Comparison of traditional and fullerene-based adsorbents for extraction of 1,4-dioxane and 2-methyl-1,3-dioxolane from milk

A. I. Kochaev1,3, R. Razavi2, S. Kaya4, M. R. A. Mogaddam5,6, N. Altunay4, M. Nemati5, K. P. Katin1,7, K. S. Grishakov1,7, A. I. Podlivaev1,7, M. M. Maslov†,1,7

†Mike.Maslov@gmail.com

1Research Institute for the Development of Scientific and Educational Potential of Youth, Moscow, 119620, Russia
2Department of Physical Chemistry, Faculty of Science, University of Jiroft, Jiroft, 7867161167, Iran
3Ulyanovsk State University, Ulyanovsk, 432017, Russia
4Sivas Cumhuriyet University, Department of Biochemistry, Sivas, 58140, Turkey
5Food and Drug Safety Research Center, Tabriz University of Medical Science, Tabriz, 5165665931, Iran
6Pharmaceutical Analysis Research Center, Tabriz University of Medical Science, Tabriz, 5165665931, Iran
7National Research Nuclear University MEPhI, Moscow, 115409, Russia

Using density functional methods, the results of the analysis of traditional adsorbents and adsorbents based on nanosized particles capable of trapping 1,4-dioxane and 2-methyl-1,3-dioxolane molecules in milk are presented. We considered the following interacting compounds: 1,4-dioxane — primary amine, 1,4-dioxane — secondary amine, 1,4-dioxane — fullerene C20, 1,4-dioxane — a fragment of the structure of activated carbon, 2-methyl-1,3-dioxolane — primary amine, 2-methyl-1,3-dioxolane — secondary amine, 2-methyl-1,3-dioxolane — fullerene C20, 2-methyl-1,3-dioxolane — a fragment of the structure of activated carbon. We determined the optimal configurations of the corresponding interacting structures, estimated their binding energies and chemical potentials. The highest binding energy was obtained for 1,4-dioxane adsorbed on C20 fullerene. At the same time, the energy gaps between the occupied HOMO and unoccupied LUMO molecular states were calculated, which makes it possible to characterize the reactivity and stability of molecules. Compounds of 1,4-dioxane and 2-methyl-1,3-dioxolane with amines have rather large gaps HOMO-LUMO. Using the concept of the electronic localization function, we found that a covalent bond is formed between 1,4-dioxane and C20 fullerene with a sufficiently high degree of electron localization in the bond region. In other cases, the value of the localization function indicates the absence of a chemical bond between the compounds. The proposed study gives recommendations on the adsorption of 1,4-dioxane and 2-methyl-1,3-dioxolane for further solid-phase microextraction, which will allow them to be found in milk by gas chromatography using a flame ionization detector.

Keywords: adsorption, dioxane, density functional theory, solid-phase microextraction.
1. Introduction

The planetary deterioration of the ecological situation is inextricably linked with the deterioration of the quality of food, the safety of which is the key to preserving human health. It is especially important to preserve the naturalness and purity of baby food as a guarantee of the preservation of infants' health, 1,4-dioxane can be transmitted to infants during lactation. According to pharmacokinetic models [2], it was shown that 1,4-dioxane, along with carbon tetrachloride, methylchloroform, perchloroethylene, has the property of easily binds to milk, which is inhaled from the ambient air. In addition, it is known that in the context of preserving children's health, 1,4-dioxane can be transmitted to infants during lactation. According to pharmacokinetic models [2], it was shown that 1,4-dioxane, along with carbon tetrachloride, methylchloroform, perchloroethylene, has the property of easily binds to milk, which is inhaled from the ambient air to nursing mothers. In this regard, the problem of determining foreign chemical inclusions and maintaining the chemical purity of breast milk is relevant and promising. The detection of 1,4-dioxane is an independent task and can be considered in conjunction with the detection of 2-methyl-1,3-dioxolane since the latter is the most frequent derivative of 1,4-dioxane, often obtained as a result of the decomposition of 1,4-dioxane and indicates its presence. Finding two substances at once in breast milk and milk products for children will more accurately characterize its purity. It is important to be able to detect these two substances simultaneously.

