Proceedings of the 2nd International Conference on Green Energy, Environment and Sustainable Development (GEESD2021), D. Dobrotă and C. Cheng (Eds.) © 2021 The authors and IOS Press. This article is published online with Open Access by IOS Press and distributed under the terms of the Creative Commons Attribution Non-Commercial License 4.0 (CC BY-NC 4.0). doi:10.3233/ATDE210345

Air Contaminants in an Underwater Vehicle Cabin During Navigation

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> Abstract. The purpose of this study is to study the air contaminants in the cabins of underwater vehicle. The basic data help for the better research of the underwater vehicle cabin environment standard and the control strategy. Pretreatment and analysis method of volatile organic compounds was preconcentration combined with gas chromatography under the condition of liquid nitrogen and detected by chromatography-mass spectrometry. The pollution of particles, carbon monoxide and carbon dioxide during the underwater vehicle voyage were monitored by online monitoring instrument. Altogether 34 kinds of pollution components were detected, most of which were low in concentration. Some are low olfactory threshold or high toxic components, such as dimethyldisulfide, benzene, carbon disulfide, trichloromethane, and several reached to ppm level. The contamination of the particles was mainly fine particles and part cabins exceeded the national standard of indoor air quality. The highest concentration of carbon dioxide in accommodation space exceeded the permissible concentration of atmosphere composition aboard diesel underwater vehicle compartments. The increase submerged time made the environment in the cabins deteriorate. The concentration of trace contaminants may close to or beyond the relevant standards with the prolonged time. The volatile organic compounds, particles, carbon monoxide and carbon dioxide aggravated the air circumstance in the cabins. It should be determined the permissible concentration of air contaminants in underwater vehicle as soon as possible.

Keywords. Air contaminants, underwater vehicle, environment pollution

1. Introduction

When the underwater vehicle sails underwater, the crew lives in a specific environment, the space is small, the activity is limited, and the cabin lacks natural light and normal air circulation, plus swing, vibration, noise, high temperature, high humidity, biological rhythm, harmful Gas, nutrients, water supply and other factors will inevitably have a certain impact on human physiology and psychology. Conducting surveys on the navigation air quality data of such underwater vehicle can provide a scientific basis for strengthening medical support and formulating corresponding health standards in the future. There are many kinds of gas in the enclosed environment of the underwater vehicle cabin, which pollutes the air inside the boat and threatens the health of the crew. There are many sources of pollution in the boat, such as ammonia, formic acid, uric acid, aldehyde, methyl mercaptan, volatile amines and other harmful substances produced by human metabolites; cooking produces a large amount of acrolein, oxygenates and aerosols; non-metallic materials such as paints and plastics Rubber, fuel, lubricating oil,

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and binders can produce a large number of harmful substances such as alkanes, olefins, halogenated hydrocarbons, aromatic hydrocarbons, oxygenates, sulfur compounds, aerosols, and the like. With the increasing number of non-metallic materials on the boat, these materials have become the main source of air pollutants in the cabin [1-4]. The harm of aerosol to human body is closely related to its particle size. Particles larger than 2.5µm are easily blocked by the respiratory tract, stimulating the local mucosa, causing allergic rhinitis, infecting the upper respiratory tract, and forming bronchial asthma, bronchitis, and allergic Pneumonia, and lead to respiratory dysfunction; and particles less than 2.5µm can directly enter the lungs, leading to lung sclerosis, and posing a great

threat to the health of the crew [5].

