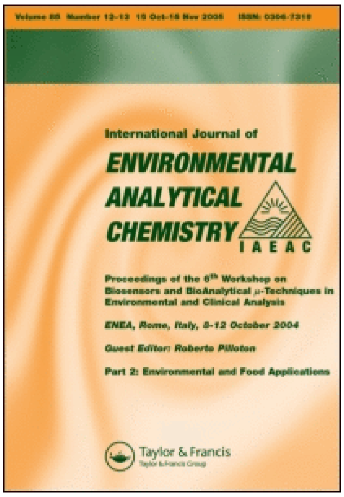

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Method for fractional solid-waste sampling and chemical analysis

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Method for fractional solid-waste sampling and chemical analysis

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Chemical characterization of solid waste is a demanding task due to the heterogeneity of the waste. This article describes how 45 material fractions hand-sorted from Danish household waste were subsampled and prepared for chemical analysis of 61 substances. All material fractions were subject to repeated particle-size reduction, mixing, and mass reduction until a sufficiently small but representative sample was obtained for digestion prior to chemical analysis. The waste-fraction samples were digested according to their properties for maximum recognition of all the studied substances. By combining four subsampling methods and five digestion methods, paying attention to the heterogeneity and the material characteristics of the waste fractions, it was possible to determine 61 substances with low detection limits, reasonable variance, and high accuracy. For most of the substances of environmental concern, the waste-sample concentrations were above the detection limit (e.g. $Cd > 0.001\,mg\,kg^{-1}$, $Cr > 0.01\,mg\,kg^{-1}$, $Hg > 0.002\,mg\,kg^{-1}$, $Pb > 0.005\,mg\,kg^{-1}$). The variance was in the range of 5–100%, depending on material fraction and substance as documented by repeated sampling of two highly different material fractions ('Vegetable food' and 'Shoes, leather, etc.'). Statistical analysis showed for the 'Vegetable food' that the variance could not be attributed to a single step in the procedure, whereas in the case of 'Shoes, leather, etc.', the first coarse shredding was the main source of variance (20–85% of the overall variation). Only by increasing the sample size significantly can this variance be reduced. The accuracy and short-term reproducibility of the chemical characterization were good, as determined by the analysis of several relevant certified reference materials. Typically, six to eight different certified reference materials representing a range of concentrations levels and matrix characteristics were included. Based on the documentation provided, the methods introduced were considered satisfactory for characterization of the chemical composition of waste-material fractions.

Keywords: Sampling solid waste; Solid-waste analysis; Theory of sampling; Direct waste analysis; Waste sampling; Waste analysis

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1. Introduction

Municipal solid waste is very heterogeneous, as it consists of many different large material fractions with different compositions and many small items of very specific composition. This makes chemical characterization of municipal solid waste difficult and costly. For example, a small piece of electrical wire accidentally mixed into a fraction of vegetable food waste would drastically affect the copper content of the vegetable food fraction, as determined by chemical analysis.

As waste management often involves source separation of specified material fractions for recycling or a central mechanical separation plant, information about the chemical composition of individual material fractions in the waste is often requested. The ability to take representative samples of individual material fractions and to perform reproducible chemical analysis of the samples is a prerequisite for obtaining reliable data to support sound decisions. In solid-waste characterization, standardized methods and well-documented case studies are few and are often limited to specific aspects. Jansen *et al.* [6] statistically demonstrated how the sampling of source-separated organic waste could be performed with good reproducibility.

This article describes how 61 chemical substances were determined in 45 waste fractions obtained by hand-sorting of Danish household waste. Subsampling procedures were developed and an array of digestion methods introduced. Repeated characterization and use of certified reference materials allowed statistical assessment of detection limits, variance, and accuracy.

The waste-material fraction samples studied were obtained from a study [1] that hand-sorted household waste from 1607 single-family dwellings and 603 multi-family dwellings into 45 material fractions, as shown in table 1. This article addressed only the handling of the material fractions after hand-sorting, thus excluding any consideration of the representativity of the original sample. The samples were deep-frozen until homogenization and subsampling.

