



IDENTIFICATION AND QUANTIFICATION OF VOLATILE ORGANIC COMPONENTS IN EMISSIONS OF WASTE INCINERATION PLANTS

K. Jay*, L. Stieglitz,
Institut für Heiße Chemie,
Kernforschungszentrum Karlsruhe GmbH,
Postfach 3640,
D-76021 Karlsruhe,
Federal Republic of Germany.

(Received in Germany 16 November 1994; accepted 27 December 1994)

Abstract

A combination of different sampling techniques was applied to cover the wide range of volatility of the various organic compounds in the emission of incineration plants: The sampling steps consist of a condensation of the water vapor, adsorption/thermodesorption and adsorption/elution on selected XAD-resins. In total ca. 250 individual compounds were identified at concentrations above 50 ng/m³. These represent ca. 42% of the total organic carbon (TOC) of the emission. Additionally ca. 58% of the TOC could be shown to consist of non-identified aliphatic hydrocarbons.

Key words

municipal waste incineration, identification, emission, organic pollutants, sampling, adsorption, thermodesorption, extraction, elution.

1. Introduction

For the emission of organic compounds from municipal waste incinerators so far two limits are set by the national or European authorities: On one side it is the Toxic Equivalent (I-TEQ) as 0.1 ng/m³ as measure for the presence of 2,3,7,8 substituted polychlorinated dibenzodioxins and -furans. On the other side organics are monitored as Total Organic Carbon (TOC), with a limit e.g. of 10 mg/m³ for Germany. Formation and release of other compounds from incinerators has been the objective of a series of studies [1-8]. Mostly, however, the investigations were restricted due to the sampling technique to compound classes of medium volatility.

This study was conducted in order to identify and quantify the relevant organic components in the clean offgas of waste incineration plants beyond the usual assays for specific classes of substances [1-6] in order to allow a balance of the organic carbon contents.

As a consequence of the low concentrations it is impossible in many cases to identify and measure directly trace components in the gas phase. The compounds to be examined must first be separated from the gas matrix by isolation and enrichment techniques to obtain a concentrate. The techniques which preferably are employed include adsorption on solids followed by elution with solvents or by thermal desorption, as well as absorption in solvents followed by concentration.

The organic substances contained in the flue gas cover a wide boiling range. Attempts made with filter techniques (XAD resins and other polymers as well as carbon-based filters) to isolate the complete contents by means of an adsorbent or by multi-bed filters failed because of the high water content of the flue gas: Cold flue gas causes the filters to be wetted and deactivated by the condensed water vapor. Also diluting the flue gas with an inert gas in order to underrun the dew point is no successful approach: The less volatile hydrocarbons can no longer be quantitatively desorbed thermally. As a consequence the filters must be eluted, which on the other hand causes the highly volatile substances to be lost in the solvent peak. For adsorption of higher-boiling substances it is also possible to pass the hot flue gas stream right through the filter, which may be heated, in order to prevent most of the water from condensing. This method lends itself particularly well to the detection of polyaromatic compounds and dioxins [9]. In order to overcome the difficulties described a combination of sampling techniques was applied taking in consideration the presence of water vapor as well as the broad range of volatility of the various compound classes.

2. Experimental

The procedures were developed and applied with two incineration facilities (A, B) which differ greatly by the composition of the feed and the incineration technology. The influence of these parameters are not discussed here. This contribution is restricted to the application of the sampling procedures, the analysis of the different compartments and the evaluation for emissions.

2.1. Sampling

In the sampling technique used the flue gas stream is passed through a cooling trap (Fig. 1).

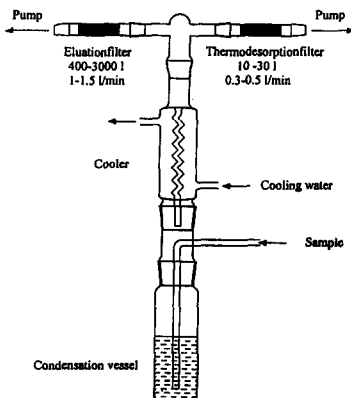


Fig. 1: Sampling Train for the Analysis of Volatile Organic Components in the Emission.

The condensate is collected in a storage vessel at approx. 2-5°C. The gas stream depleted in water vapor is drawn through two separate filters (I, II) for the analysis of components with higher and lower volatility. As a result of a detailed study of different filter materials the following filter materials were selected and used:

Filter I (for thermal desorption of highly volatile compounds): glass tube (4 mm i.d.) filled with XAD-16 (0,3 - 0,5 mm grain size), bed height 4.5 cm, 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 II (for elution of compounds with lower volatility) is a multi bed filter (4 mm i.d) consisting of equal layers in the sequence XAD-1180, XAD-16, XAD-4 (grain size 0,3 - 0.5 mm) 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.