The research on the atmospheric environment detection of underwater vehicle cabins has been valued by the navies of various countries. The US Navy ranks the importance of underwater vehicle air quality as the second only to defense preparations, which shows the importance attached to the quality of the atmospheric environment [6]. The Royal Navy also attaches great importance to the air detection technology of underwater vehicle cabins [7]. It has qualitatively analyzed 195 kinds of harmful gas components in the air of underwater vehicle cabins, and quantitatively analyzed 50 of them. Zhou Shengru used five kinds of adsorbents (Tenax, Porapak, Chromosob-103, GDX-101, and activated carbon) for concentration sampling, and 14 kinds of 266 organic substances were legally determined by color spectro scopy [8]. Xiao Cunjie divided the atmospheric components of the underwater vehicle into 12 categories, and concentrated and sampled the 12 substances using six adsorbents (Tenax, Porapak, Chromosob-103, GDX-101, activated carbon, and silica gel) [9]. Altogether 368 components were qualitatively detected, including 175 kinds of aliphatic hydrocarbons, 53 kinds of aromatic hydrocarbons, 28 kinds of naphthalenes and their homologues, 20 species of quinones and their homologues, 14 kinds of halogenated hydrocarbons, 2 kinds of nitrogen-containing compounds, 7 kinds of alcohols, 9 kinds of aldehydes, 16 kinds of ketones, 1 kinds of acid, 4 kinds of esters, 2 kinds of ethers and 37 others, by the method of Colorimetric mass spectrometry, verification tube, colorimeter and atomic absorption spectrometry, and 67 components were quantitatively detected. The Swedish Naval Institute of Defense, Lund University and other units studied the quality of the air during the dive of the Gotland-class AIP underwater vehicle, and jointly carried out a 16-day trial in which the snorkeling continued for 8 days [10]. In this experimental study, the monitor was carried out mainly including carbon dioxide (CO₂), oxygen (O₂), ozone (O₃), hydrogen (H₂), nitrogen dioxide (NO₂), volatile organic compounds (VOC), formaldehyde, suspended particulate matter (PM) and Microbial contaminants. Air temperature, total pressure and relative humidity were also monitored. Tests show that as long as the air renewal system works normally, except for carbon dioxide, all measured concentrations are much lower than the 8h occupational exposure limit standard made by Swedish Environmental Protection Agency, and the monitored air pollutants do not accumulate. Researchers from the Australian Department of Defense's National Defense Science and Technology Organization have studied the particle properties and composition of diesel-electric underwater vehicle release, and the measurement of emissions from marine-derived diesel particulates is rare, although this form of transportation causes significant air pollution. However, unlike the terrestrial environment, the maritime environment is not disturbed by other sources of combustion. The average concentration of particulate matter in the diesel engine compartment is $1500 \mu g/m^3$, and the particle size distribution is in the range of 0.5-202µm. The chemical forms of elemental carbon (EC), organic carbon (OC) and total carbon (TC) of the particulate matter are determined [11].

Researchers at the University of Antwerp in Belgium studied the contamination of particulate matter in diesel cabins, collected fine and coarse ions in the boat, and analyzed organic carbon, water-soluble organic carbon, main inorganic ion species and organic species, and estimated the concentration of sea salt particles, water soluble and water insoluble organic matter [12].

In order to study the composition and concentration of the main pollutants in the air of the Underwater Vehicle's cabin, airborne pollutants were detected and monitored for the underwater navigation test. The research on the quantitative analysis of air pollutants in such underwater vehicle s can provide a basis for future research on the standard limits of harmful gases for such underwater vehicle s and the design of marine air purification devices.

2. Methods

2.1. Sampling Point Settings

This type of underwater vehicle is equipped with an air renewal system for common air pollutants, a carbon dioxide elimination system using LiOH as an absorbent, and an activated carbon filter device for adsorbing volatile organic compounds and particulate matter. In this experimental study, volatile organic compounds (VOC), fine Particles (PM_{2.5}), inharable particulates (PM₁₀), and total suspended particulate matter (TSP) were monitored, and the temperature, humidity and pressure of air were recorded. The VOC collected a total of six representative points, accommodation space (AS), toilet (T), control room (CR), galley (G), energy source section (SS), machinery room (MR). The test was carried out tested in the later period of navigation, and the environmental equipment of each cabin of the navigation test worked well.

2.2. Gas Analysis of VOC

2.2.1. Environmental Parameters

Silicon-coated sampling tank (Entech USA) was used to enrich and measure the harmful gases in each cabin of the underwater vehicle. Before sampling, the sampling tank is cleaned and vacuumed with N_2 . The instantaneous sampling head is connected to the cleaned sampling tank by means of instantaneous sampling. After opening the valve, the air sample is automatically collected, and the 6L sampling tank is collected in 5 minutes. The environmental conditions of each compartment at the time of sampling are shown in table 1. After the collection, the sampling valve is sealed and brought back to the laboratory for quantitative analysis after the end of the navigation.