2. Theory of sampling

To obtain a representative increment (subsample), structurally correct (unbiased) sampling must be performed in compliance with the Theory of Sampling (TOS) [1, 3]. This implies avoiding Incorrect Sampling Errors (ISE), which cover all mistakes in the sampling from the first increment to the result of the analysis. ISE will, if present, add a variance of unknown and undeterminable magnitude to the results. Assuming that these errors are avoided, the Relative Standard Deviation (RSD) of measurements consists of Fundamental Sampling Error (FSE), Group and Segregation Error (GSE), and Total Analytical Error (TAE). These errors describe the errors related to the material itself (FSE), the errors related to the interaction between fragments of the material (GSE), and the errors related to inaccuracies in analytical measurements (TAE). The concepts are described in detail in [1, 4]. FSE can be minimized by particle size (d) reduction and increasing sample mass (M_{E}) as stated by Gy's equation [5]:

$$\mathrm{FSE} = \sqrt{\frac{Cd^3}{M_{\mathrm{E}}}}, \quad C = c\beta f g, \tag{1}$$

Table 1. Analytical parameters determined for 45 fractions and sampling method used.[a]

No.	Sample fraction	Sampling method[b]	Digestion method[c]	Analytes quantified			
				A1	A2	A3	A4
1	Vegetable food waste	S2	D3	X		X	X
2	Animal food waste	S2	D3	X		X	X
3	Newsprints	S2	D3	X		X	X
4	Magazines	S2	D3	X		X	X
5	Advertisements	S2	D3	X		X	X
6	Office paper	S2	D3	X		X	X
7	Other clean paper	S2	D3	X		X	X
8	Paper and carton containers	S2	D3	X	X	X	X
9	Other cardboard	S2	D3	X	X	X	X
10	Milk cartons	S2	D3	X	X	X	X
11	Juice cartons	S2	D3	X	X	X	X
12	Other dirty paper	S2	D3	X		X	X
13	Other dirty cardboard	S2	D3	X		X	X
14	Kitchen tissues	S2	D3	X		X	X
15	Soft plastic	S3	D4	X			X
16	Plastic bottles	S2	D4	X			X
17	Other hard plastic	S2	D4	X			X
18	Non-recyclable plastic	S2	D4	X			X
19	Garden waste, flowers, etc.	S2	D3	X		X	X
20	Animals and excrements	S2	D3	X		X	X
21	Nappies and tampons	S2	D3	X			X
22	Cotton buds, etc.	S2	D3	X			X
23	Other cotton, etc.	S2	D3	X			X
24	Wood	S2	D3	X		X	X
25	Textiles	S3	D3	X			X
26	Shoes, leather	S3	D4	X			X
27	Rubber, etc.	S3	D4	X			X
28	Office articles, etc.	S2	D4	X			X
29	Cigarette butts	S2	D3	X			X
30	Other combustibles	S2	D3	X	X		X
31	Vacuum cleaner bags	S2	D3	X			X
32	Clear glass	S1	D1, D5				
33	Green glass	S1	D1, D5				
34	Brown glass	S1	D1, D5				
35	Aluminium containers	S4	D2	X	X		
36	Alu-trays, alu-foil	S4	D2	X	X		
37	Metal foil (-Al)	S4	D2		X		
38	Metal containers (-Al)	S4	D2		X		
39	Other metal	S4	D2		X		
40	Soil	S2	D3	X			
41	Rocks, stones, and gravel	S1	D1, D5				
42	Ceramics	S1	D1, D5				
43	Cat litter	S1	D1, D5	X		X	X
44	Other non-combustibles	S1	D1, D5	X	X		X
45	Batteries	S4	D2	X	X		X

[a] A1: heating value, C-total, H, O and S—A2: Al and Fe—A3: Ca, Na, N, P, K and F—A4: Cl—DEPH (plastic softener) was additionally measured in some fractions.

[b] Explanation in text.

[c] Explanation in table 2.

The material constant C is described by the constitution parameter (c), the liberation factor (β), the shape factor (f) and the size range factor (g). The descriptive parameters are explained in detail in [5].

GSE theoretically can be eliminated through homogenization, and TAE can be minimized through good analytical practice and determined by parallel measurements.

If ISE is avoided and GSE eliminated, the measured RSD is the sum of FSE and TAE. But in reality, there will always be an error in sampling which will result in a combination of GSE and ISE, simply because of human or systematic errors. The determination of RSD related to the different sampling steps and analytical errors provides the possibility of further development of the sampling procedures and thus is a contribution to the validation of the overall method.

3. Sampling method

Sampling is understood as the combination of cumminution (reduction of FSE), mixing (minimization of GSE), and representative mass reduction (elimination of ISE) to the mass of the final increment. Sampling can be conducted in multiple steps if necessary for technical, economic, or otherwise practical reasons. Failure to obtain 100% correct sampling will add ISE to the final RSD of measurements. For each step in the sampling, the variance can be determined by parallel increments. The variance of multiple steps of sampling is related to the total variance (RSD) as stated in equation (2), where i is the number of sampling steps, SD is the standard variation, and $\bar{x}$ is the mean.

$$\mathrm{RSD}_{\mathrm{final}} = \frac{\sqrt{\sum_i \mathrm{SD}_i^2}}{\bar{x}}. \qquad (2)$$

