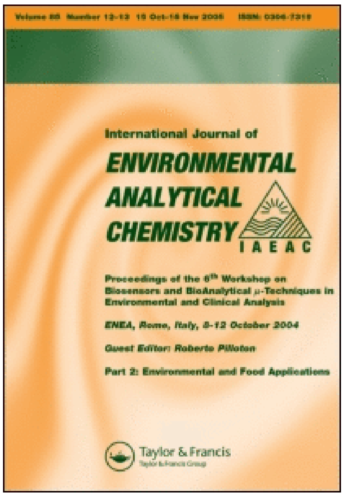

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Comparison of Four Methods for Digestion of Sewage Sludge Samples for Analysis of Metals by Atomic Absorption Spectrophotometry

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Four digestion methods were examined for the determination of cobalt, nickel, chromium, cadmium, lead, copper, zinc, manganese, iron, potassium, sodium, calcium, and magnesium in sewage 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, recovery of digested standard solutions, recovery of metal standards added to sludge samples, time consumption and laboratory safety, digestion of sewage sludge with nitric acid is considered to be the best method for routine measurements of metals by atomic absorption spectrophotometry.

KEY WORDS: Sewage sludge, sample digestion, metal determination, atomic absorption spectrophotometry.

INTRODUCTION

Characterisation of sewage sludge in terms of heavy metal content is of major importance when sludge is disposed of on land intended for agricultural production. The use of atomic absorption spectrophotometry for an analytical determination of the metals is predominating in the investigation reported in the literature. But several different methods are used for digestion of the sludge samples prior to the analytical determination.[1] The methods used basically involve either dry ashing, aqua regia, nitric acid, or sequential use of two or more acids or oxidising agents, but many variants exist due to variations in specified concentrations, temperature, pressure, and time. Several interlaboratory comparisons of metals in sewage sludge[1-4] have 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.

In order to make analytical results on metals in sewage sludge more comparable, it has been proposed, e.g. by COST 68 working party (EEC),[5] that one single method should be recommended as a standard digestion method. Aqua regia has been proposed for a standard digestion procedure, but final agreement on which method to be recommended has not yet been reached.

The aim of this article is to evaluate a few potential methods for digestion of sewage sludge samples prior to metal determination.

LITERATURE

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

Based on a Nordic (26 laboratories) and a European (15 laboratories) interlaboratory comparison of metal determination in sewage sludge samples, Tjell[3,4] concluded that the most common digestion methods showed no significant differences in metal concentration levels. Muntau and Leschber state in their summary[1] of a recent European interlaboratory comparison involving 39 laboratories, that aqua regia is suitable for digestion of sewage sludge samples. However, statistical tests (approximative *t*-test) of the observed average metal concentrations after exclusion of extreme observations support no preference of aqua regia to nitric acid. Both methods yielded higher metal concentrations of Pb, Ni, Cu, and Cr—but not of Cd, Co, and Zn—than obtained with dry ashing of the sludge samples.

Ritter and co-workers[6] digested three different sludge samples by means of dry ashing, nitric + perchloric acid, nitric acid, aqua regia, and hydrofluoric acid. They found that dry ashing, nitric + perchloric acid, and hydrofluoric acid in general resulted in the same metal concentrations, while nitric acid and aqua regia resulted in lower concentrations of the investigated metals (Cd, Pb, Ni, Cu, Zn). Dry ashing was recommended due to speed of digestion and the high precision. Thompson and Wagstaff[7] investigated several digestion methods, including minor variants of the above mentioned five methods,[6] with respect to Cd, Pb, Ni, Cu, and