Due to the high solubility of 1,4-dioxane in water, its detection seems to be a serious problem [3]. There are various physical and chemical methods of analysis. Standard analytical methods based on closed-loop stripping analysis [4] are not suitable to determine 1,4-dioxane owing to taste and odor are almost absent [3]. The physicochemical method for separating substances, based on the distribution of the components of the analysed mixture between two immiscible phases moving relative to each other (the gas chromatography method), can be very reliable in this case. 1,4-dioxane, which has the properties of volatility and thermal stability, meets the requirements of this method. The following detectors can be used to continuously measure the concentration of substances at the outlet of the chromatographic column: thermal conductivity detector, electron capture detector, mass spectrometry, and others. A detector for the determination of 1,4-dioxane must simultaneously combine the properties of versatility, non-destructive measurements, and high sensitivity to organic compounds. The Flame ionization detector reacts to all compounds that can be ionized by a flame and are a dedicated organic compound detection tool. To apply this method, a preliminary concentration of dioxane and 2-methyl-1,3-dioxolane is required.

To pre-concentrate the dioxane and dioxolane, one of three methods must be used: liquid-liquid extraction (LLE), purge and trap (PT), and solid-phase extraction [5]. The PT pre-concentration method requires extended purge time or additional heat. The reported limit for the PT method, observed in [3], was 150 ng/L. The detection limit in the LLE method was 200 ng/L [6]. The separation of solid-phase mixtures using solid sorbents in the SPE method allows one to increase the dioxane concentration to 1 µg/L [7 – 9]. A variation of the SPE method is the solid-phase microextraction (SPME) with involves the use of a fibre coated with an extracting phase. The SPME approach can be effectively used in combination with gas chromatography due to improvement in time-saving, economic factors, and detection limits [10].

The stationary phase in the gas chromatography method is solid particles, namely adsorbents with a high specific surface area (10 – 1000 m²/g). The search for such adsorbents by the methods of quantum chemistry is the subject of this article, i.e., we hope to obtain a comparative picture of the degree of adsorption of dioxane and methyl-1,3-dioxolane on known

Ключевые слова: адсорбция, дихлорэтилен, теория функционала плотности, твердофазная микроэкстракция.
materials and, based on the obtained data, to give appropriate recommendations for the selection of adsorbents based on quantum chemistry. We will take activated carbon, amines, fullerenes, and other carbon nanoparticles as the analysed adsorbents. Activated carbon as a well-known sorbent is used in the field of pharmacology, in the food industry, in the military, in devices for purifying drinking water [11,12], and in many other areas of life. The effectiveness of primary and secondary amines as adsorbents was discussed in [13], where, in particular, it was shown that the processes of adsorption and desorption for the primary, secondary, and tertiary amines proceed in opposite directions. The study of hybrid materials based on mixed amines and oxides for the capture and separation of CO\(_2\) from bio-hydrogen was carried out in [14]. Further, fullerenes are stable, biocompatible, and highly reproducible nanoparticles. It was shown in [15,16] that fullerenes, fullerene-, graphene-like materials [17], due to their large specific surface area, can chemically bind a large number of particles. Although C\(_60\) and nanotubes are more suitable due to their larger area, we consider C\(_{20}\) as the minimum fullerene, it is the most curved and therefore the most active. The efficiency of adsorption using functionalized nanoparticles by different groups is also an interesting subject for research.