			1	0	0	
Parameter	AS	Т	CR	G	SS	MR
Temperature (°C)	30.3-32.3	29.6-32.8	34.5-29.3	38.3-42.3	32.3	33.6
Pressure (KPa)	100.9±0.4	100.8 ± 0.7	100.5±0.9	101.3 ± 0.6	101.4±0.4	101.1 ± 0.8
Humidity (RH%)	78%±12%	85%±12%	73%±11%	77%±11%	69%±11%	68%±12%

Table 1. Environmental condition of sampling and monitoring.

2.2.2. The Procedure of Sample Pretreatment

The instrument parameters of the three-stage cold trap concentrator refer to the USEPA TO-15 method [13]. A certain volume of the gas containing the target compound can be analyzed by the cold trap preconcentration device, and the solvent gas (N₂, O₂, CO₂, H₂O) does not pass through the preconcentration device without entering the chromatographic analysis. Three-stage pre-concentration techniques are commonly used to analyze VOCs in humid air. The first stage of cold trap (glass beads with weak adsorption capacity) is designed to effectively remove water. The cold trap is then heated and the concentrated material is slowly carried with helium or nitrogen into a secondary trap containing Tenax sorbent for efficient removal of CO₂. The concentrated gas is heated and backflushed into the tertiary trap. The aim is to further eliminate the interference of water vapor without losing VOCs, and to freeze and concentrate the concentrated gas for rapid injection analysis. In this study, samples were concentrated using Entech Model 7100A VOCs preconcentrator.

2.2.3. The Analysis Conditions of Chromatography-Mass Spectrometry

The laboratory analytical instrument is gas chromatography/mass spectrometer (Agilent 7890/5975GC/MS, Agilent, USA), the carrier gas is high purity helium, the purity is >99.999%, the carrier gas flow is 1.2mL/min, and the tail gas is 29mL/ Min, hydrogen flow rate 30 mL/min, and air flow rate 300 mL/min. The column temperature was programmed in two steps, held at 40 °C and increased to 10 °C/min to 140°C for 5 minutes, and for 3 minutes at 250 °C at the rate of 20 °C/min. The split ratio is 10:1, the inlet temperature is 200 °C, the transfer line temperature is 230 °C, the ion source temperature is 130°C, the quadrupole temperature is 230 °C, and the mass range is 10-600 am. The column was an Agilent DB-5MS, 60 m × 0.32 µm × 1.0 µm (Agilent, USA). Standard gas (1ppm, Linde Spectra Gases Inc, Linde Co., Ltd.) was used to quantify by external standard method. All gas indexes were tested 3 times, the standard deviation analysis accuracy was ± 5 %, and the standard addition recovery rate was 91%-110%.

2.3. Particle Analysis

The aerosol mass concentrations of six different compartments were tested in the later period of the voyage. A 24-hour concentration test was performed using a portable aerosol tester (TSI8533, TSI Inc. USA) that monitors Fine Particles ($PM_{2.5}$), Inharable particulates (PM_{10}), and total suspended particulate matter (TSP). The sampling flow rate during monitoring was 3.0 L/min, the detection range was 0.001-150 mg/m³, and the average daily concentration of particulate matter was calculated.

2.4. Analysis of CO/CO₂

In this test, CO and CO₂ in the living room were continuously monitored (Konor Model JA903, Konor Electronics, Shenzhen China), the sampling flow rate was 500 mL/min, the detection range was 0-100 mg/m³, and the CO₂ was 0-3%. The monitoring time is not less than 8 hours, and the highest concentration of CO₂ was recorded per day.