Zn. Dry ashing was abandoned because of low values for Cu and methods involving sulphuric acid because of low values for Pb. No major differences were found for the other methods: nitric acid, nitric acid + hydrogen peroxide, aqua regia, hydrochloric acid, nitric acid + perchloric acid, and hydrofluoric acid (no statistical test accomplished). The nitric acid digestion was recommended as an accurate, safe and rapid digestion for sludge. The results of Delfino and Enderson[8] on comparison of five methods for sludge sample digestion are difficult to evaluate because of substantial uncertainty. However, dry ashing was considered to be unreliable with respect to Cr, Ni, Mg, and Fe. Van Loon and co-workers[9,10] found that aqua regia and perchloric acid resulted in the same metal concentrations of Cd, Cr, Pb, Zn, and Cu, but that perchloric acid resulted in higher concentrations of Ni and Fe than aqua regia did. Andersson[11] found that dry ashing the residuals from nitric acid extraction of sludge increased the observed metal concentrations 14–19% for Pb, Co, Cd, Ni, and Cr but only 3–8% for Cu, Mn, and Zn. Lester and co-workers[12-14] found that dry ashing of sludge at 450°C resulted in lower concentrations of Cd, Cr, and Cu compared to digestions with nitric acid + sulphuric acid or with nitric acid + hydrogen peroxide. No differences were observed for Ni and Zn, while the nitric acid + sulphuric acid digestion gave very low results for Pb.

As indicated by the above summarized investigations, disagreement exists as to which method should be used for digestion of sludge samples prior to metal analysis by atomic absorption spectrophotometry. The apparent contradictory recommendations found in the literature are difficult to explain, although minor differences in equipment, concentrations of reagents, temperatures, reaction times, and biased habits may account for some of the discrepancies.

EXPERIMENTAL

The investigations 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 sewage sludge, standards, and sewage sludge enriched with standards. 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 2 g of sludge was ashed at 450°C for 1 h. 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 min another 10 ml of aqua regia was added. After another 60 min the watch glass was removed, and the sample evaporated to a low volume. The residual was dissolved in 1.4 N HNO_3, filtered and diluted to volume 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.[15]

(2) **Aqua regia:** In an Erlenmeyer flask 2 g of sludge 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, filtered and diluted to volume with 1.4 N HNO_3. The method is modified after Delfino and Enderson.[8]

(3) **Nitric acid:**[11] In an Erlenmeyer flask (supplied with a watch glass) 2 g of sludge was treated at 100°C with 20 ml of conc. HNO_3. The digestion continued until brown nitrousoxide fumes ceased, but at least for 5 h. Approx. 10 ml of deionized, distilled water was added, the sample was filtered and diluted to volume with 1.4 N HNO_3.

(4) **Nitric acid + dry ashing:**[11] After treatment of the sample as described in method (3), the filter paper and residuals were transferred to a quartz crucible. 10 ml 4 N H_2SO_4 was added and the crucible kept at 130°C overnight. This was followed by ashing at 450–500°C for 45 min. After cooling, 15 ml 4.7 N HNO_3 was added, the crucible covered with a watch glass and heated for 45 min at near boiling. After filtering, the sample was diluted to volume with 1.4 N HNO_3.

Analytical Procedures

The metals (Co, Ni, Cr, Cd, Pb, Cu, Zn, Mn, Fe, K, Na, and Mg) were determined by flame atomic absorption spectrophotometry (Perkin–Elmer 300 S). The specific instrumental conditions are found in Table I.

Samples, Standards, etc.

The sludge sample consisted of dried (105°C), anaerobically stabilised sludge that was ground and thoroughly mixed before sampling. The sludge samples were digested in triplicates.

A mixed standard solution containing all 13 metals investigated was made up as a 1 N HNO_3 solution from industrial metal standards. This mixed standard solution was added to blind reference digestions and to sludge amounting to approximately 50% of the sludge sample metal

TABLE I
Analytical operation conditions for flame-AAS

Element	Line (nm)	Slit (nm)	Flame	Standards[a] (mg/l)
Co	240.7	0.2	air/C_2H_2	1–10
Ni	232.0	0.2	air/C_2H_2	1–10
Cr	357.9	0.7	air/C_2H_2	1–10
Cd	228.8	2.0	air/C_2H_2	0.05–0.75
Pb	283.3	0.7	air/C_2H_2	5–40
Cu	324.7	2.0	air/C_2H_2	1–25
Zn	213.9	0.7	air/C_2H_2	0.3–3
Mn	279.5	0.2	air/C_2H_2	0.5–3
Fe	248.3	0.2	air/C_2H_2	1–25
K[b]	766.5	0.7	air/C_2H_2	0.5–5
Na[c]	588.6	0.7	air/C_2H_2	0.1–2
Ca[d]	422.7	0.7	N_2O/C_2H_2	1–15[a]
Mg[d]	285.2	0.7	N_2O/C_2H_2	0.5–15[a]

[a]Standards adjusted to proper HNO_3 concentration.
[b]0.2% Na added to samples and standards.
[c]0.2% K added to samples and standards.
[d]0.6% La and 0.01% Na added to samples and standards.

content. Digestions including standard addition were accomplished in duplicates.

