Chemical Composition of Organic Pollutants in the Tie-Impregnating Plant Air (Tayshet city, Irkutsk Region)

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Abstract

Chromatography mass spectrometry was applied to study the qualitative and quantitative composition of pollutants in the working air of the Tie-Impregnating Plant (TIP) in the city of Taytshet (Irkutsk Region). Organic pollutants were shown to be provided by the emission of antiseptics, used in technology process. Pollutants composition varied depending on the sampling method and analytical sample pre-treatment. The most informative data were obtained, when sorption sampling was combined with extraction and thermal desorption sample pre-treatment for analysis.

INTRODUCTION

The Tie-Impregnating Plant (TIP) has essential environmental impact due to their production activity and technology peculiarities. First of all this impact is related to emission and soil accumulation of organic compounds, which are harmful to the living organisms, and thus degrade environmental situation in the region. Tayshet TIP is situated in the Irkutsk Region, and occupies 40.6 hectares. It is a source of intensive pollution, since its technology process applies antiseptics for the wood treatment. These antiseptics contain organic compounds of high volatility that are carcinogenic and toxic.

Earlier we have studied chemical composition of the following antiseptics used at the Tayshet TIP: coal oil (CO) and thermocatalytic fluid (TCF) [1]. We have shown that these antiseptic materials are complex mixtures with dominating benzene and polycyclic aromatic hydrocarbons (PAH), heterocyclic compounds and alkanes.

Pollutant emission happens at all stages of the wood impregnation process [2], since it is done with out-of-date equipment without essential sealing at impregnating cylinders recharging. Antiseptic treated product lies in the open air. Let us note that Tayshet TIP works since 1932 with no revamp and modernization. Therefore, its technical condition does not allow its environmental impact reduction. Therefore, a complex estimation of its emissions and wastes is of importance for production reengineering and environment protection.

In the present study we determine the qualitative and quantitative composition of organic pollutants in the Tayshet TIP air using a complex approach involving sampling and analysis optimisation, sample treatment procedure and chromatographic mass spectrometry (CMS) analysis.

EXPERIMENTAL

For the CMS studies we used mass spectrometer Hewlett-Packard 5972A. Ionisation was performed by electrons with energy 70 eV, scanning in a range of 40–400 a.u.m. was done each 2 s, quartz capillary column HP-5MS was 50 m long and 0.25 mm in diameter, helium being gas carrier. Organic compounds were identified regarding the following suppositions: resemblance to reference spectra, presence of typical molecular fragments, boiling point correspondence, retaining time correspondence, a priori expectation of certain compounds in such emissions.

Organic pollutants were adsorbed by Silochrom C-120 (0.3–0.5 mm) and by Petriyanov filters. Aspiration devices PA-40M-1.3, PU-3E were used for the sampling. Pollutant concentration was done by passing 10 l of air with a rate of 0.5 l/min through glass tubes 15 cm × 5 mm in size, filled with 0.2 g of Silochrom. When Petriyanov filters were used, air volume was 2 m^3, flow rate was 100 l/min. In case when sampling was done through the sorption tube, samples were exposed to thermal desorption and extraction by organic solvents. Thermal desorption was performed using vapour-phase attachment HP Headspace 7694. Diethyl ether was used for extraction. Extract was concentrated by partial solvent stripping and then analysed.

RESULTS AND DISCUSSION

Organic pollutants at the TIP were monitored during years 2003–2004, and sampling was done in different seasons. Sampling was arranged in the places of maximum pollution such as wood impregnation works and sleepers store [2].

CMS method was for the first time used to study the composition of organic pollutants in the TIP air. In contrast to other methods such as GLC, HPLC *etc*., CMS shows high selectivity, sensitivity and wide enough identification potential at ions registering, since besides separation characteristics (chromatography retaining time) one may record the mass parameters of pollutants. These parameters are determined by the structure, element composition and chemical properties of the identified pollutants. For organic air pollutants CMS identification reliability criteria and quantitative analysis peculiarities are discussed elsewhere [3–6].

