

**DETERMINATION OF LOW CONCENTRATIONS OF SARIN
AND O-ISOPROPYLETHYLPHOSPHONATE
(SARIN DESTRUCTION PRODUCT)
IN OBJECTS OF THE ENVIRONMENT
BY THE METHOD OF IR-FOURIER SPECTROSCOPY**

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ABSTRACT

Some features of IR-spectroscopy have been considered, which may be used for identification of hazardous toxicants in objects of the environment.

Sarin was studied as a toxic chemical, and O-isopropylmethylphosphonate was studied as well as its destruction product by which the agent may be identified indirectly even a long time later after it contacted with foregoing objects. Some other derivatives of methylphosphonic acid have been studied as well.

As objects contaminated by these substances the samples of soil, water and some other surfaces were studied. As a result there was found, that all mentioned substances extracted from appointed mediums by extraction or by wipe, may be quick and rather exactly identified by characteristic features (by absorption bands in IR-spectra). The method allows detect the substances being studied in soil at the level of - 0.1 mg/g, in water at the level of ~ 2 mg/ml and on the surface at the level of- 0.2 mg/cm².

INTRODUCTION

In case of contamination of environmental objects (such as air, water, soil etc.) by different toxicants (including the consequences of acts of terrorism) the main purpose is their quick identification. These methods should be quick, selective and have high sensitivity. Well-known methods of the environmental monitoring meeting these requirements [1] may be successfully applied for the identification of hazardous toxic substances [2] including toxicants assigned to chemical weapons [3-6].

IR-spectroscopy is one of them. This method is widely used for analyses of different environment objects and may be used for detecting the content of harmful chemicals in them [7-11]. In this case [9-10] the lowest detectable limits have been achieved (including such hazardous toxicant as sarin) comparable with those achieved by gas chromatography methods [10]. However, to achieve such high sensitivity it is often necessary to apply special equipment and to use rather complicated sample preparation procedure, what make the analysis to be not so operative. At the same time, for quick and effective elimination of the consequences of emergency situations and provision of first medical aid it is necessary to apply, first of all, high operative methods, and, as a rule, in these situations high sensitive methods are not required because concentrations of toxicants are sufficient for their determination by standard IR-spectrometer.

In this report the IR-spectroscopy method is considered for detecting toxic chemicals in objects of the environment in most simple variant.

EXPERIMENT

The samples of soil, water and some surfaces were picked out as the environment objects.

The above mentioned objects were contaminated by sarin and O-isopropylmethylphosphonate (IPMP), which is the first sarin destruction product.

O-isopropylmethylchlorphosphonate (IPMCP), which is a similar analogue of sarin. has been studied as well.

As it is known sarin has a rather low hydrolytic stability and may be decomposed rather quick under moisture impact both in the atmosphere and in the soil. That is why it may be difficult to detect this agent in objects of the environment in some period of time. However, it may be easily identified indirectly even after long period of time in the objects mentioned above by presence of IPMP in the sample formed by the following reaction:



The objects were prepared for the analysis in such a way. The substances mentioned above were added to the samples of water and soil in quantities providing their concentrations of 0.5-13.0 mg/l and 0.1-5.0 mg/g respectively (on the surface approximately 1-2 mg/cm²). After intermixing the substances added were extracted by carbon tetrachloride (chlorinated hydrocarbons are often used for extraction [6]). According to recommendations [12] the extraction was carried out either by shaking up mixtures for 5-10 minutes or by using an ultrasonic bath (in both cases the results obtained were similar). Weight (volume) ratios of sample: solvent were varied from approximately 4:1 to 1:1. The extraction degree, determined by comparing spectra of the extracts and standard solutions of known concentrations, varied depending on conditions and the origin of the object within the wide limits (15-65%).

IR-spectra of the sample solutions were recorded by Nicolet Avatar- 360 FTIR spectrometer with use of cells with a pathlength of 0.4 mm and KBr windows.

