ABSTRACT
Waste management lacks of quality control instruments to assess the effect of legislative, organisational and technical measures on the waste stream. In this paper results of the application of a new monitoring instrument to analyze routinely the impact of such measures on the MSW- composition are presented. Waste incineration plants transform heterogeneous wastes into much more homogeneous residues (bottom ash, filter ash, waste water, flue gas). Due to the fact, that materials tend to accumulate in certain incineration products, the chemical composition of the waste material can be determined by analysing single incineration products only. This is an easy and cost efficient method to find temporal changes in waste. The partitioning of 10 elements (C, Cl, F, S, Fe, Cu, Zn, Cd, Hg, and Pb) was examined in a modern full scale incinerator in Austria. The objective was to determine element balances by measuring inputs and outputs and analyzing the residues only. Statistical methods were used (a) to quantify uncertainties, (b) to select the appropriate incineration residues to be analyzed, (c) to determine the minimum sampling frequency of the residue, and (d) to analyze the chemical composition of municipal solid waste routinely with a given accuracy. Field measurements demonstrate, that the proposed method allows to determine annual mean waste concentrations rather accurately for a reasonable annual number of samples in the selected residues (C: ± 1%; Cl: ± 5%; S: ± 10%; heavy metals such as Cd, Zn: ± 10%, Cu and Pb: ± 20%).
INTRODUCTION

In waste management, cost effective instruments are needed to assess the effect of legislative, organizational and technical measures on the waste stream. The routinely determination of the chemical waste composition is essential to assess the effect of such measures. The knowledge of long-term trends of the metabolism of materials, determined by continuous material balances, meets the requirements of national environment plans as defined for example in Austria and the Netherlands. The knowledge of trends in waste composition is instrumental for planning and running waste treatment plants, too.

The objectives of the investigations presented in this paper were:

1. To establish a material flux analysis of a municipal solid waste incinerator plant (MSWIP), that allows to determine the flux of selected elements through the incinerator and the chemical composition of the municipal solid waste (MSW). This includes the use of methods to quantify uncertainties.
2. To establish a method to measure routinely the chemical composition of municipal solid waste by the analysis of one incineration product only.
3. To apply the proposed method routinely on the MSW incinerator plant.

MATERIALS AND METHODS

A state of the art municipal solid waste incinerator plant in Wels, Austria was investigated. The incinerator is equipped with a grade type furnace, a waste heat boiler, an electrostatic precipitator (ESP), two wet scrubbers, an activated carbon filter and a catalytic denitrification process. Solid residue products (bottom ash, waste heat boiler and ESP ash, and contaminated activated carbon) as well a waste water of the wet scrubbers are treated in further residues treatment processes (neutral bottom ash washing process, acidic fly ash washing process combined with low temperature rotary kiln process. Combustion conditions in the furnace are controlled by an automated control system. The capacity of the incinerator is 8 tons/hour of municipal solid waste (waste from household, trade and commerce). The feeding rate of the waste is adjusted according to its calorific value. Actual emissions to air and water all are very well below the actual stringent emission limit values in Austria and the European Community.

The investigations consisted of two parts:

In the first part of the investigation a material flux analysis of the municipal solid waste incinerator plant in Wels, Austria was established in July/August 1996. The flux of selected elements (C, Cl, F, S, Fe, Cu, Zn, Cd, Hg, and Pb) through the MSWIP, the chemical composition of the waste input and the partitioning of the elements in the MSWIP were determined by analyzing the products of the MSWIP (Morf et al., 1997). This approach was suggested in Brunner & Ernst (1986) and successfully applied several times (Brunner & Mönch, 1986; Vogg et al., 1986; Reinmann, 1989; Angenend & Trondt, 1990; Vehlow, 1993; Chandler et al., 1995; Schachermayer et al., 1995; Belevi, 1995) Statistical methods as suggested in Schachermayer et al. (1995) and Bauer (1996) were applied to quantify uncertainties.

In the second part of the investigation a method to measure the MSW composition routinely by the analysis of a single incineration residue was developed (Morf & Brunner, 1998).
Based on the results of the first part of the investigation, appropriate incineration residues were selected as future measuring points for routine monitoring. The selection of the residues depends on various parameters:

I. the partitioning of the elements in the MSWIP (transfer coefficients)
II. the statistical behavior of the transfer coefficients (uncertainty)
III. the concentration levels in the considered MSWIP residues
IV. the statistical behavior of the elemental concentrations in the MSWIP residues considered
V. process constellation of MSWIP in between input and considered residues
VI. practical and economical criteria

The determination of the minimum sampling frequency of the residue depends on following parameter (Müskens & Kateman, 1978; Morf & Brunner, 1998):

A) the choice of the lot to be investigated (e.g. annual amount of burnt waste)
B) the choice of required accuracy to describe the lot (e.g. annual waste concentration)
C) the choice of distance between the middle of two adjacent samples
D) the choice of the sample size
E) the time constant and variance of the „process“ (derived from the auto-correlation functions of the selected elements)
F) variance of the method of analysis (determined in first part of the investigation)
RESULTS AND DISCUSSION

Results of the first part of the investigation (material flux analysis)

The partitioning of selected elements in the MSWIP Wels are presented in Figure 1.

If the input into the furnace is taken as 100%, 98% of carbon is transferred to the flue gas, 84% of chlorine to the cleaned waste water. The metals Pb, Zn, Cu and Cd are transferred 100% into solid residues, only neglectable amounts remain in waste water and flue gas. Detailed results about the flux of the selected elements through the MSWIP and the chemical composition of the waste input during the measuring campaign are presented in Morf et al. (1997).
Results of the second part of the investigation

To apply the general method to measure the MSW composition as described in Morf & Brunner (1998), optimal residues and sampling frequencies had to be determined.

