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The MSW Incinerator as a Monitoring Tool for Waste Management

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For efficient waste management, instruments are needed to assess the impact of legislative, organizational, and technical measures on the waste stream. Since waste incineration plants transform heterogeneous wastes into more homogeneous residues, they are well suited for easy and cost-effective monitoring of the chemical composition of wastes. A method is proposed to determine changes in the chemical waste composition by analyzing a single incineration residue only. Procedures are presented to (a) select the appropriate incineration residue to be analyzed, (b) determine the minimum sampling frequency of the residue, and (c) analyze the chemical composition of municipal solid waste routinely with a given accuracy. Field measurements demonstrate that, with a reasonable effort, the annual mean concentration of Zn and Cd in MSW can be determined with an uncertainty of less than 10% and of Cu and Pb with less than 20%, respectively. The proposed method, which can be extended to nonmetals also, serves as a base to use waste incineration plants as a routine tool for quality control in waste management.

Introduction

In waste management, cost-effective instruments are needed to assess the effect of legislative, organizational, and technical measures on the waste stream. The routine determination of the chemical waste composition is essential to assess the effect of such measures. The knowledge of trends in waste composition is instrumental for planning and running waste treatment plants too. Various approaches to characterize wastes have been described previously (1). Traditionally, waste composition has been determined by sorting waste samples. This method has been used in many regional and nationwide waste characterization studies (2–7). Another approach is to collect statistical information about consumer goods that will later become wastes. This approach is mainly applicable on a national level and requires information from market research and about the different time spans needed for goods to turn into wastes. It is well suited to determine specific waste groups in the waste stream but does not directly lead to information about chemical waste composition.

As a third approach, chemical waste composition may be determined by investigating the material flux through a municipal solid waste incinerator plant (SWI) (1). Analyzing the residues of the SWI over a certain period of time allows us to determine the flux of selected elements through the SWI, to calculate the chemical composition of the waste input,

and to assess the partitioning of selected elements in the SWI. This method has been successfully applied before (8–13). To quantify uncertainties, statistical instruments were suggested in refs 12 and 14–17.

All three approaches have specific advantages and drawbacks with regard to easy and cost-effective continuous monitoring. In this paper, we present a new method to measure routinely the chemical composition of municipal solid waste by the analysis of a single incineration residue only. Procedures and examples are presented to select the appropriate incineration residue to be analyzed, to determine the minimum frequency for analyzing the residue, and to measure the chemical composition of MSW routinely. The method allows us to use waste incineration plants as an analytical tool for quality control in waste management.

Experimental Section

Mass balances of 10 elements (C, Cl, S, F, Fe, Cu, Zn, Pb, Cd, and Hg) have been determined by a series of investigations of the SWI Spittelau in Vienna, Austria, in 1994 (Figure 1). In investigation I, a provisional material balance of the Spittelau incinerator was established in order to determine the orders of magnitude of the material concentrations and material flows. In investigation II, mass balances of the elements selected were performed during 48 h with separately collected household waste as the incinerator feed. The same procedure was applied in investigation III, but ordinary, mixed municipal solid waste was incinerated. To determine the time constants and the variance for the four selected metals, 260 additional filter ash samples have been analyzed during a period of 12 months (April 1995–April 1996) (investigation IV). For the present paper, we use the data and the results of investigations III and IV and focus on the four metals (Cu, Zn, Cd, and Pb) only.

In investigations I–III, the flows of all goods (input, MSW; outputs, bottom ash, scrap metals, filter ash, wastewater, filter cake, flue gas) through the incinerator were measured. Samples were taken from all goods except the waste input and scrap metals. Cu, Zn, and Pb were analyzed by inductively coupled plasma atomic emission spectrometry (ICP–AES), and Cd was analyzed by atomic absorption spectrometry (AAS). Data about metals in the flue gas originate from a previous measuring campaign. For investigations II and III, the mean concentrations $\bar{C}_{k,p}$ of the selected metals have been determined in all relevant incineration residues as well as their variances, $\text{var}(\bar{C}_{k,p})$, the mean transfer coefficients of the selected elements into the relevant residues, $\bar{\epsilon}_{k,p}$, and their variances, $\text{var}(\bar{\epsilon}_{k,p})$. The mass balances were calculated by multiplying the flow of goods with the respective concentrations of the elements. The Spittelau incinerator and the experimental procedure are described in detail in ref 12 (investigations I–III) and 18 (investigation IV). An expanded summary of investigations I–IV is given in ref 19.

Method

The proposed method is described in three parts. First, a general method to calculate the chemical composition of the waste input by the analysis of a single incineration residue is discussed (part a). Part b presents a model to minimize the sampling frequency. In part c, those parameters are discussed, that are needed as a base in the first and the second part, such as transfer coefficients and variance of transfer coefficients. Also, a procedure to select the appropriate residue for monitoring the waste composition is presented.