2.2. Analysis of the Sampling Matrices

2.2.1. Analysis of the Thermal Desorption Filters

The analysis of the thermal desorption filters is performed in a Thermal Desorption Unit, Model 890, Dynatherm Analytical Instruments, Inc (Supelco). The adsorbed substances are desorbed at 220° C (8 minutes) and transferred into a quartz capillary (CP-Sil-5-CB 25 m, 0.32 mm i.d. coupled with DB-5, 60 m, 0.25 mm i.d.). The compounds are cryofocused in the capillary, cooled by liquid nitrogen for 10 min., then separated by a thermal program (35°C, 12 min, 3°C/min 200°C, 8°C/min 270°C), and detected with a flame ionisation detector. For identification a mass selective detector (HP 5890) was used. The application of the thermal desorption filters allows compounds such as CH₃Cl, CFC₃ and pure hydrocarbons from C₃ onwards to be enriched. Substances with a retention time up to and including toluene may be quantitatively determined using these filters. The method cannot be applied for quantitative analyses of higher-boiling hydrocarbons (>C₁₀) because of the temperature limits of 250 °C for thermal desorption, where higher-boiling substances are not desorbed completely. The recovery at 250°C e.g. was 100% for decane. One disturbing factor with XAD filters is a reaction of the polystyrene matrix with nitrous gases, which causes nitromethane to be emitted on desorption. Under plant conditions it was not possible to use carbon-based thermal desorption filters for quantitative analysis because, compared to the XAD filters, they exhibited a greatly reduced adsorption behavior. Although both filter materials have identical retention characteristics under laboratory conditions, apparently carbon filters are reversibly deactivated during sampling in the plant by the uptake of carbon dioxide and nitrous gases. One drawback of the thermal desorption method is the impossibility to repeat the analysis and the fact that, at high loading, the detection and recording system may be overloaded long before filter breakthrough.

Figure 2 is a typical spectrum of highly volatile substances in 20 l of flue gas from incineration plant A. The substances listed below were detected in the order shown here: (1) NO, (2) CO₂, (3) formaldehyde, (4) SO₂, (5) methyl nitrite, (6) methyl chloride, (7) acetaldehyde, (8) methyl propane, (9) acetonitrile, (10) acetone, (11) pentane, (12) methyl iodide, (13) dichloromethane, (14) 1,1-difluoro-1-chloro-2,2-dichloro-2-fluoroethane, (15) nitromethane (artefact), (16) butanal, (17) butanone, (18) ethyl acetate, (19) trichloromethane, (20) 1,2-dichloroethane, (21) bromochloroethene (22) benzene, (23) tetrachloromethane + cyclohexane, (24) 1-bromo-2-chloroethene, (25) bromodichloromethane, (26) bromochloroethane, (27) dibromoethene, (28) chloriodoethene, (29) toluene, (30) chlorodibromomethane, (31) tetrachloroethylene, (32) chloriodoethane, (33) chlorobenzene, (34) bromiodomethane, (35) ethyl benzene, (36) phenylacetylene + xylene, (37) tribromomethane, (38) styrene, (39) xylene, (40) benzaldehyde, (41) benzonitrile, (42) benzofurane, (43) 1,3-dichlorobenzene + 1,4-dichlorobenzene, (44) methyl isopropylbenzene, (45) 1,2-dichlorobenzene.

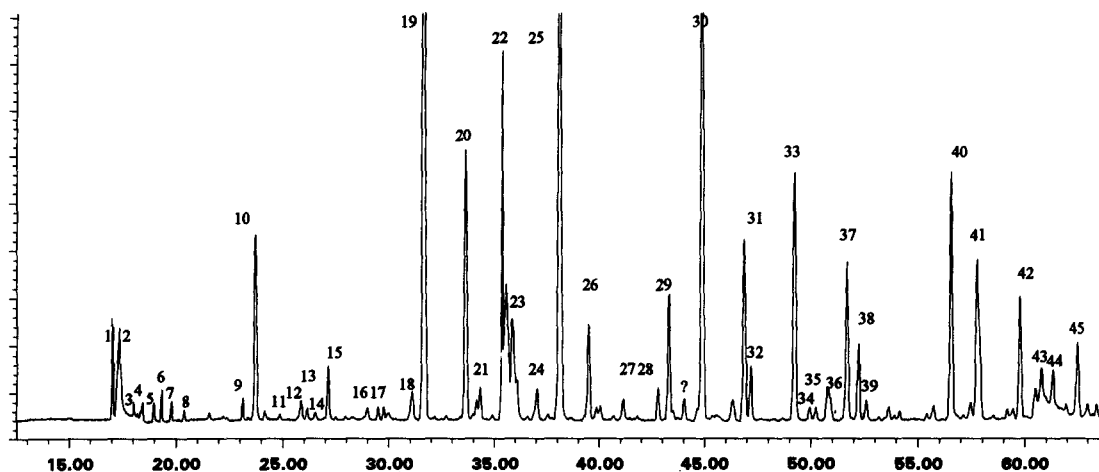


Fig. 2: Example of a Total Ion Chromatogram of a Thermal Desorption Filter of the Incineration Plant A obtained from 20 l Offgas (section).