All plastic and glass ware used was soaked overnight in 3 N HNO_3 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 a sewage sludge are shown in Table II in terms of average observed metal concentrations and in Table III in terms of coefficients of variation expressed relative to the observed averages. In Table II, 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 approximative *t*-test and a 95% 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 IV the elements are grouped in heavy metals, manganese/iron, and alkaline earth/alkali metals with and without potassium, and the average digestion efficiencies are calculated for these groups. Method (4), HNO_3 + dry ashing, showed the best over-all (13 element) efficiency of 95.6% while method (1), dry ashing, showed the lowest over-all efficiency of 87.1%. For the heavy metals, method (3), nitric acid, and method (4), were better (98–99% efficiency) than the other two methods (90–92% efficiency). Method (1) was in particular inefficient for Cr, Cd, and Cu, while method (2), aqua regia, was very inefficient for Co and Cr. All methods were better than 90% efficient for Mn and Fe, except for aqua regia in the case of Fe. For Ca and Mg all methods are considered acceptable with efficiencies better than 88%. For K and Na method (2) showed the highest concentrations. Especially K showed highly variable results, most probably a result of a varying degree of destruction of clay minerals present in the sludge.

The coefficients of variation as shown in Table III were in general very low for methods (3) and (4): 0.2–2%. Both method (1) and (2) showed high coefficients of variation for five and four elements respectively. This indicates that nitric acid or nitric acid + dry ashing are the most precise digestions methods of the four methods investigated.

TABLE II

Observed metal concentrations in sewage sludge by four sample digestion methods (average of 3 replicates)

	Metal concentration (μg/g) with method:			
Element	Dry ashing	Agua regia	HNO_3	HNO_3 + ashing
CO	113.5 B	91.0 C	115.5 B	118.5 A
Ni	370 B	375 B	375 AB	385 A
Cr	1090 C	865 C	1265 B	1280 A
Cd	66.1 C	71.9 B	75.3 A	75.3 A
Pb	1210 C	1340 A	1275 B	1275 B
Cu	985 C	1080 B	1140 A	1150 A
Zn	2215 C	2210 A	2165 B	2165 B
Mn	485 B	520 A	495 B	495 B
Fe	16590 B	13180 D	15500 C	17070 A
K	1650 C	3020 A	1460 C	2170 B
Na	700 B	1040 A	805 B	910 A
Ca	49850 B	48350 C	54800 A	54900 A
Mg	3435 C	3915 A	3475 C	3715 B

A, B, C: Observations marked with A significantly higher than the observations (for the same element) marked with B, which furthermore are higher than those marked with C. An approximative t-test and a 95% significance level have been applied.

TABLE III

Relative coefficients of variation (C.V.) for observed metal concentrations[a] in sewage sludge by four sample digestion methods

Element	C.V. (%) for metal concentrations with method:			
	Dry ashing	Aqua regia	HNO_3	HNO_3 + ashing
Co	1.9	2.0	0.2	0.5
Ni	0.9	0.9	1.3	1.3
Cr	7.9[b]	20.2[b]	0.5	0.5
Cd	0.5	0.9	0.3	0.3
Pb	0.5	1.0	0.9	0.9
Cu	3.8[b]	1.4	1.2	1.2
Zn	1.1	1.0	0.9	0.9
Mn	3.4[b]	3.3[b]	1.4	1.4
Fe	1.4	9.3[b]	0.2	0.4
K	11.7[b]	2.4	2.0	1.4
Na	5.7[b]	11.0[b]	0.2	1.7
Ca	0.5	0.8	1.8	1.8
Mg	2.2	0.1	0.9	1.5

[a]Averages of observed concentrations in Table II.
[b]Coefficients of variation considered to be unsatisfactorily high. No statistical considerations attempted, since estimates are based on only 3 replicate samples.

