

Identification and Quantification of Volatile Organic Components in Emissions of Waste Incineration Plants

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1. Introduction

Emissions of municipal waste incineration plants are currently monitored for specific compound classes, such as polychlorinated dibenzodioxins (PCDD) and -furans (PCDF) in order to ensure that the limits of 0.1 ng I-TEQ/m³ are met. Besides that also the concentrations of polychlorinated benzenes, -phenoles or polyaromatic hydrocarbons can be measured. For that purpose there exists a series of proven and certified techniques for sampling, clean-up, gaschromatographic separation and quantification.^{1, 2, 3, 4)} These compound classes, however, represent only an infinitely small fraction of the total organic carbon, for which a limit of 10 mg/m³ is e.g. set in Germany. The objective of this work is to extend our knowledge on the nature of the organic emissions by identifying and quantifying the relevant components beyond the usual assays in order to allow a mass balance of the organics in the emission and to make a contribution to the discussion on the toxicity of emissions of municipal waste incinerators.

2. Experimental

Due to the broad range of volatility of the pollutants in the off-gas a combination of sampling techniques has to be applied, combined with appropriate desorption/elution to achieve high recoveries. Furthermore the identification and quantitative determination has to be carried out.

In the sampling technique used the flue gas stream (particulate concentration < 0,5 mg/m³) is passed through a cooling trap. The condensate is collected in a storage vessel at approx. 1°C. The gas stream depleted in water vapor is drawn through two separate filters (A, B) for the collection of components with high and low volatility. (see fig. 1)

Filter A (for thermal desorption of highly volatile compounds): glass tube (6 mm o.d., 4 mm i.d.) filled with XAD-16 with an additional filling of 2 cm TENAX GR at the inlet to prevent thermal stress of the material at the hot inlet. In total 10 - 30 l are sampled at a rate of 0.3 to 0.5 l/min.

Filter B (for elution of compounds with lower volatility) is a multi bed filter, consisting of equal layers in the sequence XAD-1180, XAD-16, XAD-4 with a total filter depth of 6 cm. The sampling of 400 to 3000 l is performed at a rate of 1 - 1.5 l/min. With this procedure the volatile components, first absorbed in the aqueous condensate, are purged off in the course of the sampling and transferred to the adsorption filter.

After sampling the matrices are analyzed:

a.) The thermal desorption filters (A) are heated to 220°C, the desorbed substances cryofocused on a quartz capillary (50 m, DB-5), separated in a temperature program and quantified by a flame ionisation detector. Separately for identification the desorption unit is coupled to a mass selective detector. With this filter compounds from propene up to and including toluene are analyzed.

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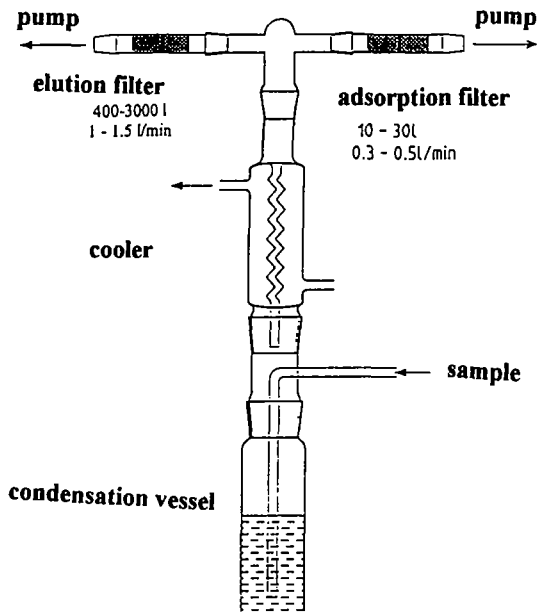


Fig. 1: Sampling train for volatile organics in the emission of incineration plants

b.) The elution filters (B), containing the less volatile compounds, are eluted with methylene chloride, containing tetracosane as internal standard.

The selection of the adsorber material was based on detailed investigations of recovery rates both by thermal desorption and elution.

c.) The condensate, after saturation with NaCl is extracted at pH 4 with methylenchloride.