2.2.2 Analysis of Condensate and Elution Filters

Analysis of the Condensate: The condensed water is transferred to a separation funnel. The residual water remaining in the cooler and in the sampling line is taken up with methanol, and after evaporation of the solvent combined with the condensate. The aqueous phase (150 to 200 ml/m³) is saturated with NaCl, adjusted to a pH of 4, n-tetracosane added as an internal standard, and extracted four times with 30-50 ml dichloromethane. After the organic layer has been dried with sodium sulphate, the volume is reduced to approximately 20 μ l. Application of head space gas chromatography to the condensate ensured that low-boiling substances covered by the solvent peak in gas chromatographic analysis are present only in traces. For specific assays for carboxylic acids and phenols, the extract is combined with the eluate of the XAD filter (see below) and subjected to an acid-base separation. For further analysis of the contents, the neutral sample can be chromatographed over alumina (basic, 10 g) with pentane, pentane/dichloromethane, dichloromethane, and methanol as eluents. Besides mononuclear and binuclear aromatics, the pentane fraction contains mainly aliphatic hydrocarbons (saturated and unsaturated). The more highly polar fractions contain enriched trinuclear and polynuclear aromatic compounds as well as aldehydes, ketones, and esters. Figure 3 is a chromatogram of the condensate from incineration plant A, where primarily mixed waste was treated. The sample was taken in the clean gas upstream of the activated carbon dioxin filter during the incineration of iodine bearing waste. The strongest signals are shown by these substances: (1) methyl butanone + benzene, (2) iodoethene, (3) toluene, (4) 2,5-cyclohexadiene-1,4-dione, (5) methyl hexanol, (6) benzaldehyde, (7) iodoalkane?, (8) chloriodopentane?, (9) naphthalene, (10) triiodomethane, (11) 2,4,6-trichlorophenol, (12) biphenyl, (13) 2,4-dichloro-4-nitrophenol, (14) C₆H₉OI aromatic compound, (15) naphthalenecarboxaldehyde, (16) 2,6-dibromo-4-nitrophenol, (17) fluorenone, (18) phenanthrene, (19) perinaphtenone, (20) dibutyl phthalate, (21) fluoroanthene, (22) pyrene, (23) internal standard (44.6 μ g tetracosane), (24) chrysene (triphenylene), (25) bis-(2-ethylhexyl) phthalate.

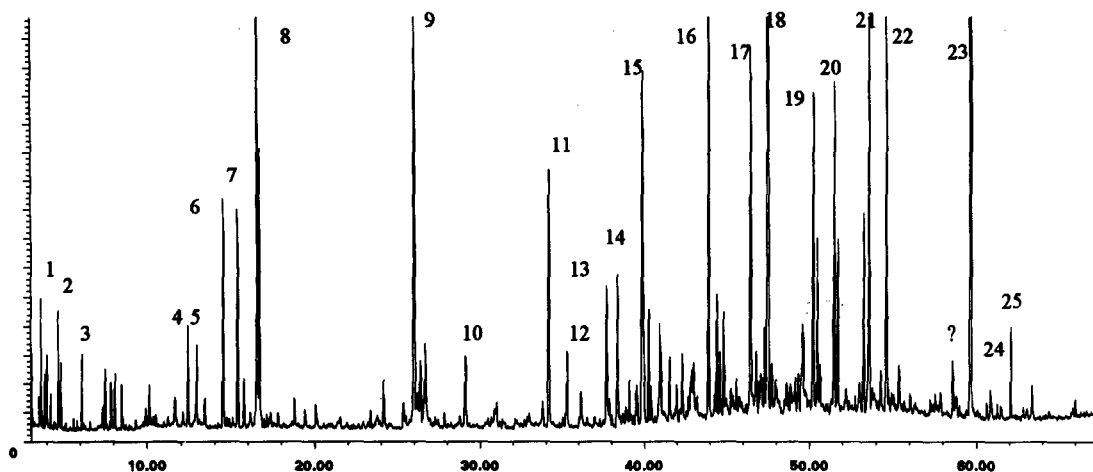


Fig. 3: Total Ion Chromatogram of the Condensate of 428 l of Offgas from Incineration Plant A.

Analysis of the Elution Filters: Substances with boiling points above toluene were enriched by means of a multibed XAD filter. These filters retain large amounts of substance (>6 mg), and are eluted with dichloromethane to which an internal standard (tetracosane) has been added. Identification was carried out with a gas chromatograph coupled to a mass spectrometer (Finnigan MAT 4500), quantification by gas chromatography over a flame ionization detector and, partly, also by mass spectrometry. Figure 4 shows the chromatogram of the eluate of the XAD filter from the same sampling event as shown in Figure 3. The most intense peaks are: (1) benzene, (2) chloriodomethane, (3) toluene, (4) elemental iodine, (5) chlorobenzene, (6) ethyl benzene, (7) xylene, (8) diiodomethane, (9) diiodoethene, (10) chloriodopentane, (11) diiodochloromethane, (12) hydroxybenzaldehyde, (13) undecane, (14) diiodobromomethane, (14) naphthalene, (16) benzoic acid, (17) trichlorobenzene, (18) triiodomethane, (19) methyl naphthalene, (20) biphenyl, (21) chloriodoethylbenzene (-xylene), (22) dibenzofuran + pentachlorophenol, (23) diiodostyrene, (24) phenanthrene, (25) hexadecanoic acid, (27) octadecanoic acid, (27) tetracosane (4.46 μ g), (28) bis-(2-ethylhexyl) phthalate.

