THE DETERMINATION OF ORGANOHALOGEN COMPOUNDS AND OTHER TRACE COMPONENTS IN LANDFILL GASES

K.Koch, M.Schreiner, O.Vierle
Bayerisches Landesamt für Umweltschutz,
Rosenkavalierplatz 3, D-8000 München 81 / F.R.G.

ABSTRACT

Samples of landfill gases of 6 Bavarian landfills have been investigated for organohalogen compounds and other trace components essentially by high-resolution gaschromatography with mass spectrometric and flame ionization detector.

INTRODUCTION

In 1987, a program was started by the Bayer. Landesamt fuer Umweltschutz (LfU, Bavarian State Office for Environmental Protection) for the investigation of gaseous effluents from six selected representative Bavarian landfills. In a schedule of quarterly tests samples should be investigated principally to get an idea about the impact to the environment and to possible commercial utilization, also about seasonal trends in the composition of landfill gases. The landfills are situated in southern Bavaria and characterized as follows (Table 1):

Table 1. Investigated landfills

landfill No.	deposit	volume Mio m^3	utilization or removal of gas
1	garbage *	5.4	open flare
2	garbage *	4.2	flame tube
3	garbage *	0.26	open flare
4	garbage *	0.14	flame tube
5	garbage *	0.33	generation of current, waste heat utilization
6/1 **	garbage */ sewage sludge	13.4	open flare
6/2 **	garbage */ industrial waste		open flare

* garbage - like industrial waste included

** two different deposit areas

EXPERIMENTAL PART

Sampling procedures

- Adsorption on activated charcoal

Two samples of landfill gas were drawn simultaneously by membrane pumps from gas wells (flow rate 500 ml/min or less, sample volume 5-10 l) through two combined tubes (1 sample tube, 1 back-up tube) each containing activated coconut charcoal, for trapping especially apolar organic trace components. Water was removed by freezing in a cold trap at about -15 degrees C. After sampling the tubes were sealed and stored at -25 degrees C until analysis.

- Adsorption on Tenax (R)

Other samples were drawn similarly through tubes, containing preconditioned Tenax (R) (Poly-2,6-diphenylphenylenoxid) (flow rate 200 ml/min or less, sample volume about 5 l) for trapping the more polar components. Storage as above.

- Other methods

Other samples of landfill gas were taken directly from gas wells with 50 l-Tedlar (R) bags for the quantitative determination of CH_4 and CO_2.

Heavy metals were collected by absorption in impingers, containing solutions of $K_2Cr_20_7$ in nitric acid. The meteorological conditions and the gas flow rates in the sampled gas wells were documented, too.

Analytical methods

- Organic trace components

The trace components adsorbed on Tenax (R) were thermodesorbed in a heated special injector block, cryofocussed on the first loop of a suitable column and identified after gaschromatographic separation by mass spectrometry (GC/MS)(Table 2).

Table 2. GC/MS-conditions

gas chromatograph:	Perkin-Elmer 9610
column:	Fused silica; DB-5, 60 m, ID 0,32 mm, film thickness 0,25 microm;
temp. program:	7 min thermodesorption at 300 degrees C with cryofocussing (liquid nitrogen): 10 min 30 degrees C isothermal; 5 degrees/min to 300 degrees C; 10 min 300 degrees C isothermal
injector temperature:	300 degrees C;
carrier gas:	Helium 5.0, 25 cm/s;
mass spectrometer:	Finnigan 4500; EI-standard conditions (70 eV);

The activated charcoal tubes were extracted for 30 min with CS_2, freshly distilled by means of "ROTARY-TAPE" distillation apparatus. 1 Microl-aliquots of this extracts were used for the quantitation of some relevant and known components by high resolution capillary gaschromatography (GC)(Table 3). The quantitation was performed using the "INNER-STANDARD"-method (1-Cl-Hexane) with flame ionization detector (FID)(Table 4). The condensates of the cold traps were extracted with diethyl ether or CH_2Cl_2 and analyzed as above.

Table 3. GC-conditions

gas chromatographs:	Hewlett-Packard 5880A, Sichromat 2;
columns:	Fused silica; DB-1, DB-5, 60 m, ID 0,25 mm, film thickness 1 microm;
detector:	FID, 280 degrees C;
carrier gas:	Helium 5.0, Hydrogen 5.0, 25-45 cm/s;
temp. program:	multilevel temperatur program;
injector temperature:	220 degrees C;
injection mode:	split/splitless (GROB);

- other components / method of detection:

CH_4, CO_2 / Fourier-Transform infrared spectroscopy (FT-IR), NICOLET 55XC;

H_2S / Sulfipac 83, DRAEGER;

Heavy metals / Atomic Absorption Spectroscopy (AAS), GBC;

RESULTS AND DISCUSSION

About 50 organic trace components (aliphatic, aromatic, terpenoid and halogenated hydrocarbons, sulphurous compounds) were identified in landfill gases by GC/MS and part of them quantitatively determined by GC/FID (Table 4). The main components are toluene, some terpenes and xylenes besides some aliphatic (C7-C14)-, alkylaromatic (C8-C9)- hydrocarbons and tri-/tetrachloroethylene. The concentrations vary, depending on the nature of deposits.

Some indications exist that landfill gases contain traces of heavy metals. In view of the ozone problem it is also intended to determine chlorofluorocarbons (CFC) in landfill gas by thickfilm capillary gaschromatography. The investigations are still in progress.

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Tabel 4. Representative concentrations of some trace compounds in landfill gas (mg/m^3) *

landfill No.	--- 1 ---	--- 2 ---	--- 3 ---	--- 4 ---	--- 5 ---	--- 6/1 ---	--- 6/2 ---
n-Heptane	0.9	4.4	4.8	4.1	1.9	4.5	11.9
n,i-Octane (sum)	0.3	12.2	3.6	3.3	3.3	7.5	17.6
n-Nonane	0.3	34.3	2.8	8.5	21.6	25.2	47.3
n-Decane	0.2	55.5	1.1	10.4	35.5	51.0	66.6
n-Undecane	0.1	13.6	0.2	3.3	10.7	35.9	43.1
n-Dodecane	0.1	7.9	< 0.1 (dl)	0.5	2.2	11.6	11.5
Benzene	1.9	2.7	1.8	0.9	0.7	6.0	30.7
Toluene	5.0	201.3	34.3	19.6	22.8	54.5	76.9
Ethylbenzene	1.4	71.7	10.7	12.7	16.4	33.7	48.6
Xylenes (sum)	1.7	154.9	18.6	25.0	37.8	71.4	130.2
C3-Benzenes (sum)	0.6	74.6	3.3	15.1	24.8	74.9	117.3
Terpenes (sum estimated)	n.d.	527.3	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroethylene	0.8	10.3	1.5	0.9	1.6	10.5	1.7
Tetrachloroethylene	0.2	24.0	1.3	2.4	2.3	2.6	1.1

* sums of the contents of condensates and associated activated charcoal tubes

n.d. = not determined

dl = detection limit