

DETERMINATION OF TOXIC ORGANIC SUBSTANCES IN CEMENT-FIXED MIXED WASTE.

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ABSTRACT

In Germany it is not permitted to deposit mixed waste in the planned final repositories for radioactive waste (1). Therefore methods are required to control the composition of the cement fixed low level radioactive waste. In contrast to the well known methods to analyze the radioactive isotopes no methods have been developed so far to determine organic substances in such waste. In this work extraction, steam distillation/extraction and dynamic headspace analysis have been investigated as possible methods to separate eight organic model substances from a cement matrix and suitable GC/MS determination methods were developed. For qualitative analysis the dynamic headspace analysis proved to be the most promising method, especially if fast response was required. The slower extraction method gave recovery rates up to 100 % and is therefore preferential for quantitative analysis. The influence of the cement matrix and of irradiation on the model substances was also investigated.

INTRODUCTION

Mixed waste is defined as waste, which contains low-level radioactive material and non-radioactive, toxic components. In former times the radioactivity content was considered bearing the main risk, but the toxic components represent an additional potential hazard, which can not be neglected. The projected final repositories in Germany are designed for cement-fixed low-level radioactive waste, but toxic substances were not regarded in the safety assessments of these sites. Therefore in Germany it is not permitted to store mixed waste in a final repository for radioactive waste (1). For this reason it is necessary to control the content of the cement-fixed, low-level radioactive waste. The radioactive isotopes can be identified by different well known spectroscopic methods. Especially γ -radioactive substances are relatively easy to detect and in this case it is even not necessary to destroy the samples (2). In this work different methods to determine organic compounds possibly present in cement-fixed low-level radioactive waste were investigated.

SAMPLE PREPARATION

Instead of real waste organic model substances were used, which were fixed with portland cement PZ35F. The organic model substances were chosen from the NAGRA report NTB 85-61 (3): tetrachloromethane (TCM), trichloroethene (TCE), tributyl phosphate (TBP), hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), fluoranthene (FLU), pyrene (PYR), Clophene^{*}, octachlorodibenzofurane (OCDF) and octachlorodibenzodioxine (OCDD). The prepared specimens had a diameter of 24 mm and a height of 35 mm. The amount of cement was 30 g and the water/cement ratio was 0.33 for all samples. The concentrations of the model sub-

stances were 1, 0.5 and 0.1 % w/w in relation to the mass of cement, except the model substances OCDF and OCDD. These were used in concentrations of about 40 and 10 ppm w/w in relation to the cement mass. The minimum hardening time of the samples was 28 days.

To simulate the influence of radiation in the low-level radioactive waste parallel samples were irradiated with a γ -dose of $5 \cdot 10^4$ Gy. This corresponds to the dose which would be absorbed in this kind of waste during about ten years. The irradiations were performed in cylindrical stainless steel containers.

Irradiated or non-irradiated samples were entirely crushed to grain sizes of < 0.1 mm and homogenized for several hours, except samples containing OCDD or OCDF. To avoid dissemination of contaminated material into the environment, drilling dust samples were prepared from these specimens. Another sample containing OCDD and OCDF was prepared with a concentration of about 100 ppb by mixing the drilling dust of the 10 ppm sample with powdered hardened cement in the relation 1 : 100. To suppress any loss of the volatile substances TCM and TCE the samples containing these substances were treated under liquid nitrogen.

The solid samples were investigated by steam distillation/extraction, extraction and dynamic head space analysis and the gas phase over the irradiated samples by gas chromatography.

STEAM DISTILLATION/EXTRACTION

The sample was boiled with water for two hours. The vapors, which were enriched with organic substances, were guided to a special condenser. In another flask hexane was boiled, the vapor was led to the same condenser and extracted the condensed water immediately. The condensates

* Clophene is a technically produced mixture of polychlorinated biphenyls (PCB) containing 20% of trichlorobenzene (TCB).

entered a separator and the extracted water was recycled. The organic substances were enriched in the liquid hexane phase and analyzed directly with gas chromatography/mass spectrometry (GC/MS). The GC/MS-conditions are listed in Table I.

EXTRACTION WITH HEXANE

An aliquot of the sample was extracted with 20 ml hexane for 2 or 16 hours. Dodecane was added to the hexane solution as internal standard. The extract was investigated with GC/MS. A clean-up of the extracts was not necessary. The GC/MS-conditions were the same as in the steam distillation/extraction method.