3. Results and Discussion

3.1. Analysis of VOC Detection Concentration in Each Compartment

A total of 34 components were quantitatively detected and divided into five categories, namely aliphatic hydrocarbons, halogenated hydrocarbons, oxygenated compounds, aromatic hydrocarbons and sulfur-containing compounds. As shown in table 2, most of the substances were low in concentration and did not exceed the conventional underwater vehicle military standard of our country (GJB11.3-91) [14] and the American Government Industrial Hygiene Committee (ACGIH) occupational exposure standards [15]. Many pollutants do not have corresponding health standards. ACGIH occupational exposure standard is a time-weighted average of 8 hours working weekday and 40 hours working weekday. While the underwater vehicle's continuous exposure time is significantly longer than 8 hours, the interval period and total exposure time are significantly shorter than the former, so the listed thresholds can only be used as a reference to accurately assess the health hazards of pollutants on boats. As can be seen from the table, the concentrations of oxygen-containing compounds and aromatic hydrocarbon compounds such as aldols are significantly higher than those of sulfides and hydrocarbons. The total amount of pollutants detected in the cabin was 32.7 mg/m³, followed by 21.5 mg/m³ in the machinery compartment, and the least in the energy source section (SS) was 18.4 mg/m³. It can be known that the pollutants produced by human activities and human metabolism account for a large proportion. The main dominant compounds with higher concentration are cyclohexane, dichloromethane, ethanol, acetone, toluene, ethylbenzene and xylene, most of which are in the ppm range, and in which the ethanol in the cabin even reaches 11.3 mg/m³, and the ethanol is too high. The concentration is estimated to be related to the crew drinking. Among these pollutants, there are some low odor thresholds such as dimethyl sulfide and dimethyl disulfide, which are higher in the toilet and other compartments, and the dimethyl disulfide detected in the toilet reaches 0.167 mg/m³, exceeding three times the concentration of the cabin, more than 8,000 times of its odor threshold [16]. These substances in this concentration range will seriously deteriorate the air quality in the cabin and have a strong stimulating effect on the human senses. It is necessary to increase the air quality improvement of these places, such as the installation of purifiers with specific chemical adsorption capacity for these odor substances. From the quantitatively detected substances, such as styrene, toluene, ethylbenzene, xylene and carbon tetrachloride are moderately toxic substances, while benzene, carbon disulfide, chloroform and dimethyl disulfide are highly toxic substances. Though the concentration was from tens to hundreds of ppb, the impact of these components on the cabin environment could not be ignored. Figure 1 shows the concentration accumulation of five types of pollutants. Non-biological sources on the boat such as aliphatic hydrocarbons, aromatic hydrocarbons, halogen and hydrocarbons, mostly are included in themselves, such as the volatilization of the lubricating oil of the ship, the leakage of the refrigerant and the release of the paint, and the natural volatilization due to temperature changes and ventilation, which are influenced greatly by environmental parameters. Bio-sources are closely related to the metabolism and decomposition of organic matter, such as organic acids, sulfides, etc., and their concentrations are significantly correlated with the microbial activity and stability parameters of the source [17]. More toxic compounds such as aromatic hydrocarbons and halogenated hydrocarbons are more important in the power and mechanical cabins. These places

include diesel engines, coolers, oil pipes, water pipes, filters and auxiliary machines. The bottom compartment of the lower part of the diesel engine is arranged to be slippery. Oil tanks, slop tanks, and diesel engine cooling fresh water tanks, these two types of nonbiological compounds are more abundant. The noise and the ambient temperature in the cabin is high which is the cabin with the worst environmental conditions on the underwater vehicle, in places where activities such as cabins and command rooms are densely populated, and a large number of oxygenated substances such as aldols are detected, which is closely related to personnel activities and diet.