Four different types of cumminution equipment were used in order to deal with all the different material properties of the 45 material fractions: cutting with a cutting mill (Retch SM 2000, Haan, Germany) and an industrial shredder (ARP SC 2000, Brovst, Denmark), crushing with a rotary disc mill (Siebtechnik IS100A, Mülheim an der Ruhr, Germany), breaking with a jaw crusher (Retch, Haan, Germany) and fragmenting by drilling (titanium drill). Mass reduction was performed by a riffle splitter (Rationel Kornservice RK12, Esbjerg, Denmark). Mixing was performed using a mechanical mixer (Raimondi Iperbet 110, Modena, Italy) or by hand. Dry ice (CO_2 (s)) and liquid nitrogen (N_2 (l)) were used to obtain required properties for the size reduction and sampling, the dry ice was certified for food production as E290, and nitrogen was of analytical quality.

The cutter mill and rotary disc mill were with heavy metal-free coating (wolfram-carbon) on all ware parts. The mills were controlled for any ware in-between usage. Cleaning of equipment between samples was assessed to be of great importance to avoid cross-contamination, and therefore considerable time was spent on this procedure, treating 45 waste fractions in several pieces of equipment.

The choice of subsampling method was a function of the material properties of the individual fractions, grouping the 45 waste fractions into four categories according to common material properties (S1–S4) as can be seen in table 1. All waste materials were frozen before treatment and kept frozen by addition of dry ice to all steps of treatment, except rotary disc milling:

- S1: Brittle fractions (e.g. glass and stone) were particle-size-reduced by jaw-crushing down to a particle size of 10 × 10 mm and thereafter mixed, mass reduced to half the mass, and further crushed to a size of 1 × 1 mm in a rotary disc mill.

- S2: Cutable fractions (e.g. paper and plastic) were particle-size-reduced in an ARP CS 2000 shredder down to a size of 20 × 20 mm and then mixed, mass-reduced to half the mass, and further treated in a SM 2000 cutter mill to a size of 1 × 1 mm.
- S3: Elastic and heat sensitive fractions (e.g. rubber and thin soft plastic) were treated as S2 but additionally cooled by liquid nitrogen ($N_{2,l}$) to facilitate cutting. Large amounts of pulverized dry ice ($CO_{2,S}$) were added during handling to ensure sufficient cooling capacity.
- S4: Strong and composite fractions (metal and batteries) were mass-reduced by titanium drilling. This method was chosen because these fractions could not be shredded, cut, or crushed due to their strength. In composite fractions such as batteries, drilling was performed on all sides of the batteries, distributed according to the surface areas of the sides. Other fractions were drilled randomly over the entire surface.

Mixing and mass reduction were done in the same way for S1, S2, and S3 by repeated mixing in a mechanical mixer (or by hand) and then mass-reduced with a riffle splitter until the required mass for chemical analysis was obtained.

The strong and composite samples (S4) were split before treatment into representative subgroups which could each be further treated. After treatment, they were mixed again by hand and mass-reduced as for the other fractions.

4. Chemican-analytical method

4.1 *Instrumentation*

A microwave digestion unit (MARS 240/50, CEM Microwave Corporation, Matthews, NC) equipped with either a MarsX carousel consisting of 40 perfluroalcoxy (PFA) lined vessels or an HP500plus high-pressure carousel (10 vessels), and a Digester 1015 open-vessel digestion system equipped with an Autostep 1012 temperature controller (Tecator, Höganäs, Sweden) were used for sample digestion.

The ICP-SFMS instrument used was the ELEMENT (ThermoElectron, Finnigan MAT, Bremen, Germany) equipped with an ASX 500 sample changer (CETAC Technologies, Omaxa, NE) and HF-resistant introduction system. The ICP-OES was the OPTIMA 5000 (Perkin-Elmer, Wellesley, MA), Details on the operating conditions and measurement parameters can be found elsewhere [7].

4.2 *Reagents and reference materials*

All calibration and internal standard solutions were prepared by gradual dilutions of single-element standard solutions (1000 and 10,000 mg L^{-1}, SPEX Plasma Standards, Edison, NJ and Promochem AB, Ulricehamn, Sweden). Analytical-grade nitric acid (Merck, Darmstadt, Germany) was used after additional purification by sub-boiling distillation in quartz still. Analytical-plus-grade hydrochloric acid and SupraPure hydrofluoric acid (all from Merck) were used as supplied. The three-stage water-purification system consisted of an ion-exchange column (SeraDest), Milli-Q water purification system (Millipore Milli-Q, Bedford, MA) and sub-boiling distillation in Teflon stills (Savilex Corp., Minnetonka, MN). Water produced by this system is referred to as distilled deionized water (DDIW) and was used exclusively for dilution of samples, blanks, and standards.