Nevertheless, it is a rather sophisticated analytical problem, and requires sampling with concentration.

According to [7, 8] adsorption is mostly used at sampling of gases and vapours, while particulate pollutants are usually concentrated on filters. At sleeper wood processing air pollutants are mostly vapours. Therefore, samples were taken with the help of the sorption tube.

We have found that analysis completeness essentially depends on the sample treatment procedure (Tables 1, 2). Thus, when thermal desorption is applied more than 30 organic compounds are registered, which is 87–92 % (see Table 1) of pollutants in total. These compounds are mostly alkanes and aromatics (alkyl derivatives of benzene, indans, PAH).

Adsorbed pollutants extraction with organic solvents appears to be more informative in comparison to thermal desorption with regard to heavier hydrocarbons. Low boiling aromatic compounds are removed along with the solvent when the sample is concentrated (see Table 2). In this case identification completeness is 85–88 %, and more than 40 compounds are identified. Beside volatile aromatics (naphthalene, alkyl naphthalenes) we have found PAN, oxygen and nitrogen containing heterocycles, phenols, and heavier alkanes. The portion of bi- tri- and tetracyclic homologues was respectively 45–50, 40–48 and 7–8 % of the total amount

TABLE 1

Content of organic pollutants in the air of Tayshet TIP, thermal desorption being used for sample treatment

Compound	Content, mass %	
	Impregnation works	Impregnated production store
Benzene, methyl	0.22	0.17
Benzene, ethyl	0.43	0.34
Benzene, dimethyl	0.83	0.71
Benzene, trimethyl	1.05	1.02
Benzene, ethyl, methyl	0.48	0.42
Benzene, ethyl, dimethyl	2.18	1.42
Benzene, tetramethyl	0.38	0.4
Benzene, methylethyl	0.25	0.35
Indan	1.96	1.8
Indene	1.5	1.7
Indan, methyl	0.5	0.3
Naphthalene	52.81	53.3
Alkanes (C_9–C_{13})	17.75	14.7
Natural compounds	1.5	0.9
Phase components	10.2	9.8
Non-identified compounds	7.96	12.67

TABLE 2

Content of organic pollutants in the air of Tayshet TIP, extraction being used for sample treatment

Compound	Content, mass %	
	Impregnation works	Impregnated production store
Naphthalene	2.85	4.87
Naphthalene, methyl	7.41	10.27
Naphthalene, dimethyl	5.1	5.22
Naphthalene, ethyl	0.9	2.0
Naphthalene, trimethyl	1.3	2.05
Anthracene/phenantrene	7.0	6.93
Fluorene	7.36	4.6
Fluorene, methyl	2.65	1.03
Acenaphthene	8.15	11.3
Chryzene	3.83	4.77
Biphenyl	3.5	3.05
Biphenyl, methyl	3.6	2.09
Dibenzofuran	5.55	5.9
Dibenzofuran, methyl	3.15	2.92
Phenol	0.21	0.17
Phenol, methyl	0.61	0.57
Phenol, dimethyl	0.68	0.42
Quinoline/isoquinoline	1.74	0.48
Quinoline, methyl	1.1	0.58
Esters	2.3	4.55
Olefins (C_6–C_8)	1.47	–
Alkanes (C_{14}–C_{28})	18.08	11.21
Non-identified compounds	11.46	15.02

of PAH. Highly sensitive CMS–SIM method detected benzene, pyrene, fluoranthene, and benz(a)pyrene in the Tayshet TIP air.

Combining sample pre-treatment methods we managed to build an impressive list of toxic compounds. Organic compounds are present in the TIP air mostly due to the antiseptics applying technology used at the site. Since our studies were going in a period of technology passing from antiseptic CO to TCF (years 2003–2004), pollutants contained compounds from both antiseptics [1]. Exclusions were natural compounds (pinene, limonene, carene), esters (butyl and pentyl esters of benzoic acid, *etc.*). Most likely, natural terpenoids detected in the samples evolve during the storage, since they enter the composition of conifer wood. Esters are likely to be the products of aromatics oxidized during the sleepers impregnation (100 °C).