Pollutant		Permissible		Concentrations (mg/m ³)	
Group	Name	Concentration [14]	TLV-TWA [15] 1-AS 2-T 3-CR4-G 5-SS 6-MR	
Aliphatic	n-Hexane		1920	0.5650.4520.5070.5530.4580.518	
	Cyclohexane		375	2.21 1.99 1.86 1.33 2.00 1.92	
	n-Heptane	75	1786	0.6670.3290.7651.03 0.7040.573	
Halogenated Chloromethane Chloroethane				0.1890.1520.1500.0580.1400.144	
				$0.019 \\ 0.019 \\ 0.019 \\ 0.017 \\ 0.010 \\ 0.017 \\ 0.015 \\ 0.017 \\ 0.015 \\ 0.017 \\ 0.015 \\ 0.017 \\ 0.01$	
	Chloroethylene			$0.007 \\ 0.008 \\ 0.007 \\ 0.00$	
	Dichloromethane	87.5	167	1.17 1.06 1.00 0.6270.9901.03	
	1,1-Dichloroethane		400	0.0280.0190.0180.0110.0140.019	
Trichloromethane 1,2-Dichloroethane			50	0.1260.0980.0930.0630.0800.100	
		87.5	400	0.2270.1490.1630.1290.1820.154	
	Tetrachloromethane		30	0.3670.3290.3040.2560.3370.322	
Trichloroethylene			292	0.0190.0150.0150.0150.0150.016	
	1,2-Dichloropropane		5	0.0360.0340.0420.0340.0400.040	
Oxygenated	Ethanol	300	2054	11.3 2.04 3.15 2.42 2.47 1.01	
	Acetone		1295	3.36 2.70 2.54 1.07 1.82 2.69	
	Methyl tert butyl ether		643	0.0640.0800.0580.0270.0370.078	
	2-Butanone			0.4250.4990.3360.3490.2900.38	
	Ethyl acetate		1571	1.24 2.45 0.6341.19 0.9102.39	
	Methyl methacrylate		223	0.5890.2590.4800.6341.06 0.527	
Aromatic	Benzene	6.0	1.5	0.3190.1670.3180.2130.3070.282	
	Toluene	40	13.5	3.88 2.69 2.55 2.07 1.92 3.91	
	Ethyl benzene	30	435	2.19 1.18 1.72 2.52 1.57 1.97	
	p-Xylene		435	1.00 0.7340.6851.46 0.6820.792	
	m-Xylene		435	0.6880.4340.6171.12 0.7010.778	
	o-Xylene		435	0.8370.4080.5830.9870.6320.682	
	Styrene		80	0.1240.0570.0870.1200.0910.097	
	4-Ethyl toluene			$0.079 \\ 0.042 \\ 0.065 \\ 0.137 \\ 0.087 \\ 0.050$	
	1,3,5-Trimethyl benzene			$0.092\\ 0.043\\ 0.068\\ 0.110\\ 0.080\\ 0.042$	
	1,2,4-Trimethyl benzene			0.3140.1540.2320.5230.3220.153	
	Chlorobenzene		55	0.1000.0720.0460.0200.0230.128	
	1,4-Dichlorobenzene		142	0.2110.2200.2890.1530.1330.334	
Sulfur	Dimethylsulfide			0.0250.0760.0750.0680.0560.066	
	Dimethyldisulfide		25.4	0.0520.1670.0850.0820.0460.109	
	Carbon disulfide		3.11	0.2230.1880.1930.2130.1940.186	

Table 2. The identified pollutants of six sampling location in this campaign.

TLV-TWA (Threshold Limit Values-Time Weighted Average), the data come from "American Conference of Governmental Industrial Hygienists (ACGIH)"; --, no reported.



Figure 1. Concentrations of five pollutant families in the six cabins.

3.2. Analysis of the Concentration of Particle

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According to the size of the particle size, the particles can be divided into three types: particles with a particle size of less than 2.5 μ m are called Fine Particles (PM_{2.5}); particles with a particle size of less than 10 μ m are called Inhalable particulates (PM₁₀); All suspended particulates with a particle size of less than 100 μ m are referred to as Total Suspended Particulates (TSP) [18]. PM₁₀ can stay in the atmosphere for a long time and is one of the main pollutants in the daily atmosphere [19]. PM_{2.5} is the most part of the PM₁₀, it has a small particle size and can absorb a large amount of toxic and harmful substances such as heavy metals and pathogenic bacteria, and it has a long residence time in the atmosphere and a long transport distance, which has an effect on visibility, air quality. and human health has a greater impact [20].

The monitoring was carried out from the 13th to the 18th day of navigation. The average concentration of $PM_{2.5}$ and PM_{10} in each compartment was higher than the concentration level at the time of mooring, indicating that certain aerosol pollution occurred in the cabin, as shown in figure 2. China's military standards do not have the limit of particulate matter. The national standard "Indoor Air Quality Standards" (GB/T18883-2002) stipulates that the daily average concentration of PM_{10} concentration limit is 0.15 mg/m³, and PM_{2.5} has no standard [21]. The cabins with daily average concentration of PM₁₀ exceeding the national standard GB/T18883-2002 have accommodation AS (0.346 mg/m³), command room CR (0.503 mg/m³), kitchen G (0.482 mg/m^3) and mechanical cabin MR (0.469mg/m³). According to the above analysis, the cabin aerosol in the submerged state of the boat belongs to fine particulate matter pollution. In the indoor environment, PM_{2.5} mainly has two forms of primary particles directly discharged in a solid form and secondary particles generated by a chemical reaction [22]. The primary particles are derived from the combustion of fuel, the emission of decorative materials and furniture surfaces, the use of equipment, the secondary suspension of fine particles, the condensation of particles less than 2.5 μ m, the air conditioning system and the activities of indoor personnel such as smoking, breathing, coughing, walking, and cleaning. The secondary particles are mainly secondary fine particles of nitrate and sulfate formed by multiphase chemical reaction. We speculate that the main sources of fine particles in the underwater vehicle cabin environment are human body emissions, material surface grinding and shedding, mechanical equipment operation and personnel operations.