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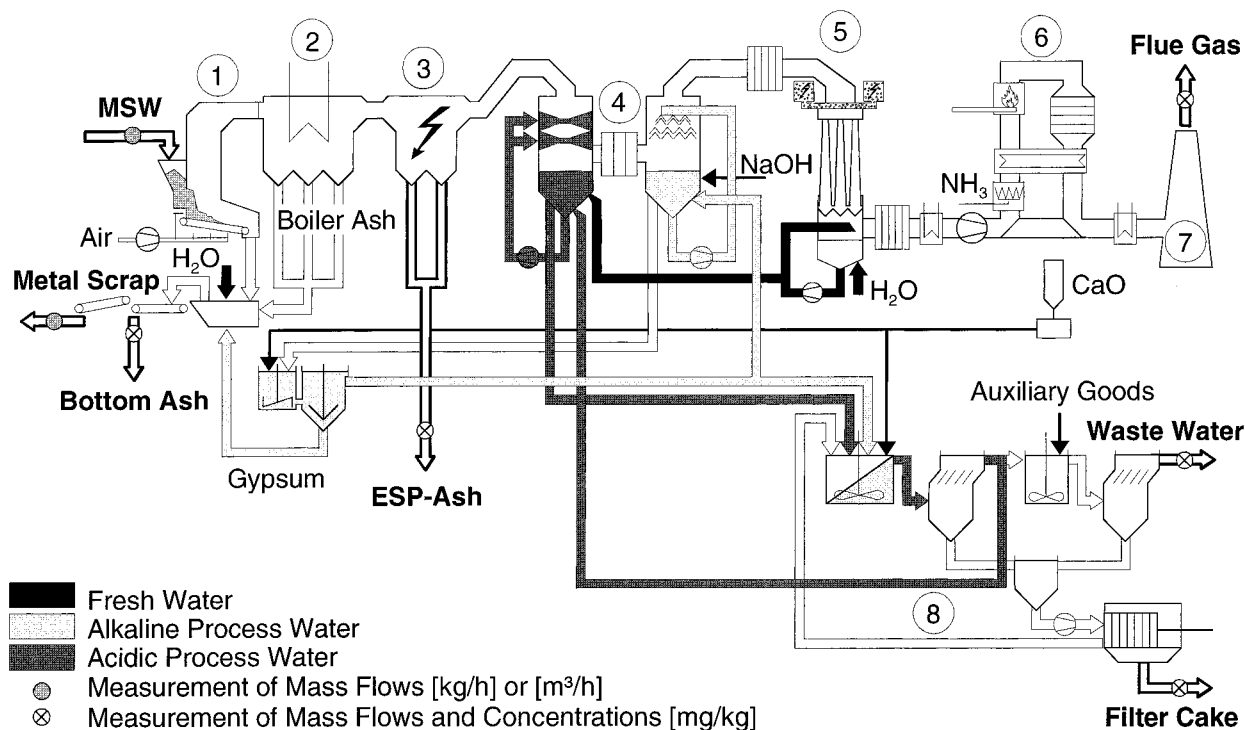


FIGURE 1. Process flow sheet for the Spittelau municipal solid waste incineration plant, Vienna, Austria; 40 t/h MSW input resulting in 9.2 t/h bottom ash, 1.1 t/h scrap metals, 0.97 t/h filter ash, 14 t/yr wastewater, 0.055 t/h filter cake, 230 t/h flue gas; 1, grate furnace; 2, waste heat boiler; 3, electrostatic precipitator; 4, two-stage wet-scrubber; 5, fine dust collection system; 6, DENOX/dioxin destruction process; 7, stack; 8, wastewater treatment plant.

In practice, part c will have to be performed before parts b and a.

(a) Determination of Waste Composition by Analysis of a Single Incineration Residue Only. The mean concentration $\bar{C}_{k,\text{waste}}$ for an element k in a waste input is calculated according to eq 1 from the measured mass flows of the residue \dot{m}_p and the waste input \dot{m}_{waste} , the mean concentration of the element k measured in the residue $\bar{C}_{k,p}$, and the mean transfer coefficient of k for the corresponding residue $\bar{\epsilon}_{k,p}$:

$$\bar{C}_{k,\text{waste}} = \frac{\dot{m}_p}{\dot{m}_{\text{waste}}} \frac{\bar{C}_{k,p}}{\bar{\epsilon}_{k,p}} = P \frac{\bar{C}_{k,p}}{\bar{\epsilon}_{k,p}} \quad (1)$$

To calculate the uncertainty of the mean concentration, $\text{var}(\bar{C}_{k,\text{waste}})$, the general law of propagation of error (eq 2) is applied on eq 1. Equation 2 may be simplified if the covariance terms prove to be small compared to the variance terms. This has to be checked individually:

$$\text{var}[f(x_1, x_2, \dots, x_n)] \approx \sum_{i=1}^n \left(\frac{\partial f}{\partial x_i} \right)^2 \text{var}(x_i) + 2 \sum_{i=1}^n \sum_{j=i+1}^n \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} \text{cov}(x_i, x_j) \quad (2)$$