The following certified reference materials were analysed: CRM 8414 Bovine Muscle Powder, CRM 1577a Bovine Liver, CRM 1547 Peach Leaves, CRM 614 Trace Elements in Glass Matrix (all from the National Institute of Standards and Technology, Gaithersburg, MD), NJV94-5 Wood Fuel (Swedish University of Agricultural Sciences, Uppsala, Sweden), CRM V-9 Cotton Cellulose (IAEA, Austria), SO-2 Reference Soil Sample (Canada Centre for Mineral and Energy Technology, Canada), BCR-681 Trace elements in Polyethylene (EU BCR, Geel, Belgium), and CRM 064-1 Nb/Ti Interstitial Free Steel (Bureau of Analysed Samples, Middlesbrough, UK).

4.3 *Sample preparation*

Taking into account the need for complete analyte recovery, the need for low limits of detection (LODs) and economic considerations (e.g. time and labour consumption, prevention of irreversible contamination of non-disposable digestion vessels, etc.), five different digestion methods were applied to oven-dried samples, as summarized in table 2. Further details concerning these digestion methods can be found elsewhere [7–9]. Internal standard (In) was added to all solutions at $25\,\mu g\,L^{-1}$ concentration. All sampling handling and analysis were performed in clean laboratory areas with a constant supply of HEPA-filtrated air.

It should be stressed that the requirement for quantitative analyte recovery combined with the wide element coverage cannot be accomplished by a single digestion method. Moreover, safe operation of high-pressure, closed vessel digestion systems puts constraints on the maximum sample size. Therefore, for selected sample types, several different digestion methods were used, and parallel preparations followed by combining of digests were performed, where the sample weight per digestion was below 0.6 g. Each digestion batch contained two preparation blanks and at least one reference material. Dilution of original digests with 1.4 M HNO_3 was used for solutions intended for ICP-OES measurements. For ICP-SFMS analysis, digests were diluted with 0.7 M HNO_3 to produce dilution factors ranging from 200 (food waste, all types of papers, cartons, cardboards, and textiles) to 20,000 (batteries).

Table 3 presents an example of calculating the Limit of Detection (LOD) as three times the standard deviation for nine digestion blanks for digestion procedures D3 and D4 (ICP-SFMS determination) analysed during three measurement sequences. Observed concentration ranges for the waste samples are given for comparison. For only 12 of 60 analytes tested were the waste sample concentrations for some material fractions below respective LODs.

5. Results

To validate the method of sampling and analysis, different approaches were used. To validate the sampling, parallel increments were obtained for all sampling steps for

Table 2. Details of operation conditions for digestion procedures.

Procedure	Sample size (g)	Reagents	Digestion conditions	Sample types
D1	0.8–1.2	5 mL HNO_3 + 5 mL HF	Open vessel, temperature 120°C, 72 h under reflux conditions, evaporation, dissolution in 7 M HNO_3	Glass, soils, ceramics, other non-combustibles
D2	1–1.5	10 mL HCl +3 mL HNO_3 + 0.1 mL HF	Open vessel, temperature 120°C, 24 h under reflux conditions	Metals and metal containers (including Al), batteries
D3	0.3–0.4	5 mL HNO_3 + 0.5 mL H_2O_2 + 0.03 mL HF	Microwave-assisted digestion, 600 W, temperature 140°C, $P < 1400$ kPa, 1 h	Food waste, all types of papers, cartons, cardboards, textiles, garden waste, soils, wood, cigarette butts, vacuum-cleaner bags, other combustibles
D4	0.3–0.4	5 mL HNO_3 + 0.03 mL HF	Microwave-assisted digestion, 1200 W, temperature 180°C, $P < 5200$ kPa, 1 h	All types of plastics, shoes, leather, rubber
D5	0.1	0.2 g $LiBO_2$	C crucible fusion, Temperature 1050°C, 45 min, dissolution of the bead in 0.7 M HNO_3	Glass, soils, ceramics, other non-combustibles

Table 3. Limits of detection (LOD) and concentration ranges for the waste samples.

