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DIOXIN EMISSION FROM COMBUSTION OF WASTE AUTOMOBILE OILS AS FUEL FOR SMALL HEATING FURNACES

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Introduction

Emission from municipal and industrial incinerators is one of the main sources of dioxin pollution in the Environment. Small municipal and industrial incinerators in hospitals etc. are very widespread because they allow utilizing quickly wastes without transportation, and frequently give heat as additional useful effect. The improvement of these incinerators is the important reserve of reduction of harmful emissions.

It is known, that the kind of combusting wastes renders the large influence on dioxin formation [1]. So, a serious source of dioxins is combustion of hospital and municipal wastes [2,3]. Motor transport as is known, also is one of the main sources of the environmental pollution. This source causes not only direct pollution of the Environment by the wide spectrum of organic and inorganic substances in exhausted gases (primary pollution), but also exploitation, service and repair automobile produce wastes (secondary pollution).

The part of automobile wastes are waste mineral and synthetic motor oils and other technological solutions and liquids. One of the ways of waste automobile oil utilisation is their use as fuel for heating furnaces of individual usage. However a problem arises to evaluate ecological effect of this process.

The purpose of this work was study of dioxin emission from special small heating furnaces for combustion of waste motor oils.

Materials and methods

The following heating furnaces were studied: Confoma Thermobile, model DAB System (Holland); LENAN (USA), model Lanair-110; Confoma Thermobile AT-500. AT-500 and Lanair-110 are open type furnaces with surface evaporation, DAB System has a sprayer. In DAB System the synthetic oil Mobile 1 SAE 5W40 was burnt, in AT-500 - mineral oil Teboil 15W40, in Lanair-110 - mineral oil CASTROL JTX3 15W40, synthetic oil Mobile 1 5W50 and mixture of various oils.

Sampling was carried out with use of mobile ecological laboratory "Kema" (The Netherlands) intended for the control of pollutants in emissions of stationary sources. The gas emissions were pumped out through the probe, then passed through two quartz fiber filters diameter of 80 mm and sorbent layer (100 ml XAD-2) at temperature 100°C. On one of the filters previously was put the mixture of the internal standards – isotope labelled dioxin analogs ($^{13}C_{12}$ -2378-TCDD - 2 ng; $^{13}C_{12}$ -12378-PeCDD - 2 ng; $^{13}C_{12}$ -123678-HxCDD - 4 ng; $^{13}C_{12}$ -1234678-HpCDD - 4 ng; $^{13}C_{12}$ -OCDD - 4 ng) in 200 ul acetone. After sampling the filter was disintegrated, placed in cartridge and was extracted with 300 ml isooctane at 100°C. The extract was passed through a microcolumn with carbon FAS-MD [4]. A column was washed with 20 ml hexane-acetone mixture (1:1), then

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reversed, placed in the microfurnace and eluted with 5 ml toluene at 80°C. The eluate was diluted by 45 ml hexane and was passed through small "multylayer" column (height of layers 1-1,5 cm) with two layers of a sulfuric acid. The column was washed with 50 ml hexane, eluate was transferred to the alumina column, washed with hexane-dichloromethane mixture (1:1) and evaporated to minimal volume (*ca.* 10-20 µl).

The analysis was carried out on GC-HRMS system including gas chromatograph Varian 3400, mass spectrometer Finnigan MAT HSQ-30, and data processing system SS 300. Fused silica capillary column 50 m x 0,32 mm with HP-5 (film thickness 0,52 μ m) was used. Temperature was programmed from 160°C (1 min) to 220°C with the rate 25°C/min and then to 280°C with the rate 5°C/min and was hold at this temperature to the end of all PCDDs and PCDFs elution; the pressure of carrier gas helium was 0,56 kgs/cm, the rate - 1,5 ml/min.

The prepared extract was dissolved in $10~\mu l$ n-tridecane, 1~ng of the internal standard, 2-fluoro-6,7,8,9-tetrachlorodibenzo-p-dioxin, was added and $1~\mu l$ was injected in gas chromatograph in splitless mode. Electron impact ionization at energy 70 eV was used, accelerating voltage was 3 kV, resolving power - about 8000. MIS (Multy-Ion Selections) mode was used for ions M^+ and $(M+2)^+$ for TCDD, TCDF and ions $(M+2)^+$ and $(M+4)^+$ for others.

Results and discussion

PCDDs and PCDFs composition in gas emissions from small heating furnaces are presented in the table.

