomic absorption spectrophotometry showed that dry ashing is unsuitable as digestion method, because of low digestion efficiency for several metals and an unsatisfactory precision. Of the other three methods investigated ((2) aqua regia, (3) nitric acid, and (4) nitric acid + dry ashing), aqua regia and nitric acid + dry ashing yielded the most satisfactory

results. The digestion efficiency for aqua regia was for no elements worse than 88%, which may make this digestion method slightly more suitable than nitric acid + dry ashing for municipal compost samples.

Milling of the compost samples prior to digestion is hardly recommendable since the milling only improved consistently the precision of the determination of K, Na, Mg and Ca, and because of the fact that wear on the mill, used in this investigation, enriched the compost sample with Cr.

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