		Waste samples	
Analyte	LOD (mg kg^{-1})	Min (mg kg^{-1})	Max (mg kg^{-1})
Ag	0.001	0.008	10
Al	0.3	70	900,000
As	0.02	<0.02	90
Au	0.001	<0.001	0.60
B	1	<1	700
Ba	0.03	0.5	7000
Be	0.02	<0.02	3
Bi	0.001	0.001	40
Br	2	<2	120
Ca	0.4	40	100,000
Cd	0.001	0.007	5000
Ce	0.001	0.02	3000
Co	0.01	0.04	5000
Cr	0.01	0.3	6000
Cs	0.0004	0.005	20
Cu	0.05	4	8000
Dy	0.0001	0.001	3
Er	0.00001	0.0007	2
Eu	0.0002	0.002	2
Fe	0.1	60	950,000
Ga	0.01	0.02	150
Gd	0.0002	0.002	150
Hg	0.002	0.002	8
Ho	0.00002	0.0003	0.5
I	1	<1	20
K	3	100	40,000
La	0.0003	0.01	2000
Li	0.03	0.06	600
Mg	2	100	15,000
Mn	0.03	2	220,000
Mo	0.003	0.1	2000
Na	2	100	50,000
Nb	0.0003	0.003	30
Nd	0.0003	0.01	1500
Ni	0.04	0.2	60,000
P	0.5	40	13,000
Pb	0.005	0.06	80,000
Pr	0.0001	0.003	500
Rb	0.007	0.07	100
Re	0.00001	<0.00001	0.1
S	4	50	8000
Sb	0.002	0.01	250
Se	0.1	<0.1	20
Si	50	<50	300,000
Sm	0.0001	0.002	3
Sn	0.02	0.04	6000
Sr	0.02	0.6	2000
Ta	0.01	<0.01	10
Tb	0.00004	0.0003	20
Te	0.002	<0.002	0.5
Th	0.002	0.005	6
Ti	0.2	1	4000
Tl	0.001	0.001	1
U	0.0002	0.007	6
W	0.001	0.01	130

(*Continued*)

Table 3. Continued.

		Waste samples	
Analyte	LOD ($\mathrm{mg\,kg^{-1}}$)	Min ($\mathrm{mg\,kg^{-1}}$)	Max ($\mathrm{mg\,kg^{-1}}$)
V	0.01	0.07	130
Y	0.0003	0.007	60
Yb	0.0003	<0.0003	2
Zn	0.1	3	250,000
Zr	0.01	0.07	200

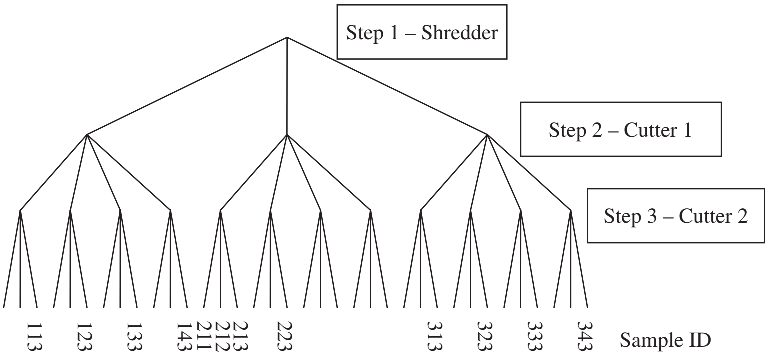

Figure 1. Design for analysis of variation for fraction 1 ‘Vegetable food waste’, including three steps.

two waste fractions: ‘Vegetable food’ and ‘Shoes, leather, etc.’. Validation of the sample digestion and analysis was performed by including eighth Certified Reference Materials (CRM) in parallel to the waste samples.

5.1 *Sampling validation*

The design for the analysis of variance in sampling of ‘Vegetable food (Material fraction 1) is shown in figure 1, and the design for ‘Leather, shoes etc.’ (Material fraction 26) is comparable with figure 1 but with four strings in step 2. Both designs are so-called staggered designs, which are aimed at analysing a hierarchical model in a reduced set-up. This test design has proven suitable for measurements of waste sampling variance [6]. The mathematical model for the measured values in both cases can be written as:

$$Y_{ijkl} = \mu + S_i + C(S)_{j(i)} + \varepsilon_{k(ij)}. \tag{3}$$

The purpose of the design is to split the variability experienced in the data into components of variance related to step 1 (S_i), step 2 ($C(S)_{j(i)}$) and from the chemical analysis level $\varepsilon_{k(ij)}$—step 3. μ is a constant, and the other terms in the model are assumed to be independent random variables with variances σ^2_{S}, $\sigma^2_{\mathrm{C(S)}}$, and σ^2_{ε}, respectively.

Using ‘Fe’ for ‘Vegetable food waste’ as a typical example, the (unbalanced) ANOVA (Analysis of variance) is as shown in table 4.

The variation of step 1 is tested against the step 2 variation, and the step 2 level variation is tested against the residual variation (ε). It is seen that the step 2 level variation is not significant, and so it can be removed from the model. The (approximate) test of step 1 variation shows a significant variation. A reduced ANOVA for this case is shown in table 5. The estimates of the components of variance are for Fe in vegetable food waste:

- step 1 $\sigma_{\mathrm{S}}^2 = (4910.08 - 545.50)/4 = 33.0^2$;
- residual $\sigma_{\varepsilon}^2 = 23.4^2$.