DYNAMIC HEADSPACE ANALYSIS

This method analyzes the gas phase over a solid or liquid sample (4). The volatile substances are distributed between the cement matrix and the gas phase corresponding to a temperature related distribution equilibrium. An inert gas with a constant flow is led through the inlet of a dual needle system into a rubber sealed bottle containing the sample and optionally a small amount of water (between 50 and 200 µl). The sample bottle is immersed in an oil bath

at constant temperature. The gas leaves the bottle through the outlet of the needle. A certain fraction of the organic material evaporates into the gas phase and is transported with the gas stream. The gas stream enters a cooled trap, filled with Tenax or another suitable absorber. After a preset time, the sample bottle is coupled off and the carrier gas flows directly through the trap into the GC system. When the trap is heated, the organic substances desorb and can be separated and detected with GC/MS. The conditions of the GC/MS and the dynamic headspace analyzer are listed in Table II. Applying this method, samples containing TBP, HCB, FLU and PYR were investigated.

ANALYSIS OF THE GAS PHASE OVER THE IRRADIATED SAMPLES

The stainless steel containers with the irradiated samples are fitted with valves, in order to investigate the gas phase over the irradiated samples gas-chromatographically. The containers are connected with the rotary gas sampling valve of the GC. The gas flows through the inlet line into the evaporated sample loop. For injection the valve rotor is switched to the carrier gas stream flowing onto the column. The GC-conditions are listed in Table III.

TABLE I
GC/MS-Conditions for Quantitative Analysis

GC	:	Siemens SiCHROMAT 2
Column	:	DB 5
Length	:	60 m
Diameter	:	0.32 mm
Film thickness	:	0.25 µm
Injector	:	On Column
Temperature	:	4 min - 30 °C, 30 - 280 °C with 10 °C/min, 5 min - 280 °C
Carrier gas	:	Helium
Pressure	:	1.0 bar
Detector	:	Finnigan MAT INCOS 50
Interface temperature	:	280 °C
Ion source temperature	:	200 °C
Ionisation energy	:	70 eV
Scan range	:	70.5- 71.5 u 99.5- 99.5 u 116.5-117.5 u 131.5-132.5 u 179.5-183.5 u 201.5-202.5 u 283.5-284.5 u
Scan time	:	0.5 sec

TABLE II

GC/MS-Conditions for Qualitative Analysis with Dynamic Headspace Analysis

GC	:	Siemens SiCHROMAT 2
Column	:	DB 5
Length	:	50 m
Diameter	:	0.32 mm
Film thickness	:	0.25 μ m
Injector	:	Dani Purge&Trap SPT 3750
Temperature	:	4 min - 30 °C, 30 - 280 °C with 10 °C/min, 10 min - 280°C
Carrier gas	:	Helium
Pressure	:	1.0 bar
Detector	:	Finnigan MAT INCOS 50
Interface temperature	:	280 °C
Ion source temperature	:	200 °C
Ionisation energy	:	70 eV
Scan range	:	98.5-100.5 u 154.5-156.5 u 179.6-182.5 u 201.6-203.6 u 281.6-284.6 u 291.6-294.6 u 323.6-328.6 u 359.6-364.6 u
Scan time	:	0.6 sec
Conditions of Dani Purge&Trap SPT 3750		
Valve Temperature	:	140 °C
Bath Temperature	:	95 °C
Residence Time of the Sample in the Oil Bath	:	10 - 610 min
Transferline temperature	:	150°C
Trap temperature (min.)	:	30°C
Trap temperature (max.)	:	280°C
Purge time	:	29 or 14 min
Injection time	:	3 min
Purge flow	:	20ml/min
Trap cool time	:	17 or 32 min
Back flow time	:	10 min

TABLE III
GC-Conditions for Gas Analysis

	A	B
GC	Siemens SiCHROMAT 2	Siemens SiCHROMAT 2
Precolumn	Porapak Q	Poraplot Q
Length	2.5 m	10 m
Diameter	1/8"	0.32 mm
Film thickness	Packed	10 μ m
Column	Molsieve 5Å	Molsieve 5Å
Length	5 m	25 m
Diameter	1/8"	0.32 mm
Film thickness	packed	30 μ m
Temperature		
Oven 1	80 °C	70 °C
Oven 2	60 °C	30 °C
Detector	HTD	HTD
Carrier gas	Argon	Helium
Pressure		
Precolumn	2.5 bar	2.2 bar
Column	2.0 bar	2.0 bar

A: for oxygen, nitrogen, hydrogen and methane

B: for hydrocarbons up to C4

RESULTS

Hydrogen was detected in the gas phase of all irradiated samples. This is not necessarily related to the presence of organic substances, because irradiation of hardened cement always results in the formation of hydrogen. The gas phase over the TBP sample contained ethane, propane and two C4-hydrocarbons. These are radiolysis products of TBP. The gas phase over the irradiated TCM respectively TCE sample contained just these constituents, but no further radiation degradation products.