DISCUSSION

The main bands of IR-spectra of compounds studied are presented in the Table. As we can see, these spectra are similar due to the present in the structure of molecules of the same fragment $\text{CH}_3\text{P}(\text{O})(\text{OC}_3\text{H}_7)_2$. However, these spectra are characterized by some evident differences (corresponding values of wave numbers are marked by bold type), by which they may be identified accurately in different objects of the environment. The IR-spectrum of sarin in carbon tetrachloride is shown in Figure 1 at 1400-800 cm^{-1} , where most characteristic bands of it are located (see Table). The IR-spectrum of the extract from water solution of sarin is presented on the same Figure. The initial concentration of sarin was 6.5 mg/ml; the volume ratio of the sample/solution was 1:1 (2 ml: 2 ml), the extraction efficiency was 37%. The extraction was carried out immediately after sample preparation and at the same time the IR-spectrum of the extract was recorded (Fig. 1).

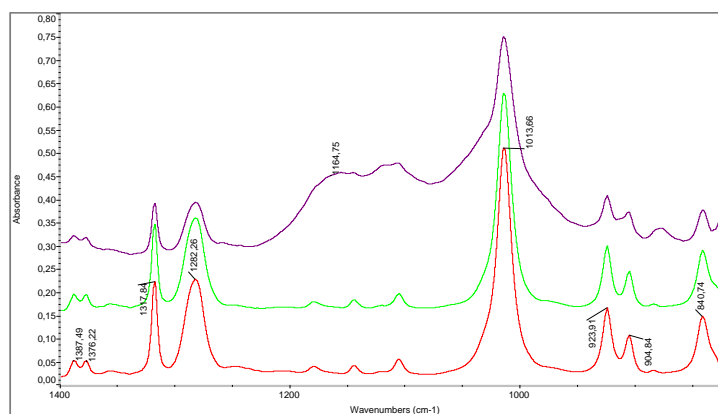


Figure 1. IR spectra of sarin (red) and its extracts from water (green) and sand (violet). Solvent and extractive was carbon tetrachloride (See Text)

As we can see, the IR-spectrum of the sample did not differ from the spectrum of the initial substance at the first moment after preparation. Thus, there was observed no noticeable interaction of sarin with water. However, the signs of sarin degradation appeared distinctly in the samples after some days of exposure. The intensity of the most specific bands of

sarin was reduced, and at the same time the bands characteristic for its degradation product (O-alkylmethylphosphonate) have appeared (see Table).

Table. The main bands of IR-spectra of molecules $\text{CH}_3\text{P}(\text{O})(\text{OC}_3\text{H}_7\text{i})\text{X}$ (cm^{-1}).
Solvent is CCl_4 .

X=F - sarin	X=OH - IPMP	X=C1 - IPMCP
2983	2979	2983
2938	2934	2935
2878	2873	2873
	2640	
	2320	
	1680	
1467	1467	1464
1455	1453	1453
1417	1417	1418
1387	1386	1387
1376	1375	1374
1318	1312	1307
1282	1202	1269
1179	1179	1180
1140	1142	1142
1105	1109	1104
1014	1009	990
	987	
924		912
905	908	889
841		
		524
508		
480	485	476

The similar phenomena was observed for the sand samples containing sarin, as well. For some hours after the sample preparation there was observed no changes on spectra of the extracts, but three days later the concentration of sarin in the sample was reduced significantly due to of hydrolysis. At the same time several bands were recorded on the mentioned spectra (Fig. 1) in the range of $1200\text{-}1100\text{ cm}^{-1}$. These bands are specific for sarin degradation product O-isopropylmethylphosphonate (the initial concentration of sarin in the soil samples was 0.19 mg/g , volume ratio sample/solution was $2.5:1$ ($10\text{ g}: 4\text{g}$) the extraction efficiency in this case was 45%). On the basis of the results described it should be concluded, that sarin may be detected in soil and water even some days later after contamination. Later, after a long time, sarin may be identified by its main destruction product O-isopropylmethylphosphonate. The main IR-spectral characteristics by which this substance may be detected in different mediums are presented in the Table. The most characteristic bands from them are strong absorption maximums located in the range of $1200\text{-}1100\text{ cm}^{-1}$ (Fig.2) corresponding to stretching vibrations of phosphoryl-group.