The interpretation of this result is that seemingly there is some variation between the results in step 1. This means that the waste is not completely homogeneous after the shredder has treated it (step 1). The analysis of 'Fe' in 'Leather and shoes' is slightly different because of the design used; see table 6. In this case, it is seen that neither the variation related to step 1 nor the variation related to the step 2 level is significant. The only remaining component of variance is the variation corresponding to the residual ε. Its variance estimate is $\sigma_{\varepsilon}'2 = 24{,}824{,}789/8 = 17{,}622 = 132.7^2$.

The above analysis was performed on all analytes. For some analytes, the variance of step 1 was significant, and for others the *p*-values were relatively small for both step 1 and step 2. To gain an overall picture, the procedure suggested by [6] was applied. We consider the *p*-values for the factor level (step 1 or 2). If, for one analyte, a small *p*-value

Table 4. Analysis of variance of 'Fe' in 'vegetable food' waste.

Source of variation[a]	df	EMS	*F*-value	*p*-value
S_i	2	$3.85\sigma_{\mathrm{S}}^2 + 1.3\sigma_{\mathrm{C(S)}}^2 + \sigma_{\varepsilon}^2$	8.22	0.015
$C(S)_{i(j)}$	7	$1.1\sigma_{\mathrm{C(S)}}^2 + \sigma_{\varepsilon}^2$	1.68	0.42
$\varepsilon_{k(ij)}$	2	σ_{ε}^2		
Total	11			

[a] The sources of variation in this case are shredder (S_i), cutter ($C(S)_{i(j)}$), and residual ($\varepsilon_{k(ij)}$).

Table 5. Analysis of variance of 'Fe' in 'Vegetable food' waste (reduced with one step).

Source of variation[a]	df	EMS	*F*-value	*p*-value
S_i	2	$4\sigma_{\mathrm{S}}^2 + \sigma_{\varepsilon}^2$	8.22	0.007
$\varepsilon_{k(ij)}$	9	σ_{ε}^2		
Total	11			

[a] The sources of variation in this case are shredder (S_i) and residual ($\varepsilon_{k(ij)}$).

Table 6. Analysis of variance of 'Fe' in fraction 'Shoes, leather, etc.' waste.

Source of variation[a]	df	EMS	*F*-value	*p*-value
S_i	3	$1.52\ \sigma_{\mathrm{S}}^2 + 1.05\ \sigma_{\mathrm{C(S)}}^2 + \sigma_{\varepsilon}^2$	0.39	0.77
$C(S)_{i(j)}$	3	$1.33\ \sigma_{\mathrm{C(S)}}^2 + \sigma_{\varepsilon}^2$	6.00	0.15
$\varepsilon_{k(ij)}$	2	σ_{ε}^2		
Total	8			

[a] The sources of variation in this case are shredder (S_l), cutter ($C(S)_{i(j)}$), and residual ($\varepsilon_{k(ij)}$).

is observed for the factor level, the corresponding variation is then statistically significant for that analyte. In table 4, for example, the p-value for the S_i variation is 0.015, indicating a significant ($\alpha = 0.015$) variation of 'Fe' related to the step 1. For the $C(S)_{j(i)}$ variation the p-value is 0.42, which indicates that little or no variation is related to step 2 for 'Fe'. If the p-values across the analytes for a level are generally small, the contents of the analytes are then unevenly distributed over the samples related to the level (step 1 or 2). Conversely, if the composition of the waste is not related to the level, the p-values will be uniformly distributed between 0 and 1. This hypothesis is tested using the standard Kolmogorov–Smirnov statistical test. For 'Vegetable food waste', the Kolmogorov–Smirnov tests are shown in figures 2 and 3.

Using 'Fe' for 'Vegetable food waste' as a typical example, the (unbalanced) analysis of variance ANOVA is as shown in table 4. The sums of squares and mean squares corresponding to the terms of the model are calculated by a general ANOVA technique. The expected mean square (EMS) column shows the theoretical value corresponding to the observed mean squares. Using the EMS column, proper statistical tests for the variance components can be constructed, and by equating the observed means squares with the theoretical mean squares these components can be estimated.