TABLE IV

Average digestion efficiencies[a] of four sludge sample digestion methods for groups of investigated elements

Elements	Digestion efficiency (%) with method			
	Dry ashing	Aqua regia	HNO_3	HNO_3 + ashing
Co, Ni, Cr, Cd, Pb, Cu, Zn	91.6	90.1	97.9	99.0
Mn, Fe	95.3	88.6	93.0	97.6
K, Na, Ca, Mg	75.1	97.0	78.6	88.6
Na, Ca, Mg	81.9	96.0	88.7	94.1
All 13 elements	87.1	92.0	91.2	95.6

[a]Digestion efficiency calculated for a specific element as observed metal concentration divided by the largest metal concentration observed for the four methods investigated.

TABLE V

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

	Recovery (%) of metal standard with method:			
Element	Dry ashing	Aqua regia	HNO_3	HNO_3 + ashing
Co	97.4	77.2[a]	94.1	94.1
Ni	99.0	97.4	104.9	104.9
Cr	97.0	87.3[a]	100.4	100.4
Cd	98.1	100.5	107.6	107.6
Pb	95.8	97.8	96.3	96.3
Cu	96.1	98.5	98.1	98.4
Zn	106.5	108.0	102.4	102.4
Mn	110.1[a]	91.0	113.2[a]	113.2[a]
Fe	99.7	87.8[a]	98.0	98.0
K	98.4	99.9	94.7	94.7
Na	97.0	102.6	99.4	99.4
Ca	103.5	97.1	105.9	105.9
Mg	97.3	104.5	100.7	100.7

[a]The recovery is worse than 90–110% of the added metal

TABLE VI

Recovery of a mixed metal standard added to sewage sludge samples digested by four methods (average of duplicates)

	Recovery (%) of metal standard with method:			
Element	Dry ashing	Aqua regia	HNO_3	HNO_3 + ashing
Co	96.6	132.3[a]	94.0	93.4
Ni	92.7	96.8	95.6	95.6
Cr	103.4	78.0[a]	93.3	94.8
Cd	88.0[a]	95.4	104.3	104.3
Pb	90.9	103.6	95.9	95.9
Cu	101.3	100.1	100.5	100.3
Zn	72.6[a]	89.7[a]	101.7	101.7
Mn	109.0	99.1	113.5[a]	113.5[a]
Fe	119.7[a]	—	103.0	98.2
K	84.5[a]	120.8[a]	107.9	101.1
Na	96.1	98.3	114.3[a]	108.0
Ca	103.9	103.0	112.6[a]	112.6[a]
Mg	106.7	122.7[a]	93.5	91.5

[a]The recovery is worse than 90–110% of the added metal.

The recoveries of known amounts of metals are shown in Table V for addition to blind reference digestions and in Table VI for addition to sewage sludge samples. 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 digestion method (2). The only substantial result from the standard addition experience is that methods (3) and (4) consistently showed good recoveries for the heavy metals: 94.1–107.6% recovery of additions to blind references, and 93.4–104.3% recovery of additions to sewage sludge.

CONCLUSION

Comparison of four methods for digestion of sewage sludge 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 digestion with nitric acid followed by dry ashing (method 4) gave the best results—in particular for the heavy metals, which are the elements of most environmental concern when sewage sludge is disposed of on land intended for agricultural production. This method resulted in the highest metal concentrations in general, in a low coefficient of variation, and in consistent and acceptable recoveries of standard additions. However the method is very time- and man-power-consuming, and it is therefore to be recommended only to use nitric acid digestion (method 3), which is identical to the first part of method (4), for routine determinations of metals in sewage sludge. Nitric acid digestion also resulted in consistent and acceptable recoveries of standard additions and in low coefficients of variation; concentrations were only 1–3% lower for the heavy metals and 5–12% lower for the other elements (except potassium) than obtained by nitric acid + dry ashing. Aqua regia (method 2) and dry ashing (method 1) are considered to be less suitable because of low digestion efficiencies for a few heavy metals, and because of inferior precision.

Nitric acid (method 3) is thus considered to be a fairly efficient method with good accuracy and precision and without severe laboratory safety problems for digestion of sewage sludge prior to determination of metals with atomic absorption spectrophotometry.

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