### 2. Computational details

The considered atomic model was driven to energy-optimal configurations using the GAMESS software package [18]. Based on the density functional theory using the set of basis functions B3LYP/6-311G, the diameter of the molecules, their total energies corresponding to a given local energy minimum, and the bond lengths were calculated. All structures are optimized while a Hellman-Feynman force convergence exceeds 10\(^{-2}\) eV/Å. Iteration tolerance is 10\(^{-5}\). The dispersion interaction was taken into account by the DFT-D2 method of Grimme [19]. The density functional theory method is also used to calculate the HOMO-LUMO sites and Electron Localization Function (ELF). The full visualization process is carried in the ChemCraft package.

### 3. Models

Fig. 1 shows the models for the considered 1,4-dioxane and 2-methyl-1,3-dioxolane, primary amines, secondary amines, fullerene C\(_{20}\), and activated carbon. All of them considered molecules were optimized as described above. The dark grey balls denote the carbon atoms, the light grey balls denote the hydrogen atoms, the red balls denote the oxygen atoms, and the blue balls denote the nitrogen atoms.

Further, we constructed the atomistic models of interacting structures: 1,4-dioxane — primary amine, 1,4-dioxane — secondary amine, 1,4-dioxane — fullerene C\(_{20}\), 1,4-dioxane — a fragment of the structure of activated carbon, 2-methyl-1,3-dioxolane — primary amine, 2-methyl-1,3-dioxolane — secondary amine, 2-methyl-1,3-dioxolane — fullerene C\(_{20}\), 2-methyl-1,3-dioxolane — a fragment of the structure of activated carbon. We performed the optimization procedure again. The initial configurations of the interacting structures were chosen so that the space between them contained as many atoms as possible.

### 4. Results and Discussions

The binding (adsorption) energy of 1,4-dioxane and 2-methyl-1,3-dioxolane molecules on primary and secondary amines, fullerene C\(_{20}\), and a fragment of the structure of activated carbon was given by [20]

\[
E_b = E_{\text{tot}} - (E_{\text{mol}} + E_{\text{ads}}),
\]

where \(E_{\text{tot}}\) is the total optimized energy of the complex interacting structures, \(E_{\text{mol}}\) is the energy of the free, relaxed 1,4-dioxane molecule (or 2-methyl-1,3-dioxolane molecule), and \(E_{\text{ads}}\) is the same energy one of four adsorbents.

As shown in [21], the density functional theory allows getting a set of physical quantities. One of them is the HOMO-LUMO gap. It is defined as the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital [21]. So, the optimized parameters for the adsorption of the 1,4-dioxane molecule and 2-methyl-1,3-dioxolane molecule on the four adsorption species were tabulated in Table 1.

As shown in Table 1, the largest bonding was found for 1,4-dioxane — fullerene C\(_{20}\), because the \(E_b = -0.435\) eV. At the same time, 2-methyl-1,3-dioxolane and secondary amine are weakly bonded. 1,4-dioxane and 2-methyl-1,3-dioxolane have a general tendency when adsorbed on the considered materials, namely, the binding energies of these molecules with “pure” carbon materials (fullerene C\(_{20}\) and activated carbon) are higher than with amines. In general, obtained
values are close to the adsorption energy of oxygen molecules physisorbed on two-dimensional tungsten disulfide [22]. As to the HOMO-LUMO gap, the compounds of 1,4-dioxane and 2-methyl-1,3-dioxolane molecules with amines have a large HOMO-LUMO gap. The HOMO-LUMO gap is reduced as one moves to other adsorbents.

To understand the bonding character of the considered interacting structures, we calculated the ELF as [23]

$$\text{ELF} = \frac{1}{1 + (D/D_0)^2},$$

where $D$ is the kinetic energy density of the considered system and $D_0$ is the kinetic energy density of a homogeneous electron gas. If ELF takes values close to 0, then such space regions contain not localized electrons and, conversely, if the value is 1, high localization of electrons can be observed. [23]. Fig. 2 shows the results of isosurfaces of ELF for all interacting structures.