Let us note the identity of pollutant qualitative composition in the air of various sites (impregnation works, store, *etc.*). The quantitative content of these compounds varies within 1–7 % (see Tables 1, 2).

The existing methods of State Sanitary and Epidemiological Inspection regulate the air sampling procedure in the working area for PAH detection with various filters. It is well known, however, that filters concentrate particulate toxicants, while gases are better caught by the adsorbents [7, 8]. In order to determine the contribution of particulate PAH into polluting exhausts we took samples using filter or/and adsorbent (Table 3). CMS analysis was done under the SIM operation (*i.e.* by characteristic

TABLE 3

Content of polycyclic aromatig hydrocarbons in the air of Tayshet TIP, data being obtained using various sampling procedures

Compound	Impregnation works		Impregnated production store	
	Filter	Adsorbent	Filter	Adsorbent
Naphthalene	0.2 ± 0.06	10 ± 1.4	0.13 ± 0.02	7.83 ± 0.75
Phenanthrene	0.51 ± 0.16	52.79 ± 3.95	0.43 ± 0.089	30.12 ± 1.3
Anthracene	0.12 ± 0.033	9.07 ± 0.77	0.08 ± 0.013	7.13 ± 0.67
Fluoranthene	0.14 ± 0.023	8.13 ± 0.92	0.14 ± 0.008	2.12 ± 0.43
Pyrene	0.13 ± 0.024	6 ± 0.7	0.11 ± 0.018	3.07 ± 0.52
Chryzene	0.2 ± 0.059	5.13 ± 0.67	0.042 ± 0.0066	3.2 ± 0.37
Benz(a)pyrene	0.019 ± 0.008	Not found	Not found	Not found

ions, thus providing the high analysis sensitivity). We have demonstrated that sampling with filters shows a lower content of PAH than sampling with adsorbents. Therefore, pollutants in the working area stay in the gas phase but not as aerosols. Quantitative analysis results were presented as the normal ones of n samples (see Table 3). Values spread around the equidistributed one was characterized by standard deviation (s).

Comparing the content of individual PAH determined by two sampling methods, we evaluated statistically reliable differences for the 95 % reliability interval using the Student criterion.

PAH concentrations on the filter probably depend on the sorption of background aerosols and vapour phase, "skip" effect being regarded. However, filter caught PAH compose only 1.5 % of all registered PAH. Therefore, sampling on the adsorbent is more preferable for monitoring the pollutants in the TIP air with regard to technology peculiarities. Sampling with filter is justified only for the benz(a)pyrene monitoring.

Minor compounds though detected appear to be the most dangerous as toxicants. By the toxic effect pyrene, phenantrene, benz(a)pyrene, benzene refer to the first and second class danger compounds. Danger class is not even stated for many aromatic hydrocarbons such as fluorene, fluoranthene, chryzene, *etc.*) [9]. Benzene and benz(a)pyrene are carcinogenic, chryzene demonstrates biological activity. According to the US EPA regulations such compounds as naphthalene, acenaphthene, fluorene, pyrene, chryzene, benz(a)pyrene and benzene are considered as priority chemical pollutants of the atmosphere.

CONCLUSION

Therefore, complex approach based on the optimised sampling and samples preparation for analysis combined with chromatographig mass spectrometry allowed the reliable detection and investigation of organic pollutants present in the air of the TIP located in the Irkutsk Region. Organic compounds are present in air as vapours and background aerosols. We have found that sampling by adsorption combined with the extraction and thermal desorption is the most reliable method to obtain both qualitative and quantitative monitoring results. CMS method has shown that organic compounds in the TIP air are provided by the evaporation and accumulation of compounds entering the composition of antiseptics used in the impregnation technology. The high concentrations of detected compounds (exemplified by PAH) prove their man caused origin. Pollutants composition analysis helped us to determine priority substances for the constant monitoring over the working area.

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