

Control of microimpurities emitted from polymer construction materials based on polyvinyl chloride

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Abstract. The aim of this article is to improve the degree control of microimpurities emitted from polymeric construction materials into the environment. It is proposed to do this through the modification of the physicochemical nature of the original (source) sorbent and, as a consequence, the improvement of the sorption capacity and the extraction ratio of highly volatile toxic substances. The proposed concentrator columns can be widely used in the analysis of microimpurities of polar organic substances released into the environment from polymeric construction materials based on polyvinyl chloride.

1. Introduction

According to the universal ecological paradigm [1], there is a current tendency when the environmental science is developing into a global knowledge system, which deals with the study of a particular subject or object in any randomly chosen natural system being closely linked with the processes taking place in the environment [2]. The latter ones perform a control function and are at the top of their hierarchical interaction. It follows that the life span and operability of any construction material, as well as items produced from this material [3-4], including structures, buildings, installations and other complexes should be designed and built, taking into account the environmental issues and parameters.

It refers not only to bio- and techno spheres, but also to a great deal of intermediate states of their interaction. It is necessary to emphasize that the requirements of biocompatibility and natural balance to the properties and behavior of materials are fundamental. The development of modern technologies, as a factor of human environment transformation is impossible without adhering to the principles of bioethics. The principle “do not harm” is one of the key factors of the construction industry, architecture, urban development and landscape architecture [5].

At present, the tendencies to develop “green” construction are becoming more popular [6]. The term “green” construction and architecture refers to the construction of civil and industrial facilities with a minimum level of power consumption, minimum use of material resources and minimal negative impact on human beings and the environment [7]. Architectural and building sites should harmoniously fit in the environment. This means that throughout the entire period of operation and maintenance of buildings, structures and construction materials, it is necessary to monitor permanently



their condition, paying attention to the systemic interaction among all the components of natural and engineering systems at the interconnected hierarchy levels of their spatial and temporal organization.

Thus, ecological compatibility (environmental friendliness) of construction materials is one of the most important qualities along with their strength, thermal conductivity and other physical, mechanical and engineering characteristics.

A wide variety of finishing materials produced on the basis of polymers have recently gained in popularity. However, in the process of their operation and maintenance under the impact of various environmental factors including external physical, chemical and biological they can emit toxic organic substances and release gaseous micro impurities into the environment causing considerable harm to people's health. This negative effect on people and environment requires taking some measures concerning the development and use of effective quality control methods for these polymer containing materials.

2. Results and discussion

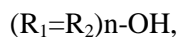
The purpose of this article is to develop chromatographic concentration methods for identification of micro impurities released in the environment throughout the whole operation and maintenance period of polymer construction materials based on polyvinyl chloride.

Concentrator columns with porous polymer sorbents are widely used for determination of trace amounts of substances in the air and water [8]. However, these concentrator columns have a number of disadvantages, among which the most significant are relatively low sorption capacity and low thermal stability of the sorbent.

There is a concentrator column known [9, 10] for its relatively high values of thermal stability and Rohrschneider's chromatographic polarity. The disadvantage of this column is its relatively low sorption capacity (V_g^{20}) concerning the range of toxic organic low (light) boiling pollutants (spirits, ketones, acids, amines, nitrates).

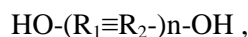
To achieve the desired goal, the reference (original) sorbent represented by styrol-divinylbenzol-copolymer was treated with ionizing radiation in a radiation polymer-monomer in the range of absorbed dose from 18 to 625 Gy at temperatures from 196 °C to 200 °C. Sorbent modification in this work was carried out in several ways. For example, the reference sorbent was exposed to radiation in a liquid monomer layer or in a monomer solution with a concentration of 0,1...95 % with respect to the weight (mass) of non-polymeric solvent, e.g. acetone or isopropanol. The copolymer can be exposed to radiation by covering its surface with a thin film of a monomer in the amount (volume) of 1...70 % with respect to sorbent weight in saturated or rarefied (low density) monomer vapor.

A special feature of the proposed technology is that the sorbent is irradiated in a hydroxyl-containing polymerizing monomer. Its common structural formula is as follows:



where: $R_1 : =CH-(-CH_2-)m-CH_3, =CH-C_6H_4-OH; R_1 = R_2; R_2 : =CH-(-CH_2-)k - ;$
 $n = 1 \dots 20; m = 0 \dots 10; k = 1 \dots 10;$

or in a monomer medium, selected from the range of substances which can be described by the following common structural formula:



where: $R_1 : CH_3, -(-CH_2-)m-C\equiv, HO-C_6H_4-C\equiv, R_1 = R_2; R_2 : -(CH_2-)k;$
 $n = 1 \dots 20; m = 1 \dots 10; k = m \dots m+1;$

or in the presence of a monomer compound taken in the ratio from 0,5/4 to 0,5/5 % to the weight of a copolymer.