As shown in Fig. 2c, the high electron localization is reached between 1,4-dioxane and fullerene C$_{20}$. In remain cases, ELF is in the range from 0.07 to 0.15, indicating the absence of covalent bonding between them. These captures are obtained for the same levels of ELF. On the contrary, Fig. 3 shows the results of maps of ELF for all interacting structures when one sees different values of ELFs. These images are designed to show the shortest distance between two molecules. The figure clearly shows the areas of covalent bonding inside the molecules depicted in red colour. At the same time, intermolecular regions considered structures (except the 1,4-dioxane — fullerene C$_{20}$) are marked in blue and green.

### 5. Conclusions

Quantum chemistry is a powerful tool for predicting the properties of new materials and their compounds. But often, the results obtained in the course of quantum chemistry turn out to be divorced from practice. In this study, we have provided an appropriate link, since the obtained results will help to understand which classical or new materials can be used for the effective adsorption of toxic 1,4-dioxane and 2-methyl-1,3-dioxolane.

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| Interacting structures | Shortest distance $l_s$, Å | Binding energy $E_b$, eV | Chemical potentials $\mu$, eV | HOMO-LUMO gap $\Delta_{HL}$, eV |
|------------------------|-----------------------------|-------------------------|-----------------------------|-----------------------------|
| 1,4-dioxane — primary amine | 2.25 | −0.291 | −2.35 | 6.20 |
| 1,4-dioxane — secondary amine | 2.52 | −0.247 | −2.19 | 6.44 |
| 1,4-dioxane — fullerene C$_{20}$ | 1.36 | −0.435 | −4.42 | 0.65 |
| 1,4-dioxane — activated carbon | 2.97 | −0.350 | −4.68 | 2.19 |
| 2-methyl-1,3-dioxolane — primary amine | 2.42 | −0.297 | −2.28 | 5.94 |
| 2-methyl-1,3-dioxolane — secondary amine | 2.09 | −0.185 | −2.38 | 6.51 |
| 2-methyl-1,3-dioxolane — fullerene C$_{20}$ | 2.45 | −0.397 | −4.66 | 0.71 |
| 2-methyl-1,3-dioxolane — activated carbon | 2.83 | −0.301 | −4.80 | 1.64 |

**Table 1.** The optimized parameters for the adsorption of the 1,4-dioxane molecule and 2-methyl-1,3-dioxolane molecule on the four adsorption species: binding energies $E_b$, shortest distance $l_s$ between the interacting compounds, chemical potentials $\mu$, and HOMO-LUMO gap $\Delta_{HL}$.

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**Fig. 2.** (Color online) Isosurfaces of ELF: 1,4-dioxane — primary amine (a), 1,4-dioxane — secondary amine (b), 1,4-dioxane — fullerene C$_{20}$ (c), 1,4-dioxane — fragment of the structure of activated carbon (d), 2-methyl-1,3-dioxolane — primary amine (e), 2-methyl-1,3-dioxolane — secondary amine (f), 2-methyl-1,3-dioxolane — fullerene C20 (g), 2-methyl-1,3-dioxolane — fragment of the structure of activated carbon (h).
2-methyl-1,3-dioxolane. This information will help to carry out solid-phase microextraction and find them in milk using gas chromatography with a flame ionization detector method.

Acknowledgments. The presented study was carried out under the project “Development of low-cost technology for efficient detection of low concentrations of dioxane and dioxolane from milk samples by micro solid-phase extraction and gas chromatography technique” with the support of the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-10-2021-107 dated September 24, 2021; Government contract identifier 0000000007521R500002).

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Fig. 3. (Color online) Maps of ELF: 1,4-dioxane — primary amine (a), 1,4-dioxane — secondary amine (b), 1,4-dioxane — fullerene C20 (c), 1,4-dioxane — fragment of the structure of activated carbon (d), 2-methyl-1,3-dioxolane — primary amine (e), 2-methyl-1,3-dioxolane — secondary amine (f), 2-methyl-1,3-dioxolane — fullerene C20 (g), 2-methyl-1,3-dioxolane — fragment of the structure of activated carbon (h).