For a solid waste incineration, it can be generally assumed that the variance of routinely measured waste and residue mass flows and any covariance terms are negligible. Thus, the propagation of error (eq 2) applied on eq 1 results in

$$\text{var}[\bar{C}_{k,\text{waste}}] = \left(\frac{P}{\bar{\epsilon}_{k,p}} \right)^2 \text{var}(\bar{C}_{k,p}) + \left(\frac{P \bar{C}_{k,p}}{\bar{\epsilon}_{k,p}^2} \right)^2 \text{var}(\bar{\epsilon}_{k,p}) \quad (3)$$

where P is the ratio of the residue versus the waste mass flow, $\text{var}(\bar{C}_{k,p})$ is the variance of the mean concentration of element k in the residue p , $\text{var}(\bar{\epsilon}_{k,p})$ is the variance of the

mean transfer coefficient of element k from the waste into the residue p . The variance $\text{var}(\bar{C}_{k,p})$ (equal to $\sigma_{\bar{C}_{k,p}}^2$ in part b), the mean transfer coefficient for the element k into the residue p ($\bar{\epsilon}_{k,p}$), and the variance $\text{var}(\bar{\epsilon}_{k,p})$ are to be determined experimentally.

Assuming normal distribution, an approximate $(1 - \alpha)$ confidence interval for the mean waste concentration of element k can be calculated by

$$f(x_1, \dots, x_n) - Z_{1-\alpha/2} \sqrt{\text{var}(f(x_1, \dots, x_n))} \leq \mu \leq f(x_1, \dots, x_n) + Z_{1-\alpha/2} \sqrt{\text{var}(f(x_1, \dots, x_n))} \quad (4)$$

x_1, \dots, x_n are the estimated mean values of the variables in eq 1, μ is the estimator of the mean concentration $\bar{C}_{k,\text{waste}}$, and $Z_{1-\alpha/2}$ is the $(1 - \alpha/2)$ percentile of the standard normal distribution. For this study, we choose $\alpha = 0.05$ and $Z_{1-\alpha/2} \sqrt{\text{var}(f(x_1, \dots, x_n))}$ was approximated by two standard deviations ($\approx 2\sigma$). The confidence interval for the mean concentration μ in the time period considered is given by

$$[\bar{C}_{k,\text{waste}} - 2\sqrt{\text{var}(\bar{C}_{k,\text{waste}})} < \mu < \bar{C}_{k,\text{waste}} + 2\sqrt{\text{var}(\bar{C}_{k,\text{waste}})}] \quad (5)$$

(b) Determination of the Sampling Frequency. Fewer samples are needed to determine the mean composition of a lot for internally or autocorrelated lots than for lots consisting of randomly distributed components. A lot is a finite part of a process (e.g., a waste stream during 1 year). The length of the lot (e.g., time period of 1 year) is defined as the lot size L . The number of samples n and their size G (time period for the sampling process of one sample) is influenced by the degree of correlation (expressed by the time constant T_x) within the lot. A process with $T_x = 0$ is totally uncorrelated (random process). Here the time variance component of the total variance is large as compared to the variability due to sample heterogeneity, sample

preparation, and analysis. A process with $T_x \rightarrow \infty$ is totally correlated, respectively. For a process with a high value of T_x both a small sampling size fraction $F (= G/L)$ and a small number of samples n are needed to describe the lot with sufficient accuracy. For a process with a very low T_x , only the relative size of the gross sample nF is determining. Therefore, it is unimportant whether nF is obtained by taking many small samples or one large sample. Factors causing this correlation can depend upon time as well as on space, e.g., changing waste properties due to new consumer products.

If for an internally correlated, one-dimensional lot of size L , the variance of the process σ_x^2 and the time constant of the process T_x are known and the desired reproducibility σ_{est}^2 of the gross sample nG , the sample size G , and the distance A between the middle of two adjacent samples, $A = L/n$, are defined, then the number of samples n can be calculated by eqs 6–10 as proposed and discussed in detail in ref 20.

The mean deviation between the estimated and real value of the lot, the variance of the deviation (reproducibility of the gross sample) σ_{est}^2 , is

$$\sigma_{\text{est}}^2 = \sigma_m^2 + \sigma_\mu^2 - 2\sigma_{m\mu} \quad (6)$$

where σ_m^2 is the variance in the composition of the gross sample, σ_μ^2 is the variance in the composition of the whole lot, and $\sigma_{m\mu}$ is the covariance between m and μ .

The procedure described is valid for Gaussian stationary stochastic processes of the first-order. For convenience, such processes may be described by a mean value $\mu = 0$, a time constant T_x , and a variance σ_x^2 . In most cases the autocorrelation functions of time series are approximately exponential, $\varphi(x) \approx \exp(-|t|/T_x)$. According to ref 20, if this is the case, eq 6 may be expressed by eqs 7–9.

