Evaluation of polychlorinated dibenzodioxins and dibenzofuran's emission from vinylchloride-monomer production

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Introduction

The present work made an attempt to estimate PCDD/PCDF 2,3,7,8-isomer emission, originated from vinylchloride-monomer production at the "Caustic" Joint-Stock Company, Ltd, the city of Sterlitamak, Russia.

The stages of ethylene oxychlorination and dichlorethane pyrolysis may be the sources of PCDD/PCDF in the vinylchloride-monomer production. Industrial waste water, distillation residues of rectification column and waste burning units may be the secondary sources of this emission.

Experimental

In the process of VCM production distillation residues and gaseous exhausts are formed which delivered to the burning units.

Vinylchloride-monomer production waste water is delivered to the water treatment facilities, where it is purified from heavy metals and then is subjected to biological purification. Sludge is delivered to the special disposal land.

The vinylchloride, purified water and sludge samples were taken for analysis.

Units for burning of liquid and gaseous waste were investigated separately. The samples of exhaust gas, scrubber and alkaline water were obtained here.

Sampling and sample preparation for analysis were conducted in accordance with recommendations USEPA 1613. For the purposes of sample preparation process control isotope-labeled standards: ^{37}Cl-2,3,7,8-TCDD, $^{13}C_{12}$-2,3,7,8-TCDF, $^{13}C_{12}$-1,2,3,4,6,7,8-TCDF, $^{13}C_{12}$-OCDD were introduced into all samples. The isotope-labeled standards were used in the form of solution in acetone or nonane depending on the sample properties. While exhaust gas sampling isotope-labeled standards were put on the filter before sampling. After exhaust gas sampling and water filtration the filters were extracted in Soxlete apparatus with acetone and toluene. Extracts were concentrated on the rotary evaporator and the solvent was substituted for hexane.

The vinylchloride-monomer samples are taken into steel bottle, then they are poured into retort for evaporation. The isotope-labeled standards are put into retort previously. Gradually vinylchloride-monomers are evaporated up to dry residual. The residual is extracted with hexane at ultrasonic bath.

Water samples are extracted with hexane, mixing at the mechanical shaking unit during two hours with three portions of hexane.

Hexane extracts purification is conducted according to the following scheme: it is washed with 20% water solution of KOH, concentrated H_2SO_4. Neutral hexane extracts are dried and purified at the multilayer silicagel and coal columns. The volume of purified extracts should be 10 μl.

The analysis was conducted, using mass-spectrometer Incos-50, equipped with chromatograph Varian 3400 and capillary column DB5-MS (60 m×0,25 mm or 30 m×0,25 mm), in the regime selective ion-determination. The inner standards $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD are used for calculation of mass-chromatograms. Analysis error is 60%.

The received results are represented in the form of isomer content from tetra- to octachlorodibenzodioxins and furans and reduced to dioxins equivalent (TEQ).

Results and Discussion

Vinylchloride is formed in the process of dichlorethane pyrolysis at 520 ^{0}C and is subjected to the system of rectification and drying. Ten samples of vinylchloride-monomer were obtained during 1997. None of the sample shows PCDD/PCDF higher limit of quantitative determination, which is 2 pg/g for vinylchloride.

It is known that isomer content of PCDD/PCDF, which is formed, while chemical waste burning, depends on the content of the waste. In the process of burning of chlorinated aliphatic hydrocarbons, which are received from vinylchloride-monomer production, the basic isomers are high chlorinated dibenzofurans. Isomer content of 2,3,7,8-isomers PCDD/PCDF in exhaust gas is represented by the following data (pg/m^3):

TetrachlorineDD	n.d.
PentachlorineDD	n.d. - 20,5
HexachlorineDD	n.d. - 271
HeptachlorineDD	n.d. - 2474
OctachlorineDD	n.d. - 5069
TetrachlorineDF	n.d. - 694
PentachlorineDF	n.d. - 461
HexachlorineDF	142 - 14253
HeptachlorineDF	291 - 61756
OctachlorineDF	343 - 119958.

The pollution of scrubber, alkaline water and soot has the same isomer content.

Waste water of vinylchloride-monomer production are delivered to the unit of purification from heavy metals. After filtration the water is delivered to the biological purification facilities. Purified water and sludge contain only polychlorinated dibenzofurans.

Thus, total emission of 2,3,7,8-isomers PCDD/PCDF from vinylchloride-monomer production is formed by technological emission from burning units, purified water and sludge. PCDD/PCDF input and distribution by flows and total emission are represented in the Table 1.

The table shows, that under the conditions of vinylchloride-monomer production equal to 8000 hours per year the annual total emission will be 2 g-TEQ of 2,3,7,8-isomers PCDD/PCDF, and only 0,8% of them goes into the atmosphere, while 93,2% to the plant purification units and 6% to the places of burial (Table 1).

Table 1.

PCDD/PCDF 2,3,7,8-isomer emission from vinylchloride-monomer production

Technological flow	PCDD/PCDF concentration				PCDD/PCDF total emission		
	measure unit	min	max	average	µg/h	µg/t	%
1. Waste water							
purified water	ng/l	0,004	0,04	0,020	0,114	0,007	0,05
sludge	ng/g	0,354	7,830	2,260	12,882	0,763	6,01
2. Burning unit of gaseous products							
exhaust gas	ng/m^3	0,00031	0,0017	0,001	0,038	0,002	0,02
scrubber water	ng/l	0,017	0,035	0,026	0,2760	0,016	0,13
3. Burning unit of waste							
exhaust gas	ng/m^3	0,020	2,315	0,500	1,680	0,100	0,78
scrubber water	ng/l	0,06	0,5	0,154	0,278	0,016	0,13
alkaline water	ng/l	0,025	10,09	2,568	1,035	0,061	0,48
scrubber water soot	ng/l	30,00	153,77	96,480	173,162	10,261	80,74
alkaline water soot	ng/l	0,99	170,25	62,01	25,010	1,482	11,66
Sum:					214,475	12,71	100