Figure 3 shows the change of aerosol mass concentration with time passing after the LiOH absorption device outside the cabin is opened (14:39). It can be found that at the instant of opening of the LiOH absorption device, the aerosol concentration of the three particle sizes in the cabin rapidly increases, and then the concentration gradually decreases, thereby it can be known that the opening of the LiOH absorption device has a large influence on the aerosol concentration of the cabin.



Figure 2. Particle mass concentration of three size in the six cabins.



Figure 3. Fluctuation of particle mass concentration during an operation of LiOH exchange in accommodation space.

3.3. Analysis of CO/CO₂ Detection Concentration

The highest concentration distribution of CO and CO_2 in the underwater vehicle cabin was shown in figure 4. CO condenses will be up to hemoglobin by breathing and forms carboxyhemoglobin after passing through the bubble membrane. The ratio of the hemoglobin affinity between to CO and to the oxygen is about 235:1. The main mechanism of toxic effects of CO on mammals is to reduce the oxygen delivery capacity of blood. Long-term CO poisoning may cause myocarditis and even myocardial infarction, and its severity increases with the increase of CO concentration in blood. China military standard (GJB11.3-91) [14] has a CO concentration limit of 23 mg/m³. During the voyage, CO is at this standard limit, and the underwater navigation concentration is higher than that of water navigation. CO_2 is one of the main components of air pollutants in underwater vehicle cabins, and high concentrations can cause asphyxiation. The underwater vehicle crew is the main source of CO_2 in the cabin [23]. Long-term exposure to high CO₂ concentrations can cause people to feel chest tightness, dizziness, and decreased response capacity. At the same time, the concentration of CO_2 is often used to characterize the degree of indoor air circulation and reflect the level of other harmful pollutants in the air. If the crew are exposed to the CO₂ environment whose condense is 3% for dozens of hours, the working ability and intellectual activity of all people are significantly reduced. If the condense is more than 5%, the environment can seriously impair vision and hearing. After exposure to 1.5% CO₂ gas for several ten days, the pH of the chronic respiratory acid and the electrolyte balance showed obvious adaptive changes. It will not fully recover even after leaving this environment for several days, which indicates that long-term exposure to this concentration may lead to change of pathology and physiological. Data collected from nine nuclear-powered ballistic missile underwater vehicle s showed that the average concentration of CO_2 was 0.35% and the concentration ranged from 0 to 1.1%. The data collected from ten nuclearpowered attack underwater vehicles showed that the average concentration of CO₂ was 0.41% and the concentration ranged from 0.03% to 1.13% [24]. The concentration of CO₂ in China's conventional underwater vehicle military standard (GJB11.3-91) is 1%, and the highest concentration of CO2 on the 18th and 35th days of navigation exceeds the standard limit, which is 1.12% and 1.21%, respectively.



Figure 4. Distribution of maximum concentrations of carbon monoxide and carbon dioxide in accommodation space.

4. Conclusion

We recommend the revision and improvement of the allowable concentration of air components in the underwater vehicle compartment, adding some standards for low odor thresholds and highly toxic components. The standards of underwater vehicle air quality should be carried out as soon as possible. Control low odor threshold gas components can improve the quality of the ambient air of the ship cabin, and further the screening of non-metallic materials used on the ship should be made. For toilets, kitchens, washrooms and other areas with strong source strength, we should strengthen hygiene and operation management and establish some special purification facilities to further improve the air quality inside the boat.

Acknowledgements

This work was financially supported by the Navy Foundation of China, National Natural Science Foundation of China (NO. 21507161).

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