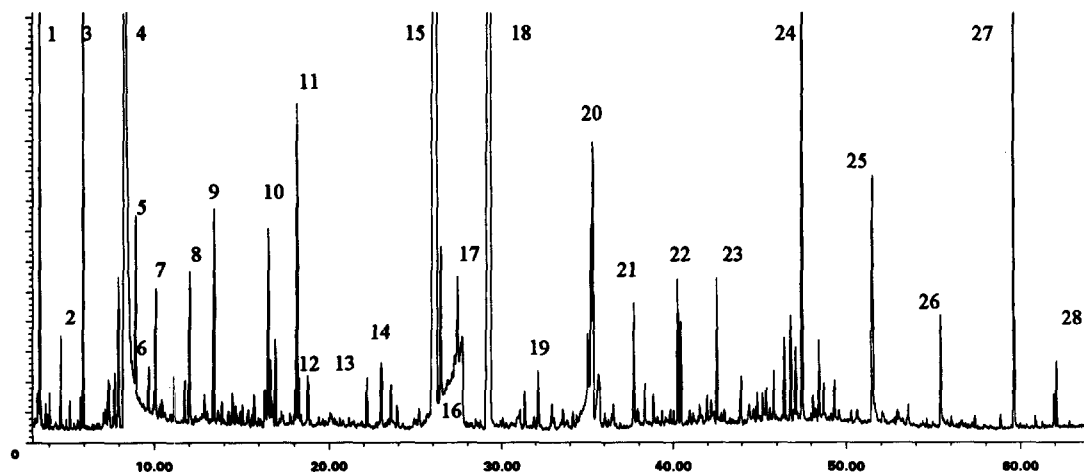


Fig. 4: Total Ion Chromatogram of the Eluate from the XAD-Filter of 361 Liters of Offgas from the Incineration Plant A.

As mentioned above, the extract of the condensate and the eluate may be combined and then analysed together. For a detailed analysis of polar compounds such as phenols and carboxylic acids an acid-base separation may be applied. The compounds identified in the acid fraction are presented in Figure 5.

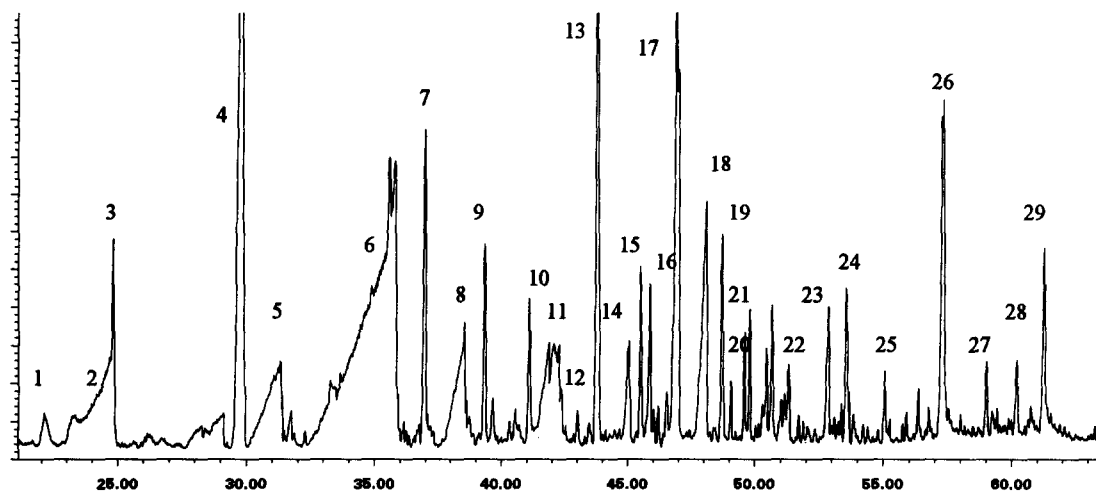


Fig. 5: Chromatogram of the Acid Compounds from the Acid Base-Separation from Incineration Plant A (section).

With this measurement 3.3 m³ of flue gas were sampled. With an emission of 2.4 mg/m³ total organic carbon the acid compounds amount to ca. 50 µg/m³. The individual substances identified are: (1) phenol, (2) hexanoic acid, (3) 2-hydroxybenzaldehyde, (4) 2-nitrophenol, (5) 2-ethylhexanoic acid, (6) benzoic acid, (7) nitrochlorophenol, (8) nonanoic acid, (9) nitrochlorophenol, (10) nitrobromophenol, (11) ethylbenzoic acid, (12) nitrobromophenol, (13) nitrodichlorophenol, (14) undecanoic acid, (15) unknown (MW = 265), (16) dinitrophenol + 4-(1,1-dimethylethyl)benzoic acid, (17) 4-nitrophenol, (18) dodecanoic acid, (19) nitrodichlorophenol, (20) dinitromethylphenol, (21) nitrodibromophenol, (25) pentadecanoic acid, (26) hexadecanoic acid, (27) naphthalenedicarboxylic anhydride, (28) naphthalenecarboxylic acid, (29) octadecanoic acid.