For mineral and synthetic oils PCDD and PCDF content in gas emissions is rather great, 1-4 ng/m³. It is necessary to note, that spraying burner of the furnace DAB System gives a little bit smaller PCDD and PCDF emission than the furnace with evaporation of fuel from open surface. PCDD and PCDF composition in gas emissions from small heating furnaces combusting automobile waste oil is similar to that of in gas emissions from other municipal and industrial incinerators [5]. The difference in PCDD and PCDF composition is noted for combustion of mineral and synthetic oils. In the case of mineral oil HxCDDs yield is less and PeCDDs, OCDD and HxCDFs is more than for synthetic oil. In the case of mixture of various oils the yield of sum PCDDs, 123678- and 123789-HxCDDs and sum of TCDFs and 2,3,7,8-TCDD are much higher

Thus, the usual mode of automobile waste oils combustion in small heating furnaces does not provide sufficient suppression of PCDD and PCDF emission and additional gas clearing is required. PCDD and PCDF composition varies depending on kind of fuel and mainly does not differ from their composition in the emissions from medical and municipal incinerators.

Acknowledgements

than for mineral and synthetic oils.

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References

- Tuppurainen K., Halonen I., Ruokojärvi P., Tarhanen J., Ruuskanen J., Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: a review. Chemosphere, 1998, 36, 1493-1511.
- 2. Pandompatam B., Kumar Y., Guo I., Liem A.J. Chemosphere, 1997, 34, 1065-1073.
- 3. Wehrmeier A., Lenoir D., Schramm K.-W., Zimmermann R., Hahn K., Henkelmann B., Kettrup A., Chemosphere, 1998, 36, 2775-2801.

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4. Soboleva E.I., Soifer V.S., Mir-Kadyrova E.Ya., Brodsky E.S., Feshin D.B., Klyuev N.A., Polyakov N.S., Petukhova G.A., Intern. J. Environ. Anal. Chem. 1997, 68, 511-522.

Table

PCDDs and PCDFs in gas emissions from small heating furnaces (pg/m³)

(1 - Thermobile AT-500, mineral oil Teboil 15W40; 2-4 - LENAN (USA), model Lanair-110, mixture of various oils, mineral oil CASTROL JTX3 15W40, synthetic oil Mobile 1 SAE 5W40, respectively; 5 - Confoma Thermobile, model DAB System (Holland)).

Sample	1	2	3	4	5
2,3,7,8-TCDD	166,1	46,3	40,3	118,6	23,9
1,2,3,7,8-PeCDD	327,8	961,7	87,6	750,7	207,2
1,2,3,4,7,8-HxCDD	540,4	< 20	148,4	105,3	254,1
1,2,3,6,7,8-HxCDD	1429,3	5725,1	1564,4	235,9	766,1
1,2,3,7,8,9-HxCDD	327,0	3354,3	1348,3	< 20	745,6
1,2,3,4,6,7,8-HpCDD	5446,6	5373,3	6661,3	6315,5	4715,7
OCDD	6079,1	6079,4	5929,4	10097,5	8755,3
2,3,7,8-TCDF	338,8	3294,9	< 20	109,1	235,4
1,2,3,7,8- PeCDF	146,8	746,1	210,0	395,9	323,3
2,3,4,7,8- PeCDF	507,5	1150,5	320,9	698,4	288,8
1,2,3,4,7,8-HxCDF	2152,3	1160,1	2634,3	8775,2	754,3
1,2,3,6,7,8-HxCDF	682,3	10304,2	1387,5	4212,4	377,0
2,3,4,6,7,8-HxCDF	625,5	3663,7	529,1	1681,3	387,4
1,2,3,7,8,9-HxCDF	176,3	1181,9	196,7	1593,8	127,0
1,2,3,4,6,7,8-HpCDF	1753,8	4156,0	4516,2	7648,8	1821,4
1,2,3,4,7,8,9-HpCDF	162,2	95,2	< 50	347,1	272,8
OCDF	2503,2	1801,3	1802,4	1680,4	2963,8
Other TCDDs	510,7	926,8	709,4	157,9	<25
Other PeCDDs	2382,5	4919,8	1133,4	1700,1	1100,5
Other HxCDDs	9009,8	19777,8	5805,9	65091,2	2959,2
Other HpCDD	2849,6	3386,1	4405,6	6315,5	3139,9
Other TCDFs	308,6	6447,5	180,7	50,0	1087,4
Other PeCDFs	3602,5	8794,8	3246,8	3681,4	1640,9
Other HxCDFs	577,4	3176,0	1928,3	22358,4	<30
Other HpCDFs	305,3	713,3	1383,1	1504,4	781,6
TEQ	1442,0	4112,2	1155,4	3031,4	811,4