The use of a styrene-divinylbenzene copolymer exposed to ionizing radiation in the specified interval of absorbed doses and temperatures in the presence of a radiative polymeric hydroxyl-containing monomer as a sorbent considerably improves the operating characteristics of the concentrator column. Radiation-chemical modification of a hydroxyl-containing monomer enables its vaccination (immunization) to the reference styrene-divinylbenzene copolymer. It is necessary to point out the

variation of Rohrschneider's chromatographic polarity of the sorbent and the possibility to form specific sorbate/ sorbent bonds. Different ways used to bring the monomer to the copolymer/ monomer contact area allow performing vaccination (immunization) both on the surface of sorbent granules and macro-, meso – and even micro-pores of styrene-divinylbenzene copolymer. Moreover, it enables one to create three-dimensional polymer meshes from graft monomer, which result in increasing their sorption capacity.

Laboratory tests of concentrator columns for different variants of the proposed technology have shown substantial improvements of operating characteristics compared to the known methods used for micro impurities concentration. The results of these tests are shown in tables 1-3. The consideration of the modification features of the reference sorbent and the technology of the monomer preparation are described in examples 1-7.

Example 1. A sample of a polymeric sorbent based on a styrene-divinylbenzene copolymer Polysorb-1 (Specification-6-09-10-1834-88) with fraction 0.125-0.250 mm is filled up with a liquid monomer till the full coverage of the sorbent layer. Then it is exposed to Co⁶⁰ radiation at 100 °C till the absorbed dose of 200 gr. After completing the exposure to radiation, the sorbent is placed in a U –shaped column. To obtain the concentrator column, it is necessary to determine the operating characteristics. Ethanol (also called alcohol) CH₂=CH-OH (if n=1, R₁= CH₂=; R₂= =CH-; general structural formula) is used as a monomer.

Example 2. All tests (operations) are carried out as in the first example, except that sorbent is filled up with a monomer solution, which takes up 20 % from the solvent mass (isopropanol). The exposure to radiation is performed by impulse electron beams in the argon atmosphere at 20 °C till the absorbed dose of 100 gr.

Example 3. All tests are carried out in the same way as it has been done in example 1, except that the sorbent was covered by 50% monomer (from the sorbent weight). The exposure to radiation is conducted at 196 °C (liquid nitrogen) using X-rays till absorbed dose of 30 gr, and phenyl ethenol HO-(C₆H₄)-CH=CH-OH (if n=1; R₁= HO-C₆H₄-CH=, R₂= =CH-, general structural formula) is used as a monomer.

Example 4. All tests are carried out in the same way as in example 1, except that during the radiation the saturated steam of the monomer is blown through the sorbent at 25 °C and the exposure to radiation is performed till absorbed dose of 600 gr. Phenylbutenal vapor OH-(C₆H₄)-CH=C₃H₇-OH (if en=1; R₁= HO-C₆H₄-CH=; R₂= =C₃H₇-; general formula) is used as a monomer.

Example 5. All tests are carried out in the same way as in example 1, except that during radiation the rarefied monomer vapor is allowed through a sorbent layer (vacuuming the flow at the output), the radiation is performed by impulse electron beams at 23 °C till the absorbed dose of 50 gr, and butene-2-diol-1,4, HO-CH₂-CH=CH-CH₂-OH (if n=1, R₁=R₂= -CH₂-CH=; general formula) is used as a monomer.

Example 6. All tests are carried out in the same way as in example 1, except that the sorbent is filled up with a monomer compound in the ratio ½ on the monomer mass, the radiation is performed at 10°C till the absorbed dose of 100 gr. Propanol CH₂=CH-CH₂-OH (if n=1; R₁= CH₂=; R₂= =CH-CH₂-) and phenylethinol taken in ratio 0,5/4,0 from the sorbent mass are used as a monomer.

Example 7. All tests are carried out in the same way as in example 1, except that the exposure to radiation is conducted by X-rays at -50 °C till absorbed dose of 400 gr. Phenylbutenol HO-(C₆H₄)-CH=C₃H₇-OH, (if n=1, R₁= HO-(C₆H₄)-CH=; R₂= =C₃H₇-) is used as a monomer.

Rohrschneider's chromatographic polarity coefficients (Table 1), the value of the sorption capacity (Table 2), as well as the mean extraction ratio of homolog substances from the concentrator (Table 3), were determined for all developed concentrator columns.

In order to assess the polarity, the concentrator columns have determined Kovach's retention indices for compounds from Rohrschneider's series (benzol, ethanol, methylethylketone, nitromethane, pyridine).