The composition of the fraction with neutral compounds from the acid-base separation is presented in Figure 6. The major compounds are: (1) butenal, (2) trimethyloxirane, (3) pentenol, (4) toluene, (5) ethyl propyl carbonate, (6) methoxybutanol, (7,8) unknown, (9) benzonitrile + 1,1-dimethylethylbenzene + benzofurane + chloriodopentane, (10) ethyl benzaldehyde, (11) naphthalene, (12) benzo[b] thiophene, (13) trichlorobenzene, (14) 1-phenoxypropanediol acid, (15) methyl naphthalene, (16) tridecane, (17) tetrachlorobenzene, (18) biphenyl, (19) 2-nitroethenylbenzene, (20) unknown, (21) naphthalenecarboxaldehyde, (22) dibenzofurane + pentachlorobenzene, (23) benzophenone, (24) tributylphosphate, (25) hexachlorobenzene, (26) fluorenone + dibenzothiophene, (27) phenanthrene, (28) perinaphthenone, (29) butyl-2-methylpropyl phthalate, (30) anthracinone + phenylnaphthalene, (31) fluoranthene, (32) pyrene, (33) internal standard, (34) chrysene (triphenylene), (35) 7H-benz[de]anthracen-7-one, (36) di-(2-ethylhexyl) phthalate, (37) benzofluoranthene (benzpyrene), (38) benzpyrene (benzfluoranthene) + 4H-cyclopenta(def)chrysen-4-one.

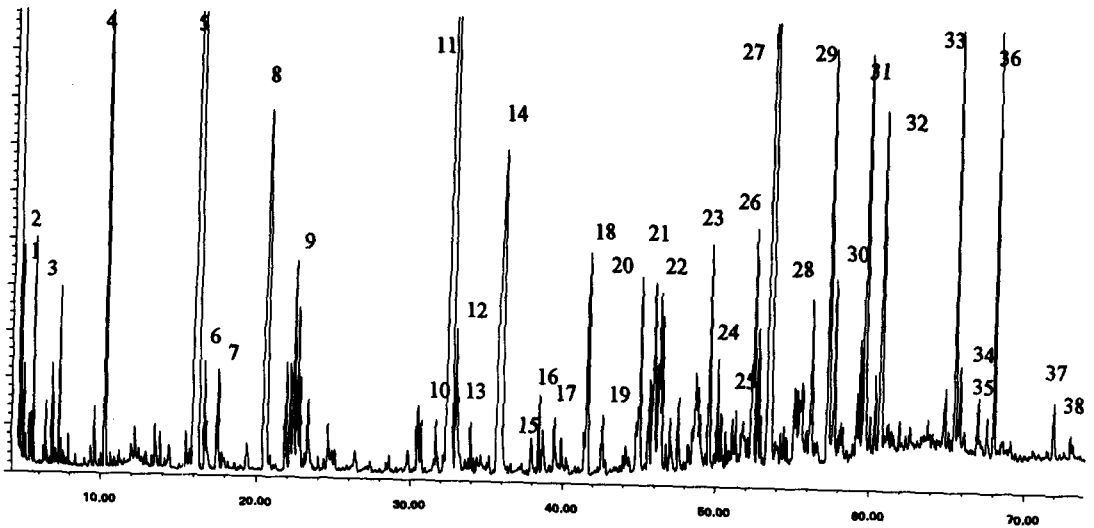


Fig. 6: Chromatogram of the Neutral Fraction from the Acid-Base Separation of Condensate and Eluate from Incineration Plant A.

The neutral fraction was further fractionated by liquid chromatography on basic alumina with pentane and pentane with rising portions of dichloromethane as eluents. In the unpolar pentane fraction mainly aliphatic hydrocarbons are found, with one and two-ring aromatics. In Figure 7 the part of the homologue series from heptadecane to tricosane is presented. The drift of the base line is caused by compounds which are not separated by the gas chromatographic column. This is a not negligible part of the total emission. The mass spectra show fragments typical for alkanes and alkenes, the compounds, however, cannot be identified unambiguously. The main peak is the internal standard. Also in this fraction is hexachlorbenzene (right from C-17), and small amounts of phenanthrene (left of C-18) and pyrene (right of C-21).

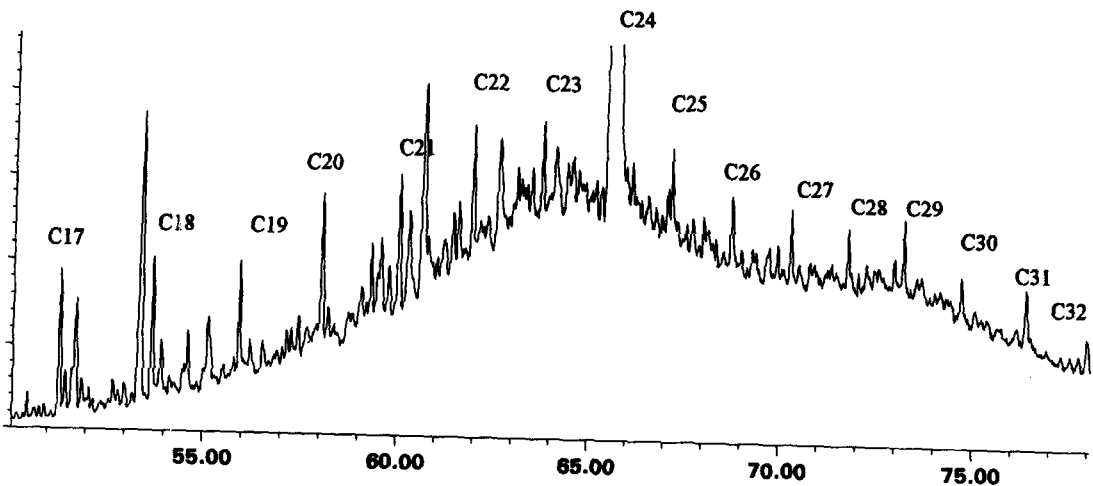


Fig. 7: Hydrocarbons in the pentane fraction from Incineration Plant A (section).