Variance σ_m^2 in the composition of the gross sample:

$$\sigma_m^2 = \frac{2\sigma_x^2 T_x^2}{nG^2} \times \left[\frac{G}{T_x} - 1 + \exp\left(-\frac{G}{T_x}\right) + \left\{ \exp\left(-\frac{G}{T_x}\right) + \exp\left(\frac{G}{T_x}\right) - 2 \right\} \times \left\{ \frac{\exp\left(-\frac{A}{T_x}\right)}{1 - \exp\left(-\frac{A}{T_x}\right)} - \frac{\exp\left(-\frac{A}{T_x}\right)(1 - \exp\left(-\frac{P}{T_x}\right))}{n(1 - \exp\left(-\frac{L}{T_x}\right))^2} \right\} \right] \quad (7)$$

Variance σ_μ^2 in the composition of the whole lot:

$$\sigma_\mu^2 = (2\sigma_x^2 T_x^2 / L^2) [L/T_x - 1 + \exp(-L/T_x)] \quad (8)$$

Covariance $\sigma_{m\mu}$ of the lot and gross sample (between m and μ):

$$\sigma_{m\mu} = \frac{\sigma_x^2 T_x^2}{nLG} \left[\frac{2nG}{T_x} + \left(\exp\left(-\frac{G}{T_x}\right) - 1 \right) \frac{1 - \exp\left(-\frac{L}{T_x}\right)}{1 - \exp\left(-\frac{A}{T_x}\right)} + \left(\exp\left(\frac{G}{T_x}\right) - 1 \right) \frac{1 - \exp\left(-\frac{L}{T_x}\right)}{1 - \exp\left(-\frac{A}{T_x}\right)} \right] \quad (9)$$

If the number of subsamples for chemical analysis for every

sample is N and the variance of the analysis sample is σ_a^2 , then the total uncertainty σ_L^2 of the mean value μ of the lot is the sum of σ_{est}^2 and σ_a^2/N . To calculate a $(1 - \alpha)$ confidence interval, with $\alpha = 0.05$, it follows for the relative error Δ_L :

$$\Delta_L = \frac{t_{b-1, 1-\alpha/2} \sigma_L}{\bar{C}_L} \quad (10)$$

whereas $t_{b-1, 1-\alpha/2}$ is Student's t for a confidence level of 0.05 and b degrees of freedom. \bar{C}_L is equal to $\bar{C}_{k,p}$ during the defined time period (lot size L), the variance σ_L^2 is equal to $\text{var}(\bar{C}_{k,p})$ in part a.

Since the concentrations of the element k in the waste stream are not measured, but the concentrations are determined from a corresponding and appropriate incineration residue, eqs 6–10 are used to determine the sampling strategy for this residue. The variance σ_L^2 , which corresponds to the optimum sampling strategy, is then introduced into eq 3 to estimate the uncertainty of the mean waste composition.

(c) Determination of the Incineration Residue Best Suited for Waste Composition Monitoring. Due to their homogeneity, element enrichment, and accessibility, the different residues of incineration offer various possibilities to determine the waste composition. In order to select the best suited incineration residue for a certain element, the following procedures are suggested:

Theoretically, the appropriate product stream is determined by minimizing the left side of eq 3 in part a of this paper. In practice, other important aspects such as the design of the incinerator plant, available resources, and desired accuracy influence the choice of the appropriate incinerator residue too. For MSW incineration, the ratio P of the mass flow of the incinerator residue versus the waste input has to be a minimum. The partitioning of the element k from the waste input into the chosen incinerator residue (transfer coefficient $\bar{\epsilon}_{k,p}$) has to be a maximum. For the metals investigated, the influence of the concentration level of the chosen incineration residue, $\bar{C}_{k,p}$, and the variation of the transfer coefficient, $\text{var}(\bar{\epsilon}_{k,p})$, are nearly negligible. The variation $\text{var}(\bar{C}_{k,p})$ of the concentration in the residue considered has to be a minimum. As a result, a homogenous incineration residue with a low specific mass output rate and a high accumulation rate with minimum variance is to be preferred for monitoring waste composition. Ideally, these conditions are fulfilled for many elements in a single incineration residue.

In order to select the best suited incineration residue, to design the sampling strategy, and subsequently to calculate the waste composition, the following parameters have to be determined experimentally: The transfer coefficients ($\bar{\epsilon}_{k,p}$), the variation of transfer coefficients $\text{var}(\bar{\epsilon}_{k,p})$, the variance of the concentration σ_x^2 , and the time constant T_x of the considered system. Further details are given in refs 12, 14, 18, 22 and 23.

Results and Discussion

$\bar{C}_{k,p}$, $\text{var}(\bar{C}_{k,p})$, $(\bar{\epsilon}_{k,p})$, and $\text{var}(\bar{\epsilon}_{k,p})$ of Bottom Ash and Filter Ash. Table 1 shows the mean transfer coefficients (with approximate 95% confidence interval) determined in the Spittelau incinerator. The values are based on investigation III and the application of the law of propagation of error without considering variances of mass and covariance terms. With the exception of Pb, the mean values of the transfer coefficients are comparable (relative difference less than $\pm 10\%$) with results of other measuring campaigns on MSW incinerators (12, 13). The mean transfer coefficients appear to depend on the applied technology and the plant design. This hypothesis is supported by a comparison of the results

TABLE 1. Mean Transfer Coefficients (with Approximate 95% Confidence Interval [$\approx 2\sigma$]) Determined in the Spittelau Incinerator (Experiment III)