It can be seen that the hypothesis of uniformly (0,1) distributed p-values was accepted for step 2 for both types of waste but rejected for step 1 for 'Vegetable food' (but not for

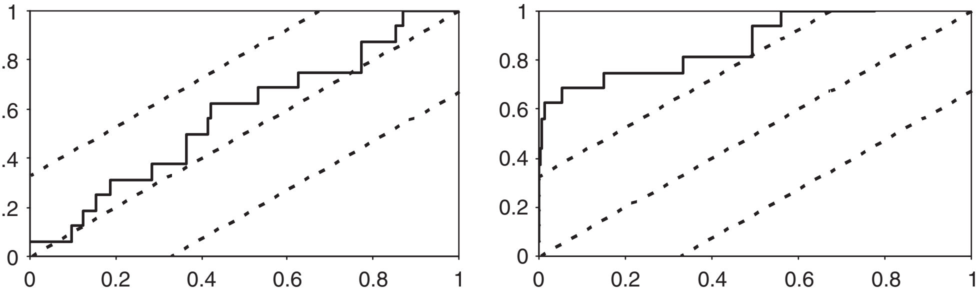

Figure 2. Illustration of the Kolmogorov–Smirnov test (Vegetable food waste) for step 1 (left) and step 2 (right), showing the empirical distribution of p-values (thick line) and 95% confidence limits (dotted lines). The x-axis shows observed p-values and the y-axis cumulative probability.

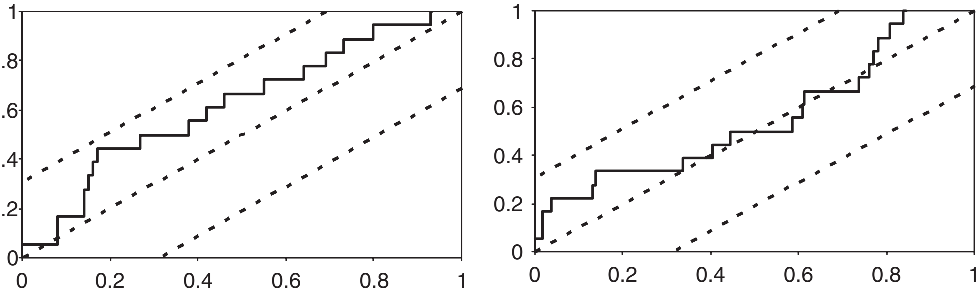

Figure 3. Illustration of the Kolmogorov–Smirnov test (Shoes and leather) for step 1 (right) and step 2 (left), showing the empirical distribution of p-values (thick line) and 95% confidence limits (dotted lines). The x-axis shows observed p-values and the y-axis cumulative probability.

Table 7. Relative sampling error (RSE) from ANOVA on sampling of two fractions and contribution by a sampling step 1 as a percentage of the total variance.

	Vegetable food		Shoes, leather, etc.
Analyte	Sampling step 1 (%)	Total (%)	Total (%)
S	56	2.29	5.4
Al	20	77.4	14.1
Fe	59	16.3	84.0
Ca	–	21.5	13.6
Na	85	6.25	4.3
Mg	74	5.00	6.6
P	47	1.70	7.7
K	77	9.79	9.0
As	–	–[a]	38.1
Cd	–	–[a]	12.7
Cr	85	116	9.7
Cu	–	5.99	84.9
Hg	37	46	20.1
Mn	67	7.3	32.7
Mo	58	17.2	27.7
Ni	–	20.2	28.3
Pb	–	19.6	9.5
Zn	62	7.0	13.0

[a] Affected by detection limits.

'Leather, shoes, etc.'). The critical limits correspond to a level of significance $\alpha = 0.05$ in all four cases. It is concluded that the vegetable food waste cannot be considered completely homogeneous after the shredder treatment (step 1). The step 1 accounts for 20–85% of the total variance in the analysis, as stated in table 7, where the total RSD of the two analysed fractions is also shown.

The results shown in table 7 indicate that the analytes likely to be found as primary liberated solid particles, such as a piece of solid metal, in the samples show substantially larger variances. Comparing the variances of the two fractions and measured concentration levels, it can be seen that for Al, Fe, Cr, Cu, Mn, and Mo, the variance is largest in the fraction with the highest fraction of liberate solid metal. This indicates that the liberation factor (β) plays a more important role than expected in the material constant C in equation (1). In fact, the liberation factor for fractions with a high fraction of liberated solid metal will have the liberation parameter as the determining factor for the overall heterogeneity. Normally, particle-size reduction is seen as the most important parameter in eliminating sample heterogeneity, but this does not reduce the material constant in equation (1), which was suggested above as very important in some fractions. Only chemical alternation of the sample or sorting out the solid particles will alter the material constant, but the total uncertainty might also be lowered by increasing the digested (sample) mass, M_{E}.

5.2 *Chemican-analytical validation*

The most straightforward approach for accuracy evaluation is the analysis of well-characterized CRMs with a matrix composition similar to the samples. In total, certificates for the eighth CRMs used to contain 220 certified, and recommended values

Table 8. Comparison between found and certified concentrations based on analysis of nine reference materials.