3. Results

The results from measurements at a municipal waste incineration plant (plant B) are presented in Table 1. Some of the data were obtained with a flame ionisation detector without correction factors for the internal standard. A probable error of 50 % must be encountered in these cases, the data may provide, however, a rough overview.

The emissions of total organic carbon varied between 1.2 mg/m³ and 5.4 mg/m³ in various measurements. In this measurement the level was 1.2 mg/m³. Of this quantity, some 0.5 mg, i.e. approx. 42 %, were detected as individual compounds.

Table 1: Concentration ($\mu\text{g}/\text{m}^3$) of Individual Compounds in the Emissions of a Municipal Waste Incineration Plant (n.q. = not quantified).

Substance	$\mu\text{g}/\text{m}^3$		
Pentane	1.00	Ethylcyclohexane	n.q.
Trichlorofluoromethane	2.00	2-Methyloctane	0.12
Acetonitrile	13.70	Dimethyldioxane	n.q.
Acetone	17.60	2-Furanecarboxaldehyde	0.18
Iodomethane	0.50	Chlorobenzene	2.11
Dichloromethane	20.00	Methyl hexanol	0.20
2-Methyl-2-propanol	n.q.	Trimethylcyclohexane	0.05
2-Methylpentane	3.20	Ethyl benzene	2.56
Chloroform	2.00	Formic acid	n.q.
Ethyl acetate	4.80	Xylene	7.77
2,2-Dimethyl-3-pentanol	7.00	Acetic acid	n.q.
Cyclohexane	1.70	Aliphatic carbonyl	0.19
Benzene	15.00	Ethylmethylcyclohexane	0.07
2-Methylhexane	3.60	Xylene	1.79
3-Methylhexane	2.70	2-Heptanone	n.q.
1,3-Dimethylcyclopentane	1.00	2-Butoxyethanol	0.23
1,2-Dimethylcyclopentane	1.00	Nonane	0.57
Trichloroethene	4.00	Isopropyl benzene	0.11
Heptane	4.70	Propylcyclohexane	0.16
Methylcyclohexane	4.70	Dimethyloctane	0.07
Ethylcyclopentane	1.00	C ₁₀ H ₂₂ HC	0.27
2-Hexanone	1.60	C ₁₀ H ₂₂ HC	0.18
Toluene	34.00	Pentanecarboxylic acid	1.31
1,2-Dimethylcyclohexane	0.03	Propyl benzene	0.28
2-Methylpropyl acetate	0.23	C ₆ H ₁₂ O HC	0.11
3-Methyleneheptane	n.q.	Benzaldehyde	1.32
Paraldehyde	n.q.	5-Methyl-2-furane carboxaldehyde	0.15
Octane	n.q.	1-Ethyl-2-methylbenzene	1.26
Tetrachloroethylene	0.16	1,3,5-Trimethylbenzene	0.34
Butanoic acid ethyl ester	0.08	C ₁₂ H ₂₆ O alcohol	0.13
Butyl acetate	5.72	Trimethylbenzene	0.42