	Cu	Zn	Cd	Pb
bottom ash	0.94 ± 0.01	0.43 ± 0.03	0.08 ± 0.02	0.75 ± 0.04
ESP ash	0.06 ± 0.01	0.57 ± 0.03	0.92 ± 0.02	0.25 ± 0.04
filter cake	<0.01	<0.01	<0.01	<0.01
wastewater	<0.01	<0.01	<0.01	<0.01
flue gas	<0.01	<0.01	<0.01	<0.01

TABLE 2. Determination of Uncertainty of Waste Composition Calculated

		bottom ash no. of samples: 38 (mass ratio $P = 0.231$)				ESP ash no. of samples: 30 (mass ratio $P = 0.024$)			
		Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb
mean concn	mg/kg	1400	1470	2.6	1870	890	17800	370	6010
variance of the mean concn	(mg/kg) ²	3960	9030	0.16	56200	1130	951000	420	134700
mean transfer coeff		0.94	0.43	0.08	0.75	0.06	0.57	0.92	0.25
variance of mean transfer coeff		2.5E-05	2.3E-04	1.0E-04	4.0E-04	2.5E-05	2.3E-04	1.0E-04	4.0E-04
calcd variance of the mean waste composition	(mg/kg) ²	240	2120	1.58	3030	1060	2080	0.3	3370
approximate 95% confidence interval	%	9	12	33	19	18	12	11	20

with other measurements (8) and with measurements on a MSW incinerator plant with similar state of the art technology but a different plant design (e.g., type of grate, geometry of combustion chamber, operating control) (17). Several authors (8, 11, 12–14) have suggested that the partitioning of metals in MSW incinerators depends on the waste input and on the incineration process (applied technology and plant design). Up to now, these hypotheses cannot be tested with the available data. The rather low level of uncertainty in Table 1 is due to a well-designed sampling plan for the measuring campaign.

Nearly 100% of the input flow of the four metals is transferred into the two incineration residues bottom ash and electrostatic precipitator (ESP) ash. This is due to state of the art technology applied in this plant. The two residues are possible monitoring goods for the metals selected. Further investigations were carried out to distinguish which of the two residues is best suited for each metal. Table 2 shows the calculation of the approximate uncertainty of waste composition for each metal.

Hourly composite samples (five samples of 2 kg each per hour) of bottom ash as well as ESP ash (four samples of 2 kg each per hour) were taken. The composite samples were homogenized, and two samples of the same size were taken and pulverized. Duplicate analysis was performed on each pulverized sample. When comparing the approximate 95% confidence interval of the waste composition calculated with bottom ash on one hand and with ESP ash on the other hand, the following has to be considered: Bottom ash was sampled during 19 1-h measuring periods (38 total number of samples), and ESP ash was sampled only during 15 1-h periods (30 total number of samples). This enhanced program for the sampling of bottom ash was chosen based on the results of investigation I, which showed that the filter ash was more homogeneous than the bottom ash. Taking this into account and since ESP ash is a material easy to sample and to pretreat for analysis, ESP ash serves best to determine Cd, Pb, and Zn in the waste feed. Approximate uncertainty for the calculated waste composition is equal or less than 20% for all selected metals. Cadmium, which is highly enriched in ESP ash, can be determined even more accurately.

Time Constant T_x and Variance σ_x^2 for the Selected Metals. The time constants T_x and the variance σ_x^2 for the four selected elements (Cu, Zn, Cd, and Pb) have been

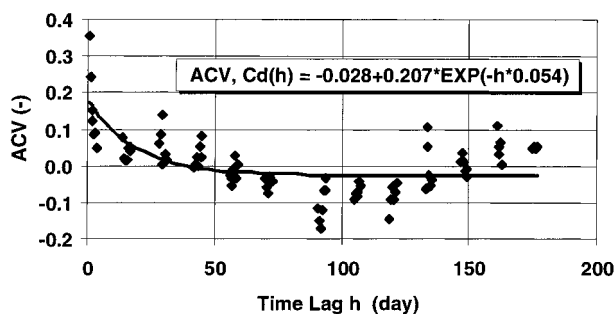


FIGURE 2. Auto-covariance (ACV) function (including the fitted function) of time lag h for Cd ($h = 24$ h); the corresponding functions for Cu, Zn, and Pb are [ACV, Cu(h) = $0.065 + 0.42 \exp(-h \times 0.052)$]; [ACV, Zn(h) = $0.073 + 0.441 \exp(-h \times 0.035)$]; [ACV, Pb(h) = $0.037 + 0.303 \exp(-h \times 0.030)$].

determined in investigation IV. ESP ash was sampled every second week for 5 days during the time period of 1 year. Twice a day, a 12-h composite sample was taken, consisting of four 1.5-kg grab samples each. The composite samples were homogenized, subsampled, and prepared for analysis. Two samples were analyzed. In total, 256 mean concentration values for the selected metals evenly distributed during a 1-year period were determined. The model of part b was applied to these data. The autocorrelation functions were calculated for the time series of all four metals. All measurements were included for the calculations. No transformation was applied to the data sets. Assuming a Gaussian stationary stochastic process of the first-order for the data sets, the time constants T_x and the variances σ_x^2 were determined with the autocorrelation functions of the time series approximated with an exponential function, $\varphi(x) \approx \exp(-|t|/T_x)$. In Figure 2, the calculated autocorrelation function values and the approximated exponential function for Cd are presented.