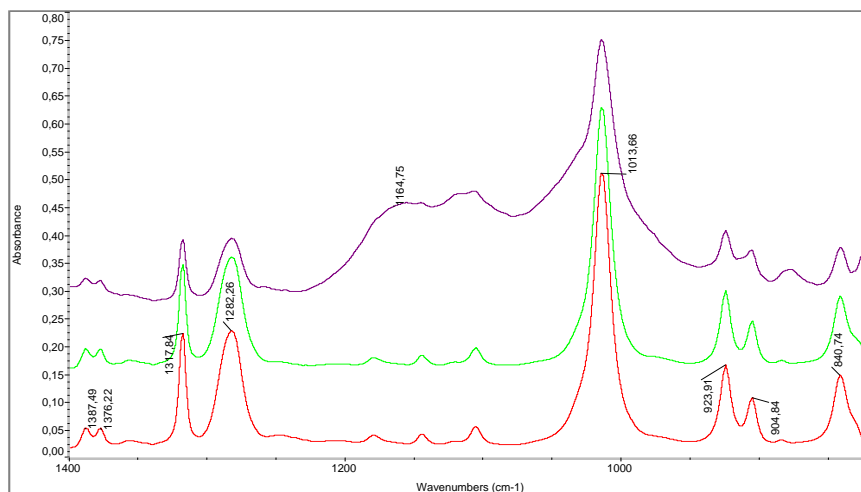


Figure 2. IR-spectra of O-isopropylmethylphosphonate (C= 0.01 %) (red) and its extracts from water (violet), sand (blue) and from the surface (green). Solvent and extractive was carbon tetrachloride.

Due to great susceptibility of this substance to formation of intermolecular complexes with hydrogen bond and the differences in their natures depending on another partner [13, 14] the structure of this absorbance may be changed (see examples on Fig.2). IR-spectra of O-isopropylmethylphosphonate and of its extracts from the samples of water, sand and the surface plate of organic glass are presented on Figure 2. We can see that when concentration of IPMP in the initial samples was 1.8 mg/ml, 0.075 mg/g and 0.22 mg/cm² correspondingly this substance may be identified confidently (the extraction efficiency from the sample was taken into account at estimation of threshold concentration).

When the substance is characterized by high susceptibility to hydrolysis, we can estimate its presence in the sample (in the past) only by indirect signs. Such situation takes place in case of O-isopropylmethylchlorphosphonate (IPMCP) that is nearest analogue of sarin.

IR-spectrum of this compound (C= 0.03%) and of the extracts from samples of water and sand with the initial concentration of IPMCP at the level of 0.52 mg/g and 0.12 mg/ml correspondingly are presented on Figure 3. Spectra of the extracts were obtained in an hour after the samples were prepared. As we can see from Fig. 3. in both cases the IR-spectra of the extracts does not have the bands characteristic for the initial substance, and the new bands (1312 cm⁻¹, absorption in the area of 1200-1100 cm⁻¹ and etc.) appeared instead, which are characteristic for IPMP. At the same time the spectra contain another bands such as 1261, 950-960 cm⁻¹, which indicate the presence in the samples of the other conversion product of the initial substance. This product was identified by the available data as isopropylmethylpyrophosphonate [CH₃P(O)(OC₃H₇i)]₂O.

