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Optimal acid digestion for multi-element analysis of different waste matrices

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Abstract

Informed planning and assessment of waste management systems requires accurate data on physical and chemical characteristics of the waste materials. For many parameters analytical standard methods already exist; however, most of these methods do not account for the specific properties of the distinct waste materials and recyclables. The purpose of this study is to evaluate the performance of different standardized microwave assisted acid digestion methods on waste samples and subsequent multi-element analysis. Six acid digestion methods were applied on a Paper & Cardboard and Composite waste matrix preparing four replicates per method. The digestates were subsequently analyzed for 20 elements using ICP-MS and ICP-OES. The measurement results were statistically evaluated using ANOVA and a ranking procedure. The ANOVA shows a significant difference between the digestion methods for 12 elements in the Paper & Cardboard matrix and for 10 elements in the Composite matrix. The ranking procedure points to different methods to be the most optimal digestion methods in the tested waste matrices. The recovery rates can vary by more than 90% among the tested digestion methods depending on the individual element. The selection of an appropriate method is therefore crucial.

1- INTRODUCTION

Informed planning and assessment of waste management systems requires accurate data on physical and chemical characteristics of the waste materials. For many parameters analytical standard methods already exist; however, most of these methods are directed towards a range of different and often non-waste materials (e.g. soil, ashes, mixed waste) and does not necessarily account for the specific properties of the distinct waste materials and recyclables. Overall, very few chemical compositional data exist for household waste and the available data in literature may often be obtained using different analytical methodologies. This makes compositional data difficult to compare. Characterization of the inorganic constituents of materials sampled from waste typically starts with microwave assisted acid digestion of the samples in order to dissolve the solid sample. Various digestion methods exist using different mixtures of acids (e.g. hydrochloric, nitric and hydrofluoric acid). Each digestion method provides a different recovery rate of waste matrix constituents (e.g. metals) and consequently the selection of an acid digestion method for the final composition data may be important and affecting the results. This consequently affects our understanding of the waste materials' chemical composition, our interpretation of contamination of recyclables, related environmental burdens and it also affects the applicability of specific waste treatment technologies and re-use options for the waste materials. (e.g. use-on-land of digestate from anaerobic digestion of organic waste). Existing waste characterization studies have applied a range of different digestion methods: e.g. Riber et al. [1], Skutan & Aschenbrenner [2] and de Abreu et al. [3]. A systematic comparison of digestion methods on relevant waste materials is needed to enable a proper selection and to ensure that not only a few elements show high recovery rate, but for finding methods suitable for multi-element analysis. The purpose of this study is to evaluate the performance of selected standardized microwave assisted acid digestion methods for waste sample digestion and subsequent multi-element analysis of selected waste materials, and thereby provide the basis for improved selecting of acid digestion methods. This paper presents preliminary results of the investigations for two waste materials.

2- MATERIALS AND METHODS

Six different acid digestion methods were selected to be applied on the waste samples (Table 1). The list of tested methods included four standard methods widely used in literature for chemical waste characterization, all involving different mixtures of acids. Acid digestion method E is based on a study by Riber et al. [1], who used material matrix specific acid digestion method for the chemical analysis of different waste fractions from household waste. The last acid digestion method is based on reviewed literature and the recommendations of the digestion equipment producer for (non-waste) materials. The six methods were applied on two waste samples representing the waste fractions *Paper & Cardboard* and *Composites.* Four replicates per digestion method were prepared each involving 250 mg of solid sample.

The waste samples were obtained in a sorting campaign on household waste from a Danish city in spring 2013 during which, collected waste was hand sorted. The samples were dried and milled to particle sizes < 1 mm before analysis. The digestion was performed in a microwave sample preparation system using temperature and pressure control. The digested samples were analysed for 20 elements using ICP_MS and ICP_OES.

To evaluate the influence of the digestion methods on the measurement results an analysis of variance (ANOVA) was performed, returning whether the difference between the results from the different digestion methods was statistically significant or not. In a next step the average responses for each method were calculated resulting in six average values per element. In order to make the results from different elements comparable a rank between 1 and 6 was assigned to all six averages; 6 for the highest average and 1 for the lowest. The methods were then compared calculating the overall average rank for each of the six digestion methods for multiple elements.