Table 3 shows the variances σ_x^2 and time constants T_x , estimated with the autocovariance functions in Figure 2. σ_x^2 was estimated conservatively with the variance of the actually measured values (lag $h = 0$). T_x was equalized 0.37 times the estimated value of σ_x^2 using the fitted value at lag $h = 0.5$ days (\approx lag $h = 0$).

Sampling Frequency. The parameters determined in investigation IV (Table 3) were applied to the model discussed

TABLE 3. Auto-correlation Values at Lag $h = 0.5$ days [ACV(0)], Estimated Time Constants T_x , and Process Variance σ_x^2 for Time Series of the Four Selected Elements

	Cu	Cd	Pb	Zn
$\text{var}(x)^a$	25 700	12 900	2 189 000	20 068 000
$\text{ACV}(0)^b$	0.341	0.174	0.261	0.360
σ_x^2	14 790	4 570	1 046 000	11 238 000
$T_x (= 0.37\sigma_x^2)$	15.2	15.0	27.4	21.8

^a The variance of all measurements during the whole year was taken as a basis for determination of σ_x^2 . ^b ACV of fitted values at lag $h = 0.5$ days, basis for determination of T_x .

TABLE 4. Relative Error Δ_L (95% Confidence Intervals $\approx 2\sigma$) for Mean Metal Concentration in ESP Ash, Determined During the Time Period of 1 Year as a Function of Sampling Frequency

no. of samples n per time period L	Cd	Pb	Zn	Cu
1	3.94	2.36	3.22	2.32
2	0.91	0.52	0.73	0.54
4	0.39	0.21	0.30	0.24
8	0.20	0.10	0.15	0.13
16	0.13	0.07	0.10	0.09
32	0.10	0.06	0.08	0.08
64	0.09	0.05	0.07	0.07
128	0.09	0.05	0.07	0.07

TABLE 5. Relative Error Δ_L (95% Confidence Intervals $\approx 2\sigma$) for Mean Cd Concentration in ESP Ash, Determined During the Time Period of 1 Year as a Function of Sampling Frequency for Different Sampling Sizes G (days)

no. of samples n per time period L	sampling size G (days)						
	$<<1$ day	7 days	14 days	30 days	60 days	90 days	180 days
1	3.94	3.62	3.35	2.86	2.25	1.86	1.20
2	0.91	0.83	0.77	0.64	0.48	0.37	
4	0.39	0.35	0.31	0.25	0.16		
8	0.20	0.18	0.15	0.12			
16	0.13	0.11	0.10				
32	0.10	0.09					
64	0.09						

in part b to evaluate the uncertainty of the mean waste composition as a function of the number of samples in the ESP ash. With a sampling period of $L = 365$ days, the number of analysis $N = 1$ per sample, and the variance of analysis σ_a^2 equal to $0.02\sigma_x^2$ (as determined in investigation III), the approximate relative 95% confidence intervals were calculated for the mean ESP ash concentration during the defined time period as a function of the sampling frequency. The results are presented in Table 4.

To assure a relative error width of less than 10%, with a 95% confidence for all four metals, approximately 30 ESP ash samples have to be taken during 1 year. The final choice of the optimal number of samples is due to considerations regarding accepted uncertainty for the mean waste composition for the selected elements and costs.

The influence of the sampling size G on the results above is shown by the example of Cd. With a sampling period $L = 365$, number of analysis $N = 1$ per sample, the variance of analysis σ_a^2 equal to $0.02\sigma_x^2$, and the same reference values for Cd as in Tables 2 and 3, the effect of G on the result is calculated (see Table 5). By increasing the sampling size G , the uncertainty level can be kept constant with a significantly decreased number of samples. This means, that the best sampling strategy is to take a few samples only (2–3) per month over a full year. In practice, the sampling strategy is

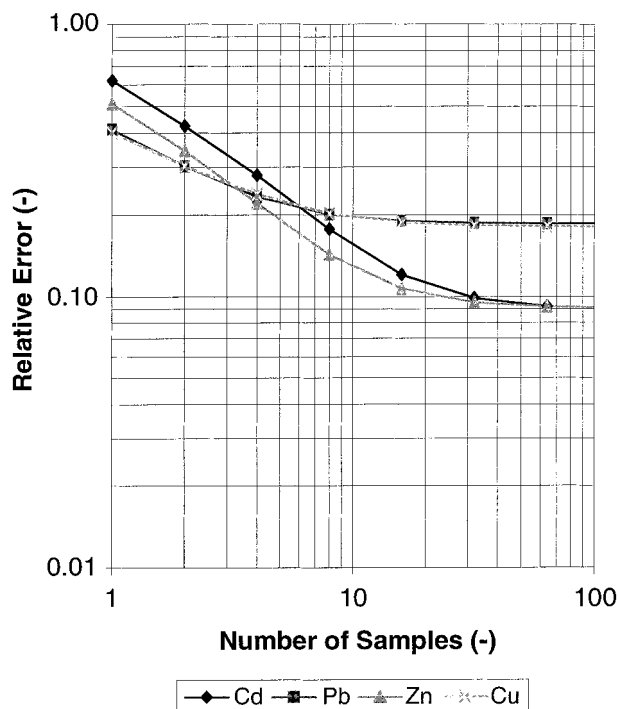


FIGURE 3. Relative error (95% confidence interval $\approx 2\sigma$) for the calculated annual mean waste composition of the selected metals as a function of the sampling in the ESP ash ($L = 365$ days, $G < 1$ day, $N = 1$, $\sigma_a^2 = 0.02\sigma_x^2$).