Benzonitrile	0.30	Ethyl benzaldehyde	1.81
Methylpropylcyclohexane	0.02	2,4-Dichlorophenol	2.39
Methylpropylcyclohexane	0.24	1,2,4-Trichlorobenzene	0.55
2-Chlorophenol	0.53	Naphthalene	1.51
1,2,4-Trimethylbenzene	1.17	Cyclopentasiloxanecamethyl	0.06
Phenol	1.40	Methyl acetophenone	0.76
C ₁₀ H ₂₀ HC	0.04	C ₉ H ₈ O aromatic compound	0.11
1,3-Dichlorobenzene	0.21	Ethanol-1-(2-butoxyethoxy)	0.08
1,4-Dichlorobenzene	0.51	4-Chlorophenol	1.25
Decane	0.94	Benzothiazole	0.31
Hexanecarboxylic acid	1.07	Benzoic acid	100.92
1-Ethyl-4-methylbenzene	0.22	Octanoic acid	0.28
2-Methylisopropylbenzene	2.19	2-Bromo-4-chlorophenol	0.47
Cyclotetrasiloxaneoctamethyl	n.q.	1,2,5-Trichlorobenzene	0.12
1,2-Dichlorobenzene	0.02	Dodecane	0.14
Benzyl alcohol	3.97	Bromochlorophenol	0.23
Trimethylbenzene	n.q.	2,4-Dichloro-6-methylphenol	0.16
1-Methyl-3-propylbenzene	0.10	Dichloromethylphenol	0.26
2-Ethyl-1,4-dimethylbenzene	0.10	Dichloromethylphenol	0.15
C ₆ H ₁₀ O ₂ aliphatic carbonyl	0.26	Hydroxybenzotrile	0.08
2-Methylbenzaldehyde	1.87	Tetrachlorobenzene	0.28
1-Methyl-2-propylbenzene	0.12	Methylbenzoic acid	4.23
Methyl decane	0.06	Nitrogen compound, m.w. 269	2.04
C ₁₂ H ₂₆ HC	0.05	C ₉ H ₁₈ O ₃ aliphatic compound	0.30
4-Methylbenzaldehyde	0.96	Trichlorophenol	0.18
C ₁₃ H ₂₈ HC	0.34	2-(Hydroxymethyl)benzoic acid	0.50
1-Ethyl-3,5-dimethylbenzene	n.q.	2-Ethyl-naphthalene-1,2,3,4-tetrahydro	0.08
1-Methyl-(1-propenyl)benzene	0.21	2,4,6-Trichlorophenol	9.55
Bromochlorobenzene	n.q.	4-Ethylacetophenone	0.59
4-Methylphenol	0.43	2,3,5-Trichlorophenol	0.49
Benzoic acid methyl ester	0.12	4-Chlorobenzoic acid	1.16
2-Chloro-6-methylphenol	0.10	2,3,4-Trichlorophenol	0.48
Ethyl-dimethylbenzene	0.00	1,2,3,5-Tetrachlorobenzene	0.30
Undecane	0.67	1,1'-Biphenyl (2-ethenyl-naphthalene)	0.64
Heptanecarboxylic acid	0.50	3,4,5-Trichlorophenol	0.04
C ₈ H ₁₄ O cyclohexanone derivative	0.16	Chlorobenzoic acid	0.91
1-(Chloromethyl)-4-methylbenzene	0.28	2-Hydroxy-3,5-dichlorobenzaldehyde	0.03
1,3-Diethylbenzene	0.15	2-Methylbiphenyl	0.20
1,2,3-Trichlorobenzene	0.07	2-Nitrostyrene(2-nitroethenylbenzene)	0.76
C ₄ alkylbenzene	0.05	Decanecarboxylic acid	1.44
C ₅ alkylbenzene	0.03	Hydroxymethoxybenzaldehyde	0.12
4-Methylbenzyl alcohol	0.95	Hydroxychloroacetophenone	0.07
Ethylhexanoic acid	0.60	Ethylbenzoic acid	35.31

C ₉ H ₈ O aromatic compound	0.05	Tetradecanecarboxylic acid	15.08
2,6-Dichloro-4-nitrophenol	0.05	Octadecane	0.91
Sulphonic acid, m.w. 192	0.58	Phthalic ester	0.17
4-Bromo-2,5-dichlorophenol	1.20	N-bearing aromatic compound, m.w. 405	2.08
2-Ethylbiphenyl	0.17	Tetradecanoic acid isopropyl ester	0.20
Bromodichlorophenol	0.33	Caffeine	0.14
1(3H)-Isobenzofuranone-5-methyl	0.11	12-Methyltetradecanecarboxylic acid	2.71
Dimethylphthalate	0.32	Phthalic ester + C ₁₅ acid	1.06
C ₈ H ₅ O ₂ N	0.12	Pentadecanecarboxylic acid	1.41
Si organic compound	0.24	Methylphenanthrene	0.06
2,6-Di-tertiary-butyl-p-benzoquinone	0.20	N-bearing aromatic compound, m.w. 405	0.58
3,4,6-Trichloro-1-methyl-phenol	1.50	Nonadecane	0.48
2-Tertiary-butyl-4-methoxyphenol	1.23	9-Hexadecene carboxylic acid	1.92
2,2'-Dimethylbiphenyl	0.78	Anthraquinone	0.14
2,3'-Dimethylbiphenyl	1.72	Dibutylphthalate	7.66
Pentachlorobenzene	0.42	Hexadecanoic acid	36.78
Bibenzyl	0.82	Elemental sulphur, S ₈	1.87
2,4-Di-tertiary-butylphenol	1.77	Eicosane	0.28
2,4'-Dimethylbiphenyl	0.67	Methylhexadecanoic acid	1.97
C ₈ H ₅ BrCl ₃ , aromatic compound, m.w. 284	0.24	Fluoroanthene	0.19
1-Methyl-2-phenylmethylbenzene	0.68	Pentachlorobiphenyl	0.21
Benzoic acid phenyl ester	0.35	Aliphatic alcohol?	0.88
2,3,4,6-Tetrachlorophenol	4.42	Heptadecanecarboxylic acid	n.q.
Tetrachlorobenzofurane	0.26	Pyrene	0.25
Fluorene	0.01	Heneicosane	0.31
Phthalic ester	0.05	Octadecadienecarboxylic acid	0.00
Dodecanecarboxylic acid	0.94	Octadecadienal	1.67
3,3'-Dimethylbiphenyl	0.72	Pentachlorobiphenyl	0.16
3,4'-Dimethylbiphenyl	1.01	Aliphatic amide	0.74
Dimethylbiphenyl	0.14	Octadecanecarboxylic acid	2.23
Hexadecane	0.50	Hexadecane amide	1.20
Benzophenone	1.16	Docosane	0.35
C ₁₁ H ₁₅ O ₂ N aromatic compound	0.53	Hexachlorobiphenyl	0.30
Tridecanoic acid	0.14	Benzylbutylphthalate	2.80
Hexachlorobenzene	0.11	Aliphatic amide	26.67
Heptadecane	0.36	Diisooctylphthalate	11.23
Fluorenone	1.69	Hexadecanoic acid hexadecyl ester	0.48
Dibenzothiophene	0.19	Cholesterol	0.70
Pentachlorophenol	1.92		
Sulphonic acid, m.w. 224	0.27		
Phenanthrene	1.09	Total (µg/m ³)	525.48