Kovach's retention indices were calculated applying the following equation:

$$J = 100 \cdot (\lg t_{RX} - \lg t_{RZ} / \lg t_{RZ+1} - \lg t_{RZ}) + 100Z, \quad (1)$$

where: t_{RX} is the corrected confinement time for a compound from Rohrschneider's series on the exposed to radiation sterol divinylbenzole copolymer;

t_{RZ} – the corrected confinement time for n-alkane with a Z number of atoms;

t_{RZ+1} – the corrected confinement time for n-alkane with Z+1 numbers of atoms.

Rohrschneider's polarity coefficients were determined by the following equation:

$$\Delta R = (J_x - J_B) / 100, \quad (2)$$

where: ΔR – Rohrschneider's polarity coefficient; J_x –Kovach's retention index for a steroldivinylbenzole copolymer exposed to radiation; J_B –Kovach's retention index with a nonpolar carbonic Carbocap B

Test substances describe different variants of specific intermolecular sorbent / sorbate interactions: benzene (ΔR_x) – π - π interaction, ethanol (ΔR_y) – the formation of hydrogen bond with electron-donor functional groups of the sorbent, methylethylketone (ΔR_z) –orientation interaction, a donor- acceptor complex formation, nitromethane (ΔR_u) – orientation, proton-acceptor interaction, pyridine (ΔR_s) – the formation of hydrogen bond with electron- acceptor sorbate groups. The numerical values of the coefficients $\Delta R_{x, y, z, u, s}$ specify the force of such molecular interactions, and $\sum \Delta R$ - the total polarity of sorbent.

The sorption capacity of the Vg^{20} concentrator column for substances (Table 2) was determined by extrapolating the linear section of the retention diagram of the substance $\lg Vg^{20} = f(1/T)$ to the concentration temperature.

The thermal desorption of the concentrated substances in Examples 1-7 was carried out at 280-300 °C.

The extraction (desorption) ratio of the substance from the concentrator column Z_{mean} (%) (Table 3) was determined by the following formula:

$$Z_{\text{mean}} = (1 - A_2/A_1 \cdot F) \cdot 100 \%, \quad (3)$$

where A_1 is the peak area of the analyzing substance after the first desorption;

where A_2 is the peak area of the analyzing substance after the second desorption;

F is the component volatility, which is determined as follows:

$$F = P_i \cdot M / RT\rho, \quad (4)$$

where P_i is the pressure of saturated steam at the concentration temperature (20 °C);

M is the molecular weight of the component; ρ is the substance density; R is the universal gas constant; T is the concentration temperature, K.

Table 1. Rohrschneider's polarity coefficients

Implementation examples	Rohrschneider's polarity coefficients ΔR , at 150 °C					Total polarity $\sum \Delta R$
	Benzol X	Ethanol Y	Methyl-ethyl- ketone Z	Nitro- methane U	Pyridine S	
Control	1.57	3.21	2.27	3.16	3.65	13.86
Example 1	1.62	3.43	3.27	3.54	3.75	15.61
Example 2	1.63	3.78	3.31	3.93	3.72	16.37
Example 3	1.73	3.73	3.29	3.52	3.77	16.04
Example 4	1.65	3.39	3.33	3.99	3.95	16,31
Example 5	1.72	3.55	3.19	3.48	3.81	15.75
Example 6	1.83	3.96	3.50	3.79	3.69	16.77
Example 7	1.75	3.87	3.66	3.79	3.72	16.79

Table 2. Sorption capacity of concentrator column

Implementation examples	Sorption capacity of concentrator column V_g^{20} , l/g									
	Methanol	Formaldehyde	Acetone	Benzene	Phenol	Chloroform	Acrylonitrile	Hexene-1	Xylene	Styrene
Control	69	65	29	95	316	25	59	62	54	89
Example 1	87	95	42	99	369	85	84	92	84	154
Example 2	95	103	117	98	383	240	98	152	95	175
Example 3	92	119	125	95	391	382	113	160	114	184
Example 4	105	122	156	97	395	310	135	168	110	172
Example 5	98	112	138	99	362	479	131	155	135	167
Example 6	112	97	120	95	381	212	136	145	113	180
Example 7	99	110	139	101	358	263	105	138	130	184

Note: substances, presented in Table 2 are chosen as the major eco toxins which control is required in the objects of the environment in accordance to Instructional Lines (IL) 2.1.2. 1829-04 (the subordinate regulatory act having the validity of a law).