Choice of the optimal residues

The results of the first part of the investigation together with sufficient knowledge about parameter II-VI allowed to determine the optimal sampling points (residues) for selected elements as described in Morf & Brunner (1998) (Tab. I). CO₂ in flue gas serves well to determine carbon in the MSW. Chlorine and even sulfur can be measured efficiently in waste water. Additional knowledge (Morf et al., 1997) about the partitioning of heavy metals into untreated ash fractions (ESP ash and boiler ash) allowed further considerations about the choice of the optimal sampling point for these elements.

Tab. I: Optimal monitoring points for selected elements

<table>
<thead>
<tr>
<th>Monitoring Point (Residue)</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>flue gas</td>
<td>carbon</td>
</tr>
<tr>
<td>waste water</td>
<td>chlorine, sulfur</td>
</tr>
<tr>
<td>ESP ash</td>
<td>atmophilic metals (Cd, Zn, Pb, Cu)</td>
</tr>
</tbody>
</table>

Determination of optimal sampling frequency

To guarantee a defined accuracy for the sampling results in the selected residues, optimal sampling frequencies have to be determined. They depend on the parameters A to F. Figure 2 shows the relative error as a function of the sampling frequency (annual number of samples) for chlorine in waste water and carbon in flue gas of the MSW plant in Wels (Morf, 1998).

Figure 2: Relative error (95% confidence intervals =2σ) for the mean chlorine concentration in waste water and carbon concentration in the flue gas, determined during the time period of 1 year as a function of sampling frequency in the residue; (Morf, 1998).
Achievable accuracy for the mean MSW composition during a selected time period

The uncertainty of the mean MSW composition during a selected time period, depends on the parameters I to VI and A to F. Fig. 3 shows approximate, achievable accuracy for the annual mean MSW concentration of carbon, chlorine and sulfur by analyzing 20 samples in the selected residues annually (Tab. I).

Figure 3: Uncertainty [%] for the annual mean MSW composition (approximate width of 95%-confidence intervals) incinerated in the MSWIP Wels, Austria for carbon, chlorine and sulfur by analyzing 20 samples annually in the flue gas and waste water, respectively; Morf, 1998.

Thus, the annual mean concentration for all three elements can be determined fairly accurate for a reasonable annual number of 20 samples by the proposed method. Other elements in the waste stream can be monitored rather accurately as well. The mean annual waste concentration of selected heavy metals can be determined with an uncertainty of ±10% (for Cd and Zn) and ±20% (for Cu and Pb) with 20 annual samples in electrical precipitator ash of the incinerator (Morf & Brunner, 1998).

Routinely measured chemical waste composition: First Results

Chlorine and sulfur have been monitored routinely in the waste water stream of the MSWI plant in Wels, Austria. Daily composite samples have been analyzed. Online measurements of CO$_2$ in flue gas have been used to determine carbon in the MSW. Applying the method proposed in Morf & Brunner, 1998, the MSW composition for these substances can be monitored routinely. The data set available allows to investigate time series with a high resolution on a daily or weekly basis. Figure 4 shows first results of the calculations. A trend for weekly mean values of the chlorine concentration in MSW during the time period between December 3$^{\text{rd}}$, 1996 and December 30$^{\text{th}}$, 1997 is displayed. Each weekly mean value including its uncertainty is determined by the analysis of seven automatically collected daily waste water composite samples, input mass, waste water flux and the transfer coefficient including its uncertainty.
Figure 4: Time trend for the weekly mean values of chlorine waste concentration incinerated in die MSWIP Wels, Austria between December 3rd, 1996 and December 30th, 1997; including lower and upper limit for an approximate 95% confidence interval); w.s... wet substance; Morf, 1998.

Figure 4 shows values for the chlorine concentration in the MSW between 4000 and 11000 mg/kg(w.s.). This are rather high variations of the chlorine content in the waste burnt in the MSWIP Wels. This is probably due to temporary variations in the amount of commercial waste including more chlorine in general. To evaluate trends over longer time periods or detect fluctuations more data is needed. The mean value of the year [7600 mg/kg(w.s.)] is in the range of results of point measurements in Switzerland [7000 mg/kg(w.s.)] (Brunner & Mönch, 1986) and [6900 mg/kg(w.s.)] (Belevi et al., 1995) and in Germany [7000 mg/kg(w.s.)] (Angenend & Trondt, 1990), and in Austria [6400 mg/kg(w.s.)] (Schachermayer et al., 1995). The uncertainty of the weekly mean values can be kept on a rather low level (<±10%). Missing values in Figure 4 are related to plant or sampling equipment shutdowns due to maintenance work.

CONCLUSIONS

- MSWIP can be used as an efficient monitoring tool to measure to chemical composition of MSW easy and cost efficient.
- Flue gas is a suitable MSWIP product to detect carbon, waste water is suitable for measuring chlorine and sulfur. Heavy Metals, such as Cd, Zn, Pb and even Cu can be monitored by analyzing electrostatic precipitator ash only.
- The proposed method allows to calculated the mean annual waste composition accurately for a reasonable annual number of 20 samples by the proposed method (C: ±1%; Cl: ±5%; S: ±20%; heavy metals <±20% depending on the element).
- For elements that are monitored online in a appropriate residue to a reasonable cost (e.g. carbon in the flue gas, chlorine in the waste water), time trends of the chemical waste composition can be determined very efficient by the proposed method.
- Further MSWIP should include hard and software to apply the proposed method for monitoring purpose.
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