determined by the uncertainty accepted, the reliability of sampling equipment for long sampling periods, and the costs of sampling and analysis.

Applying the model in part a to the data in Tables 1–3 (with a sampling period of $L = 365$ days, sampling size $G < 1$ day, the number of analysis $N = 1$ per sample n , and the variance of analysis σ_a^2 equal to $0.02\sigma_x^2$), the approximate relative 95% confidence interval ($\approx 2\sigma$) was calculated for the mean waste concentration $\bar{C}_{k,\text{waste}}$ during the defined time period (lot size L) as a function of the sampling frequency. The results are presented in Figure 3.

Depending on the sampling strategy, the uncertainty of the mean concentration for the selected metals can be kept small. As in eq 3, due to an increased sampling effort, the variance $\text{var}(\bar{C}_{k,p})$ is minimized and the second product term on the left side of eq 3 becomes influential. This results in lower values of $\text{var}(\bar{C}_{k,\text{waste}})$ for the two elements Cd and Zn. Thus, the annual mean concentration for all four metals can be determined accurately for a reasonable annual number of samples by the proposed method. Applying the method and the results of this study in practice, the MSW incinerator Spittelau serves as a fine tool to monitor routinely and cost effectively the concentrations of selected metals in the municipal solid waste of Vienna, Austria.

Our experience shows that the method can be extended to other elements (e.g., carbon monitored in the flue gas, chlorine monitored in the wastewater). For all substances studied in investigations I–IV, the uncertainty level of the annual mean remains in the range of the results presented in Table 2. It is essential to use good data, to select the appropriate incineration residue, and to design an optimal sampling strategy for each element in order to assure reasonable uncertainty levels. Up to now, the hypothesis for a generalization of the results has not been verified yet. Therefore parts b and c of the proposed method have to be applied for every new plant to assure defined uncertainty levels for the estimators of the means. Further investigations

about the dependency of transfer coefficients on the waste input, process conditions, and plant design as well as on the time series of elemental concentrations in the waste stream may help to reduce sampling and costs (21). We suggest using waste incineration plants as an analytical tool for quality control in waste management.

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Symbols

A	distance between the middle of two adjacent samples, $A = L/n$
$ACV, k(h)$	auto-covariance (correlation) function of element k (time lag h)
$\bar{C}_{k,p}$	mean concentration of element k in the incineration residue (product) p , referring to the defined time period (lot size L)
$\bar{C}_{k,waste}$	mean waste concentration for an element k , referring to the defined time period (lot size L)
F	size fraction ($F = G/L$)
G	sample size (time period for the sampling process of one sample)
k	chemical element of interest
L	length of the lot (e.g., time period of 1 year), a lot is defined as a finite part of the process (e.g., waste stream during 1 year)
N	number of samples for chemical analysis for every sample n
n	number of samples during the defined time period (lot size L)
P	ratio of the actual measured incineration residue and waste mass flux, referring to the defined time period (lot size L)
p	incineration residue (product)
T_x	time constant of a Gaussian stationary stochastic processes of the first-order
$t_{b-1,1-\alpha/2}$	student's t for a confidence level of 0.05 and b degrees of freedom
$\text{var}(\bar{C}_{k,p})$	variance of the mean concentration of the element k in the considered incineration residue p , referring to the defined time period (lot size L)
$\text{var}(\bar{\epsilon}_{k,p})$	variance of the mean transfer coefficient
$\text{var}(\bar{C}_{k,waste})$	uncertainty of the mean waste concentration of element k , referring to the defined time period (lot size L)
$Z_{1-\alpha/2}$	$(1 - \alpha/2)$ percentile of the standard normal distribution
α	probability of error
$\bar{\epsilon}_{k,p}$	mean transfer coefficient (ratio of the flux in the residue p and the total flux through the SWI for the selected element k)
$\varphi(x)$	auto-covariance (correlation) function (fitted values)

μ	estimator of the mean concentration $\bar{C}_{k,p}$ of element k in the residue p
σ_a^2	variance of analysis
σ_{est}^2	mean deviation between the estimated and real value of the lot (variance of the deviation), referring to the defined time period (lot size L)
σ_L	total uncertainty of the mean value μ of the lot (sum of the variables σ_{est}^2 and σ_a^2/N) [equal to $\text{var}(\bar{C}_{k,p})$], referring to the defined time period (lot size L)
σ_m^2	variance in the composition of the gross sample (nF)
$\sigma_{m\mu}^2$	covariance of the lot and gross sample (between m and μ)
σ_x^2	variance of a Gaussian stationary stochastic processes of the first-order deviation (reproducibility of the gross sample)
σ_μ^2	variance in the composition of the whole lot, referring to the defined time period (lot size L)
Δ_L	relative error of the mean value μ of the lot (sum of the variables σ_{est}^2 and σ_a^2/N), referring to the defined time period (lot size L)