Table 3. Mean extraction ratio (desorption) from concentrator column

Implementation examples	Mean extraction ratio (desorption) from concentrator column, Z %						
	Alcohol (spirits)	Ketones	Chlorine-alkanes	Xylenes (xylols)	Styrenes	Aldehydes	Phenols
Control	78	76	63	51	68	62	70
Example 1	88	86	79	65	70	75	85
Example 2	97	73	75	77	69	79	89
Example 3	98	81	75	83	78	73	86
Example 4	93	82	74	85	77	72	88
Example 5	99	87	77	87	75	75	83
Example 6	95	85	73	84	73	73	84
Example 7	92	85	78	83	85	70	87

3. Conclusions

The data represented in tables 1-3 obtained during this research show the possibility to develop concentrator columns with a much better range of operating characteristic, namely with a greater chromatographic polarity (Table 1), higher sorption capacity (Table 2), and higher values of extraction ratio from the specified polymeric construction materials (Table 3) [11, 12].

Table 4. Key technical and economic characteristics of polymer construction materials based on polyvinyl chloride.

Parameter	Obtained value
Radiation safety	Complies with Sanitary Regulations and Standards 2.6.1.2523-09
Chemical safety	Ensured through the stability of pH medium
The coefficient of mean thermal linear expansion in the range of 60 °C, °C ⁻¹ (mm/m)	$3.36 \cdot 10^{-5}$

Compressibility	Unavailable (absent) at pressure less than 45 kg/cm ²
Tear force (breaking load) of threaded coupling, H	1160
Water absorption, %	2.4
Mass variation in corrosive media (aggressive environment), not greater than, %	1.8
Density, g/cm ³ *	-0.6
Thermal conductivity, W/m*K*	-0.076

Note: * for sheet (laminar) polyvinyl chloride (PVC) (8-10 mm)

The improvement of the quality control of operating characteristics of polymeric construction materials enables one not only to extend their arsenal and the field of their engineering application, but also to increase the quality of the environment [13].

References

- [1] Park S, Park S & Park Y B 2018 *An architecture framework for orchestrating context-aware IT ecosystems: A case study for quantitative evaluation*. Sensors (Switzerland) **18**(2)
- [2] Ikonnikova K, Ikonnikova L, Koltunova E 2016 AIP Conference Proceedings 1772 020010
- [3] Ikonnikova K, Ikonnikova L, Koltunova E 2015 *Turkish Online Journal of Educational Technology* **2015** 485-488
- [4] Ikonnikova K, Ikonnikova L, Koltunova E 2015 *Turkish Online Journal of Educational Technology* **2015** 557-560
- [5] Mkrtychyan T, & Lokhova E 2017 *Ecological effectiveness as an essential quality requirement of innovational construction*. Paper presented at the MATEC Web of Conferences **106**
- [6] Meshcheryakova T 2017 *Problems of the development of international standards of "green building" in Russia*. Paper presented at the IOP Conference Series: Earth and Environmental Science **90**(1)
- [7] Orlov AK 2017 *Implementation of megaprojects for the creation of tourist clusters in Russia based on the concept of energy efficiency and sustainable construction*. Paper presented at the IOP Conference Series: Earth and Environmental Science **90**(1)
- [8] Shojaeimehr T, Rahimpour F, Schwarze M, Repke J, Godini H R, & Wozny G 2018 *Use of RSM for the multivariate, simultaneous multiobjective optimization of the operating conditions of aliphatic carboxylic acids ion-exclusion chromatography column: Quantitative study of hydrodynamic, isotherm, and thermodynamic behavior*. Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences **1083** 146-159
- [9] Cropper P M, Goates S R, & Hansen J C 2015 *A compact gas chromatograph and pre-column concentration system for enhanced in-field separation of levoglucosan and other polar organic compounds*. Journal of Chromatography A **1417** 73-78
- [10] Li Y, Zhang R, Wang T, Wang Y, Xu T, Li L, Luo J 2016 *Determination of n-alkanes contamination in soil samples by micro gas chromatography functionalized by multi-walled carbon nanotubes*. Chemosphere **158** 154-162
- [11] Guo X, Wang X, Zhou X, Kong X, Tao S, & Xing B 2012 *Sorption of four hydrophobic organic compounds by three chemically distinct polymers: Role of chemical and physical composition*. Environmental Science and Technology **46**(13) 7252-7259
- [12] Gus'kov V Y, Ivanov S P, Khabibullina R A, Garafutdinov R R, & Kudasheva F K 2012 *Gas chromatographic investigation of the properties of a styrene-divinylbenzene copolymer modified by 5-hydroxy-6-methyluracil*. Russian Journal of Physical Chemistry **A86**(3) 475-478
- [13] Kinoshita T, & Furuya E 2017 *Novel modification method to prevent tailing behaviors within synthetic resin adsorbents*. Journal of Environmental Chemical Engineering **5**(1)