The data of the individual compounds are summed up by compound classes. The sums are presented in Table 2.

Table 2: Organic Pollutants in the Emission of Incineration Plant B.

compound class	concentrations ($\mu\text{g}/\text{m}^3$)	
	aliphatic	aromatic
hydrocarbons, identified	45.5	80
halogen compounds	31	5
esters	11.5	24
aldehydes, ketones	24	9
carboxylic acids	68	140
hydroxy compounds (ROH)	9	33
sum	189	291

In the evaluation some arbitrary assignments had to be made: So chlorphenols are listed as hydroxycompounds rather than as chlorocompounds. Some substances such as nitriles, thiophens and amides are omitted in the summary. In total ca. 250 individual compounds are identified with concentrations ranging from 0.05 to 100 $\mu\text{g}/\text{m}^3$. With regard to the total organic carbon in the emission this corresponds to ca 42% of the TOC. Not included in this evaluation is the fraction of aliphatic hydrocarbons not separated by gas chromatography, as shown in Figure 7. From a different classification the following fractions are obtained for the measurements of the emission at the municipal waste incineration plant B:

aromatic hydrocarbons	7%	ketones	3%
aliphatic hydrocarbons (identified)	4%	halides	3%
aliphatic hydrocarbons (not identified)	58%	esters	3%
acids	18%	phenols	3%
alcohols	1%		

4. Summary

The detection of the organic traces in the emissions of incineration plants requires a combination of enrichment techniques. A number of adsorbers have been examined for isolation of particularly volatile compounds and subsequent thermal desorption. XAD-16 resin has been found to be suitable for this purpose. Less volatile components stripped from the condensate can be collected with good recovery on a multi-bed XAD filter, from where they can be eluted with methylenechloride. The substances contained in the condensate are extracted from the aqueous matrix, and, depending on requirements, combined with the eluate from the adsorption, can be further fractionated by acid-base separation followed by column chromatography. The combination of all these methods allows the volatility range starting from C_3 -alkanes and methyl derivatives, respectively, to be investigated. Compounds with concentrations as low as 0.05 $\mu\text{g}/\text{m}^3$ may be identified and quantified.

5. Acknowledgement

The authors would like to thank the Project PWAB Water, Waste, Soil Project of the State of Baden-Württemberg for the financial support. Thanks are due to Mr. Bigga for performing the experiments and to Mr. Roth and Mr. Zwick for recording the mass spectra.

6. Literature

- [1] VDI-Kommission Reinhaltung der Luft: Dioxin, eine technische, analytische, ökologische und toxikologische Herausforderung. VDI-Bericht 634, VDI-Verlag, Düsseldorf, 1987.
- [2] W. Schäfer, K. Ballschmiter, *Chemosphere* 15, 755-63 (1986).
- [3] U.G. Ahlborg, K. Victorin, *Waste Management & Research* 5, 203-24, 1987.
- [4] Environment Canada: The National Incinerator Testing and Evaluation Program, Two Stage Combustion, Prince Edward Island. Summary Report, EPS3/VPI, Sep. 1985.
- [5] P.H. Brunner, M.D. Müller, S.R. McDow, H. Mönch, *Waste Management & Research* 5, 355-66, 1987.
- [6] VDI-Kommission Reinhaltung der Luft: Messen gasförmiger Emissionen. VDI-2457, Blatt 2, Vorentwurf, June 1991.
 VDI-Kommission Reinhaltung der Luft: Messen von Reststoffen. VDI-3499, Blatt 1, March 1990.
 VDI-Kommission Reinhaltung der Luft: Messen von Reststoffen. VDI-3499, Blatt 2, Vorentwurf.
 VDI-Kommission Reinhaltung der Luft: Messen von Reststoffen. VDI-3499, Blatt 3, Vorentwurf.
 VDI-Kommission Reinhaltung der Luft: Messen von Reststoffen. VDI-3499, Blatt 4, Vorentwurf.
- [7] J. Wienecke, H. Kruse, O. Wassermann, *Chemosphere* 25, 437-447, 1992
- [8] J. Wienecke, H. Kruse, O. Wassermann, *Chemosphere* 25, 1889-1895, 1992
- [9] W. Funcke, H. Linnemann, *Chemosphere*, 24, 1563-72, 1992.
- [10] K. Jay, L. Stieglitz in: Bericht über das 3. Statuskolloquium am 18./19. Februar 1992, KfK-PWAB 13, June 1992, pp. 191-201.