All model substances except HCH could be identified qualitatively applying any of the mentioned separation methods. HCH is quantitatively dehydrochlorinated in the cement matrix to TCB, which could be detected by qualitative analysis. The model substances TCM and TCE were recovered only in trace amounts.

To increase the sensitivity of the dynamic headspace analysis water was added to the samples. The amount of water was varied between 50 and 200 μ l. More than 200 μ l should not be added, because this shifts the retention time and overcharges the multiplier of the mass spectrometer, resulting in a lower detection sensitivity rate. The peak areas of parallel samples, containing FLU and PYR, with different amounts of water are shown in Fig. 1. The areas increase

proportional to the amount of water. In another test series water aliquots were added sequentially to the same sample and analyzed after each water addition. Figure 2 shows the relative peak areas of the single analysis in per cent of the total peak areas in the four analysis after adding 50, 100, 100 μ l of water and finally 100 μ l of a saturated NaCl solution. Relative peak areas higher than 50 % after the addition of the initial 50 μ l water express that this amount of water is sufficient to separate the major fraction of the model substances from the cement matrix.

Quantitative analysis was performed using the extraction and the steam distillation/extraction method. The results of quantitative analysis are expressed as recovery rate in per cent. The calculation of the recovery rate is described in Eq. 1.

$$RR = A_m/A_t \cdot 100 \quad (\text{Eq.1})$$

RR: Recovery rate in per cent

A_m: Measured amount of the model substance

A_t: Theoretical amount of the model substance

For the estimation of the necessary extraction time parallel samples were extracted for 2, 7, 17 and 20 hours. Fig. 3 shows the recovery rates of the model substances TBP, HCB, FLU, PYR and TCB for different extraction times. The relative error of the recovery rate is between 7.8

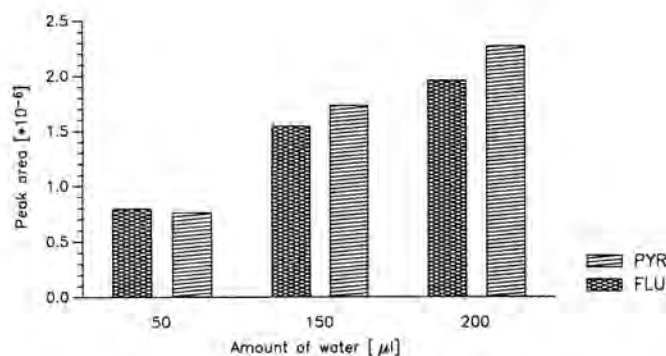


Fig. 1. Sensitivity of dynamic headspace analysis. Peak area, depending on the amount of water added.

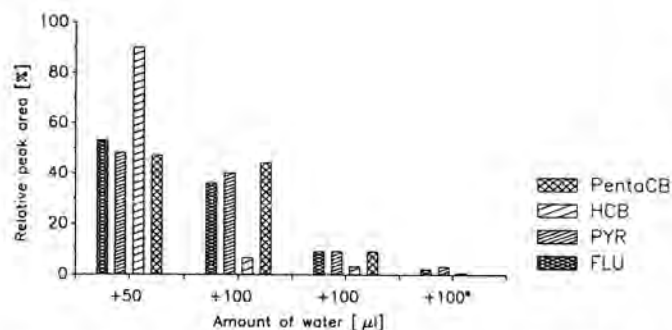


Fig. 2. Dynamic headspace analysis. Sequential addition of water to one sample. *Saturated NaCl solution.

% (for TBP) and 16.5 % (for FLU) depending on the model substance. Within this error range the recovery rates are equal for all extraction times. The extraction can be considered total after two hours. The only explanation for recovery rates higher than 100% is an inhomogeneous distribution of the organic substances in the sample. For these extractions selected pieces of the crushed samples were used. For the following extractions the entire samples were powdered and homogenized to avoid sampling errors due to the inhomogeneous distribution of the model substances in the cement block. Figure 4 shows an example of recovery rates obtained with such a homogenized powder sample. The concentra-

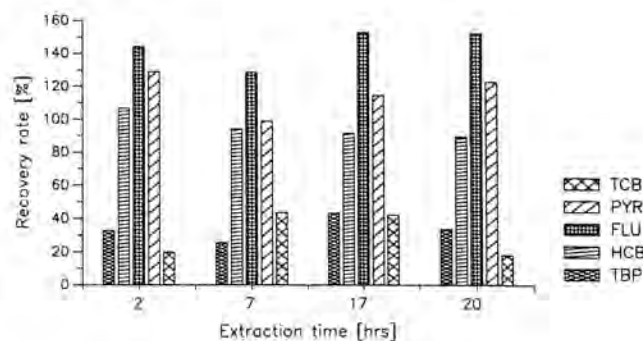


Fig. 3. Recovery rate of extraction depending on extraction time.