Method ID	Standard/ Reference	Acids involved
A	US EPA 3051[4]	10 ml HNO_3
C	Aqua Regia	3 ml HNO_3 + 9 ml HCl
B	US EPA 3052 [5]	6 ml HNO_3 + 2 ml HCl+ 2 ml HF
D	CEN 13656:2002[6]	2 ml HNO_3 + 6 ml HCl+ 2 ml HF
E	Riber et al. 2007 [1]	5 ml HNO_3 + 0.5 ml H_2O_2 + 0.3 ml HF
F	Matrix specific	7 ml HNO_3 + 2 ml H_2O_2

Table 1: Overview on applied microwave assisted acid digestion methods

3- RESULTS AND DISCUSSION

The results of the ANOVA show that in the waste matrix *Paper & Cardboard* 12 and in *Composites* 10 out of 20 analysed elements are significantly influenced by the digestion methods applied. When considering all significantly influenced elements, the overall average ranks for the individual digestion methods show similar values between 3.1 and 4.6 for both samples except for Method F (Table 2). This means that when taking all significantly influenced elements into account the methods obtain in average similar results for this waste matrix, however, the individual elements point to different methods, so that in average only a low rank can be obtained. In the *Paper & Cardboard* sample method B scored highest with a rank of 4.5 whereas in the *Composite* sample method C obtained the highest rank of 4.6. Furthermore the two best performing methods in the *Composite* sample obtained very similar ranks of 4.6 and 4.5.

Matrix	n_{sig}	A	B	C	D	E	F
PnC	*12*	3.3	4.5	3.8	4.1	3.1	2.3
Comp	*10*	3.7	3.6	4.6	4.5	3.3	1.7

Table 2: average method ranks of all significant elements for the applied digestion methods on both waste matrices (PnC = paper & cardboard; Comp = composites)

When calculating the overall average ranks for two distinct groups of elements e.g. macro-elements and toxic elements, the results point to methods C and D for the macro-elements (Table 3) in both matrices, whereas in the toxic element group for the *Paper & Cardboard* matrix methods D and C are not among the highest ranking methods, but A and B (Table 4). For the *Composite* matrix in the group of macro-elements a high average rank of 5.0 points to method C, closely followed by the rank for method D. For the analysis of macro-elements in the *Paper & Cardboard* matrix also method D and C are the two best performing methods but here method D obtains the highest rank and the difference between D and C is bigger than in the *Composite* matrix. Toxic elements in *Paper & Cardboard* show best results using digestion method B or A, neither of this methods does contain hydrofluoric acid (HF). However, for the analysis of toxic elements in a *Composite* material the use of HF is preferable indicated by the highest ranks of 4.8 for method C and 4.3 for method D.

Matrix	n_{sig}	A	B	C	D	E	F
PnC	*6*	2.2	3.8	4.0	4.8	3.3	2.8
Comp	*3*	3.0	2.3	5.0	4.7	4.0	2.0

Table 3: average method ranks of elements in the group macro-elements (including 8 elements) on both waste matrices (PnC = paper & cardboard; Comp = composites)

Matrix	n_{sig}	A	B	C	D	E	F
PnC	*6*	4.3	5.2	3.7	3.3	2.8	1.7
Comp	*7*	3.7	3.7	4.8	4.3	2.8	1.7

Table 4: average method ranks of elements in the group toxic elements (including 15 elements) on both waste matrices (PnC = paper & cardboard; Comp = composites)

The variation of recovery rates among the tested methods was for some elements very large. The recovery rates for e.g. Si ranged between 4 and 100% and for As between 1 and 100%.

This makes sense considering that hydrofluoric acid is needed to ultimately destroy silicon bonds. If there is no HF involved at all, as e.g. in method A, the recovery rate for silicon is as expected very low because the silicon-bound silicon can just not dissolve. In a case where Arsenic is of special importance obviously special care must be taken when choosing the digestion method because a wrong choice of method can obviously lead to a tremendous underestimation of its concentration.

4- CONCLUSIONS

The obtained results show that the measured content of more than half of the analysed elements is significantly influenced by the choice of acid digestion method. The performance of the tested digestion methods depends on the specific element as well as on the waste material matrix characteristics. It was shown that the influence of the waste material matrix can lead to different best performing acid digestion methods for the same element. Furthermore, it was shown that an uninformed choice of digestion method can result in tremendous underestimation of toxic elements. Consequently a proper selection of acid digestion methods is crucial for the results of chemical waste characterization.

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