The concentrates from operation b) and c.) may be combined and then subjected to an acid-base separation in order to analyze carboxylic acids and phenoles. The neutral fraction is chromatographed over alumina, with pentane, pentane/dichloromethane, dichloromethane and methanol as eluents.

With the sampling volumes as specified concentrations from $0,05 \mu\text{g}/\text{m}^3$ to $500 \mu\text{g}/\text{m}^3$ may be detected as single compounds.

3. Results and Discussion

The methods were applied in two different plants (A, B) which differ greatly by the composition of the feed and the incineration technology. The data are summarized as follows:

Plant A, feed mixed waste: With emission of $2.3 \text{ mg}/\text{m}^3$ total organic carbon some 400 components have been identified so far, representing $1.7 \text{ mg}/\text{m}^3$, i.e. ca 70% of the organic carbon could be identified. The concentrations of the compounds are summarized in table 1

The fraction of the compound classes in percent of the TOC was: aromatics 54%, aliphatic hydrocarbons identified 3%, aliphatic hydrocarbons not-identified 27%, ketones 5%, halides 5%, esters 2%, carboxylic acids 2%, phenoles 1%, alkoholes 1%.

Table 1: Concentrations of organic compounds ($\mu\text{g}/\text{m}^3$) in the emission of a plant for thermal treatment of mixed waste

	concentration $\mu\text{g}/\text{m}^3$	
	aliphatic compounds	aromatic compounds
hydrocarbons	56	1200
halogen compounds	99	20
esters	1	42
aldehyde, ketones	0,5	90
carboxylic acids	8	29
hydroxy compounds	2,6	20

Plant B, municipal waste: The emission was $1.2 \text{ mg}/\text{m}^3$. From this $0.5 \text{ mg}/\text{m}^3$ i.e. ca 44% could be identified as ca. 250 individual species. The data are summarized in table 2.

Table 2.: Concentrations ($\mu\text{g}/\text{m}^3$) of organic components in the emission of a municipal waste incineration plant

	concentration $\mu\text{g}/\text{m}^3$	
	aliphatic compounds	aromatic compounds
hydrocarbons	45.5	80
halogen compounds	31	5
esters	11.5	24
aldehyde, ketones	24	9
carboxylic acids	68	140
hydroxy compounds	9	33

The percentage of the compound classes of the emission is: aromatic hydrocarbons 7%, aliphatic hydrocarbons identified 4%, not-identified aliphatic hydrocarbons 58%, ketones 3%, halides 3%, esters 3%, acids 18% phenoles 3%, alcohols 1%.

In both cases the fraction of the non-identified aliphatic hydrocarbon is a major part of the emission and may be only evaluated by fractionating the neutral extract via liquid chromatography. A chromatogram of the pentane fraction is presented as section from heptadecane to tricosane in fig. 2. In spite of high resolution gas chromatography the chromatogram consists mainly of unresolved peaks. The mass spectra in this range show fragments typical for aliphatic hydrocarbons, a further identification was, however, not achieved.

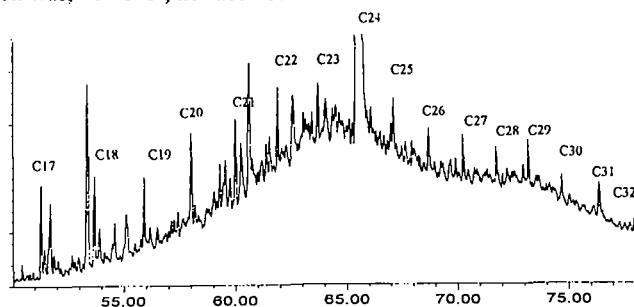


Fig. 2: Chromatogram of the pentane fraction of the combined extract from the emission of plant A.

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4. Conclusions

- A very detailed identification and quantitation of volatile organic compounds in the emissions of incineration plants is achieved by the combination of special adsorption filters with subsequent thermal desorption and elution. With these techniques 44 to 70% of the organic emission may be determined as single components
- An additional major fraction is represented by aliphatic hydrocarbons, which are not identified as individual compounds due to serious overlapping of the gas chromatographic peaks
- With these techniques available a contribution to the discussion of the toxicity of emissions is possible

5. References

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