Literature Cited

- (1) Brunner, P. H.; Ernst, W. R. *Waste Manage. Res.* **1986**, *4*, 147.
- (2) Barghoorn, M.; Dobberstein, J.; Eder, G.; Fuchs, J.; Goessele, P. *Bundesweite Müllanalyse 1979–80*; Forschungsbericht 103 03 503; TU Berlin, 1980.
- (3) Greiner, B.; Barghoorn, M.; Dobberstein, J.; Eder, G.; Fuchs, J.; Goessele, P. *Chemisch-physikalische Analyse von Hausmüll*; UBA Berichte 7/83, Forschungsbericht 103 03 502, UBA-FB 83-033; ARGUS-Arbeitsgruppe Umweltstatistik: TU Berlin, 1983 (See review by Obrist, W. *Waste Manage. Res.* **1985**, *3*, 177).
- (4) *Abfallerhebung*; Bundesamt für Umweltschutz: Bern, Switzerland, 1984; Schriftenreihe Umweltschutz No. 27.
- (5) Maystre, L. Y.; Viret, F. *Waste Manage. Res.* **1995**, *13*, 207.
- (6) *Waste Analysis, Testing and Evaluation (Waste) Program: Effect of Waste Stream Characteristics on MSW Incineration: The Fate and Behavior of Metals, Final Report of the Mass Burn MSW Incinerator Study (Burnaby, B.C.): 1993*; Chandler, A. J. & Associates Ltd., Compass Environmental Inc., Rigo & Rigo Associates, The Environmental Research Group University of New Hampshire, Wastewater Technology Center: 1993.
- (7) *Characteristics of Municipal Solid Waste in the United States, 1960–2000: 1986*; Prepared for the U.S. Environmental Protection Agency, Office of Solid Waste by Franklin Associates Ltd., July 1986.
- (8) Brunner, P. H.; Mönch, H. *Waste Manag. Res.* **1986**, *4*, 105.
- (9) Reimann, D. O. *Waste Manage. Res.* **1989**, *1*, 57.
- (10) Agenend, F. J.; Trondt, L. *VGB Kraftwerkstechnik* **1990**, *1*, 36.
- (11) Vehlouw, J. Paper Presented at the DAKOFA Conference, Copenhagen, Denmark, September 6, 1993.
- (12) Schachermayer, E.; Bauer, G.; Ritter, E.; Brunner, P. H. *Messung der Güter- und Stoffbilanz einer Müllverbrennungsanlage*, Monographien Bd. 56; Bundesministerium für Umwelt: Wien, Österreich, 1993.
- (13) Belevi, H. *EAWAG News* **1995**, *40D*, 19.
- (14) Bauer, G. Ph.D. Dissertation, University of Technology, Vienna, 1996.
- (15) Bauer, G.; Schachermayer, E. *Environ. Sci. Pollut. Res.* **1996**, *3* (1), 10.
- (16) Bauer, G.; Brunner, P. H. *Müll Abfall* **1996**, *1*, 96.
- (17) Morf, L.; Ritter, E.; Brunner, P. H. *MAPE III "Online Messung der Stoffbilanz einer MVA als Instrument der Erfolgskontrolle in der Abfallwirtschaft", Teil A: Güter- und Stoffbilanz der MVA Wels*; Final Report; Institute for Water Quality and Waste Management, University of Technology, Vienna, Austria, 1997.
- (18) Schachermayer, E.; Bauer, G.; Ritter, E.; Brunner, P. H. *Entwicklung einer neuen Methode, um aus den Produkten der*

Müllverbrennung Spittelau kostengünstig die Veränderung der Zusammensetzung des Wiener Mülls zu bestimmen; Final Report; Institute for Water Quality and Waste Management, University of Technology: Vienna, Austria, 1996.

- (19) Brunner, P.H.; Morf, L.; Schachermayer, E.; Ritter, E.; Bauer, G. Institute for Water Quality and Waste Management, University of Technology, Vienna, Austria, Manuscript in preparation.
- (20) Kateman, G.; Müskens, P.J.W.M. *Anal. Chim. Acta* **1978**, 103, 11.
- (21) Morf, L.; Brunner, P.H. The Effect of input and operating condition variations on the partitioning of selected metals in a MSW incinerator plant. Manuscript in preparation.
- (22) Müskens, P. J. W. M.; Kateman, G. *Anal. Chim. Acta* **1978**, 103, 1.
- (23) Switzer, P.; Eynon, B. P.; Holcombe, L. J. *Pilot Study of Time Variability of Chemical Concentrations in Power Plant Ash*; Final Report EA-2959; Electric Power Research Institute: Palo Alto, CA, 1993.

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