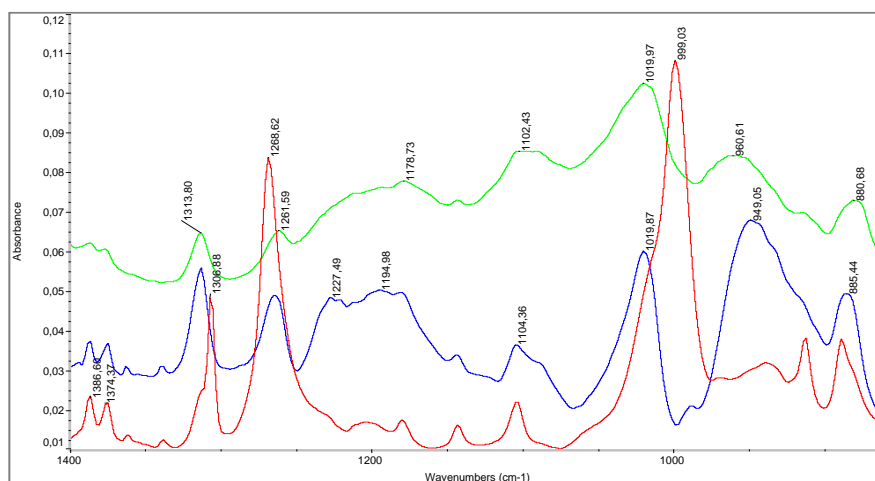


Figure 3. IR-spectra of O-isopropylmethylchlorophosphonate (red) and its extracts from water (blue) and sand (green). Solvent and extractive was carbon tetrachloride.

CONCLUSION

The study conducted showed that the IR-spectroscopy method may be applied successfully for identification of toxic chemicals and their destruction products in the environment. The method is characterized by high selectivity, and the presented variant differs by quick response as well: operations connected with sample preparation and spectrum recording takes less than half an hour. The method is characterized by high sensitivity as well. Detection limits for sarin and IPMP in the system substance/sand was about 0.1 mg/g, and for the system substance/water was about 2 mg/ml. On the surface this substance may be detected at the level of about 0.2 mg/cm².

The above stated detection limits correspond to the concentration of toxic chemical in extracts not less than 0.03 %. All analytical bands are located within the interval of optical density from 0.02 to 0.14. However, these bands may be reliably identified even at concentration of the substance in carbon tetrachloride at the level of 0.003% (Fig.4). This fact allows supposing that sensitivity of determination of substances in the environment objects by the method of IR-spectroscopy may be increased in some times.

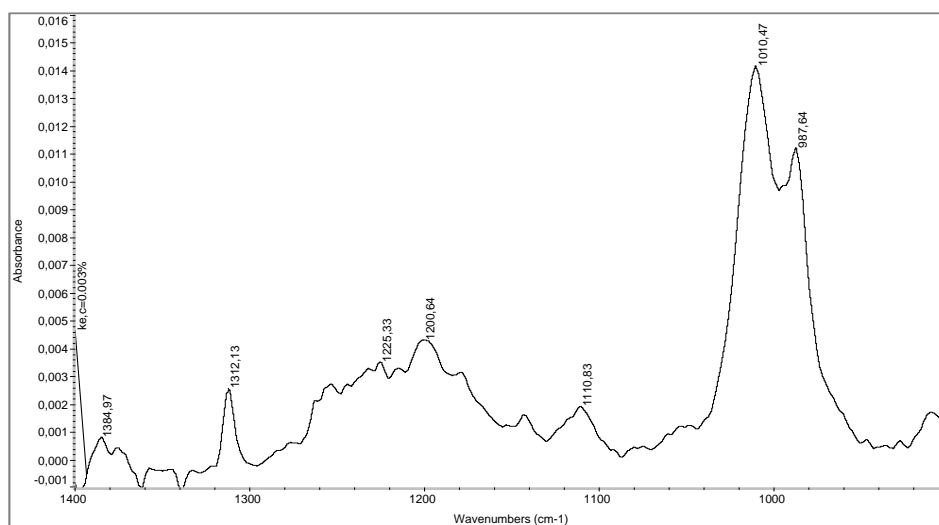


Figure 4. IR-spectra of O-isopropylmethylphosphonate in carbon tetrachloride, (C= 0.003 %)

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