Analyte	N	Found *vs*. certified concentrations		
		Slope	Intercept (mg kg^{-1})	R^2
Ag	2	1.04	0.002	1
Al	6	1.02	−9	>0.999
As	6	0.95	0.1	>0.999
Au	3	1.07	−0.0003	>0.999
B	3	1.03	−0.2	>0.999
Ba	5	1.03	−2	>0.999
Be	1			
Bi	1			
Br	4	1.09	−3	0.998
Ca	6	1.04	−20	0.998
Cd	7	1.00	0.007	>0.999
Ce	3	1.01	−0.0002	>0.999
Co	6	0.97	0.2	0.998
Cr	8	0.98	0.8	0.999
Cs	2	1.08	−0.01	>0.999
Cu	8	1.03	0.05	>0.999
Eu	2	1.18	−0.001	1
Fe	6	1.02	2	>0.999
Gd	1			
Hg	6	1.02	0.003	>0.999
I	3	0.91	−0.02	0.994
K	6	1.01	−100	0.994
La	4	1.05	−0.02	>0.999
Li	2	0.95	0.002	1
Mg	6	1.04	−30	0.998
Mn	7	1.00	6	>0.999
Mo	6	0.97	−0.04	0.998
Na	6	1.03	−10	>0.999
Nb	3	1.06	0.0004	>0.999
Nd	3	0.93	−0.0003	>0.999
Ni	7	0.96	0.5	0.999
P	6	0.98	−40	0.999
Pb	9	1.06	−0.02	0.998
Pr	2	0.88	0.00002	1
Rb	5	1.05	−1	0.999
S	5	0.99	40	>0.999
Sb	4	1.07	0.003	>0.999
Se	3	0.98	−0.02	0.999
Si	3	1.08	−4	>0.999
Sm	1			
Sn	3	1.01	−0.006	>0.999
Sr	6	1.05	−2	0.998
Tb	1			
Th	4	1.04	0.004	>0.999
Ti	6	0.96	1	>0.999
Tl	3	0.98	−0.0002	>0.999
U	4	1.01	0.001	>0.999
W	2	0.88	−0.0001	1
V	5	0.99	−0.01	>0.999
Y	2	1.10	−0.001	1
Yb	1			
Zn	5	1.04	−0.5	0.999
Zr	1			

for 53 elements were used. Hence, the accuracy of the analytical procedures can be assessed for a relatively wide range of elements presented in these samples from sub-$\mathrm{ng\,g^{-1}}$ to % concentrations. Considering all results obtained for these reference materials, the weighed regression between certified and found values is given by the following equation (see table 8):

$$\text{Found}\ [\mathrm{mg\,kg^{-1}}] = (1.001 \pm 0.005) \times \text{certified}\ [\mathrm{mg\,kg^{-1}}] + (0.0001 \pm 0.0001)[\mathrm{mg\,kg^{-1}}],\quad R^2 = 0.9994. \tag{4}$$

Since both ICP-SFMS and ICP-OES results were available for a number of the elements analysed, cross-checking for accuracy of the instrumental determination was possible. Generally, where ICP-OES LODs were not limiting, results obtained by the two ICP techniques agreed well (data not shown). Measurement precision, assessed as the relative standard deviation for replicate preparation/analysis of CRMs (representing homogenous matrixes), was as a rule better than 5%.

6. Conclusion

Subsampling of 45 material fractions sorted from Danish household waste was conducted in compliance with the Theory of Sampling. Well-organized handling routines and special equipment for size reduction and mass splitting were introduced to eliminate ISE and to minimize GSE and FSE. Four different sampling methods were used according to the material properties of the waste fractions.

Five digestion methods were introduced for the various fractions as the basis for total chemical analysis. Determination of digest chemical composition was done with ICP-SFMS and ICP-OES. Acceptably low levels of detection were obtained, allowing for quantification of many elements in most waste fractions.

Two waste fractions were selected for sampling-accuracy determination because of their difference in nature, expected chemical composition, and level of heterogeneity. For each step of sample handling, parallel increments were taken from the two fractions to estimate the added variance. By analysis of the variances in an ANOVA model, sampling steps with significant influence on the overall variance of results were found. A Kolmogorov–Smirnov test on the results concluded that only one step (for one fraction) added significant variance when all analytes were taken into account. The added variance accounted for 20–85% of the total variance for the fraction. Lowering the variance will require a larger mass for chemical digestion or a lowering of the liberation parameter by chemical alteration of the sample matrix, for example.

The accuracy and variability of the chemical characterization were good, as determined by the analysis of several relevant certified reference materials. The method described for subsampling, digestion, and analysis is laborious but seems well suited for chemical analysis of heterogeneous waste fractions.

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