tions of the model substances were 0.1 % w/w. The highest recovery rates of up to 100% were obtained for the model substances HCB, FLU and PYR. PCB52 represents the class of the tetrachlorobiphenyles, PCB101 the pentachlorobiphenyles and PCB153 the hexachlorobiphenyles. They were chosen as examples from more than 30 PCB isomers found in qualitative analysis. The determination limit was in the range of 100 ppb, tested with the model substances OCDD and OCDF. The recovery rates of these compounds are listed on Fig. 5. Figure 6 shows the recovery rates obtained with the steam distillation/extraction method. A comparison of the extraction and the steam distillation/extraction shows, that the extraction method results in higher recovery rates. Furthermore the spread between parallel samples is higher in the case of steam distillation/extraction.

CONCLUSIONS

All three separation methods are applicable for qualitative analysis. The dynamic headspace analysis proved to be the most promising method, when fast response is required; the sample can be analyzed without extensive sample preparation and the method is independent of the sample matrix. Additional analysis of the gas phase over the waste material is necessary to detect substances with a low vapor pressure like tetrachloromethane. The qualitative analysis of the irradiated samples shows, that the irradiation dose was too low (although realistic) to cause significant degradation of the model substances.

An exception is TBP, which is quite susceptible to irradiation as compared to other model substances. The dehydrochlorination of HCH, which is relatively stable

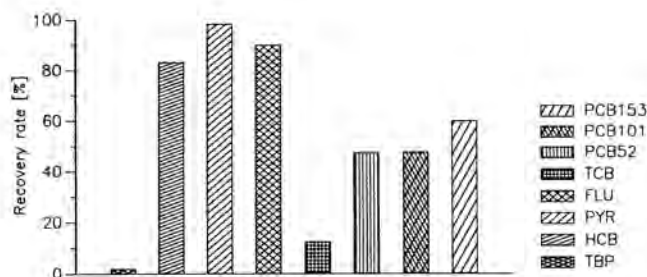


Fig. 4. Extraction of a homogenized sample.

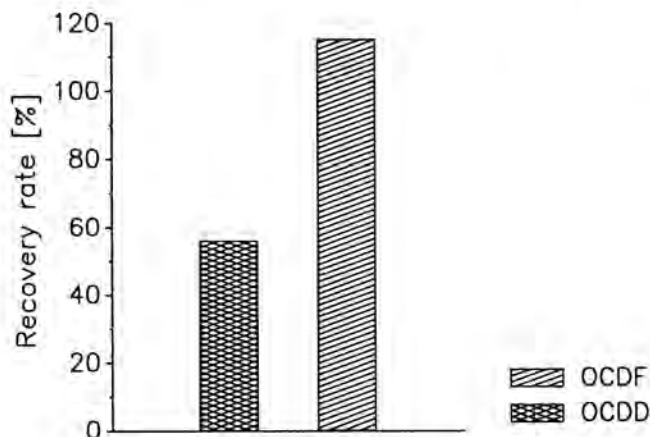


Fig. 5. Extraction of samples containing OCDD/OCDF. Concentration range: 100 - 140 ppb.

against irradiation, is an example of an effective chemical degradation in an alkaline medium.

The best quantitative results were obtained applying the hexane extraction method. Recovery rates up to 100 % with a relative error of about 10 % were found. Steam distillation/extraction also results in high recovery rates, but the reproducibility of parallel samples is poorer than with the extraction method.

Dynamic headspace analysis gives good results in qualitative measurements. The advantages of this method, espe-

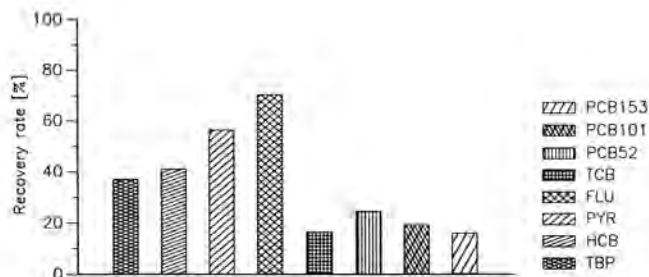


Fig. 6. Steam distillation/extraction of a homogenized sample.

cially in reducing the sample preparation work, justify its development into a quantitative procedure for the control of mixed waste. The analytical technique is, however, not the main problem. Real low-level radioactive waste is normally fixed in barrels with a volume of 200 liters. Because of the almost certain inhomogeneous distribution of organic substances it will be very difficult to collect representative samples. Further emphasis should therefore be directed towards the development of adequate sampling techniques.

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