

SOLID ADSORBENTS USED IN GAS MASKS IN JAPAN

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INTRODUCTION

I have prepared this report partly to present the general aspect of current gas masks in Japan and the Japanese Industrial Standard of Gas Masks (JIS T8152) and partly to present the solid adsorbents used in the canisters and cartridges which have been traditionally used and newly developed.

Gas masks and chemical cartridge respirators for occupational uses have the history since about 1920 in Japan. The first Japanese Industrial Standard of gas masks (including chemical cartridge respirators) was established in 1955 which was revised in 1962, 1968 and 1972. The new revision of the current JIS T8152 is about to be published.

The principal concept of gas mask, i.e., the required functions, the classification of type and kind of facepieces, canisters and cartridges and the gas-removing capacities of canisters and cartridges did not much change all through the revisions of JIS, though the materials constructing facepieces, canisters and cartridges have been improved and the designs were refined to better satisfy the user's requirements. On the other hand, the need for respirators in industry seems increasing to cope with the variety of harmful chemicals handled there.

Regulations of the Ministry of Labor for the purpose of protecting occupational diseases due to chemicals stipulate that the employers ought to supply gas masks to the workshops under the regulations and the operation-chief among the workers ought to manage the application and maintenance of the masks.

The quality of gas masks is certified by National Approval Tests which are performed by National Institute of Industrial Health entrusted from the Ministry of Labor. The criteria for the approval and the test conditions are almost coincided with JIS T8152. The examinations for the certification are carried out on 3 articles of gas masks (facepieces and canisters or cartridges in combination) to measure the following properties: the air flow resistance of inhalation valves, exhalation valves, breathing tubes, canisters and cartridges; the air tightness of facepieces, canisters and cartridges; the dead volume of facepieces; and the visual field of facepieces. The service lives of canisters and cartridges are measured on 13 articles from a kind of a type of each brand. The materials such as plastics, metals and rubber are examined for their heat resistance, cold resistance, mass reduction due to heating, corrosion resistance, tensile strength, etc.

CLASSIFICATION OF GAS MASKS IN JIS T8152¹⁾

Gas masks including chemical cartridge respirators are classified in JIS T8152 into three types according to their construction and applicable environmental conditions shown in Table I.

Among these masks, canisters of separate type have the largest gas-removing capacity with weight about 600 g - 1000g. The canisters are further classified into ten kinds according to the kind of applicable gas. The kinds of separate type canisters are presented in Table II. Their gas-removing capacities are tested against the test gases at certain concentrations mixed

with a conditioned air stream of 30 l/min at 20°C and 50% of relative humidity. The test gas for each kind of canister, the minimum requirement for the service life and the maximum allowable penetration limit are presented in Table II.

Direct connection type canisters include 8 kinds, the same with the kinds of separate type canisters except those for fire fighting and for carbon monoxide. The canisters of this type have middle gas-removing capacities which are applicable to the environmental toxic gases at fairly high concentrations for short period. For instance, this type of canister for organic vapors which is packed with active carbon has the total weight about 300g and service life of 30 minutes or more for carbon tetrachloride vapor at 0.3% concentration in the test air stream.

Small size chemical cartridges are classified into 7 kinds which are shown in Table II. The cartridges are only applicable to dilute gases for relatively long periods. For instance, a cartridge for organic vapors is about 100g. It serves for 50 minutes or more for carbon tetrachloride vapor at 0.03% concentration in the conditioned air stream.

TABLE I. Classification of gas masks and chemical cartridge respirators according to JIS T8152

Type	Applicable environmental condition	Construction requirement
Separate type	In atmosphere containing toxic gas of 2% or less (3% or less for ammonia)	A facepiece* A breathing tube A canister
Direct connection type	In atmosphere containing toxic gases of 1% or less (1.5% or less for ammonia)	A facepiece* Canister(s) directly connected to the facepiece
Chemical cartridge type	In atmosphere containing toxic gases of 0.1% or less	A facepiece* Cartridge(s)

* Facepieces used in the above three types may be either full facepieces or quarter masks, which must have inhalation valve(s) and exhalation valve(s).

TABLE II. The properties of canisters and cartridges and their test conditions according to JIS T-8152.

Kinds of canisters and cartridges	Kinds of test gases and particles	Maximum allowable penetration limits*	<u>Separate type canisters</u>		<u>Direct connection type canisters</u>		<u>Chemical cartridges</u>	
			Test gas concentration	Minimum service life**	Test gas concentration	Minimum service life**	Test gas concentration	Minimum service life**
For halogen gases	Cl ₂	1 ppm	0.5%	60 min	0.3%	15 min	0.02%	40 min.
For acidic gases	HC1	5 ppm	0.5%	100 min	0.3%	80 min	0.03%	80min.
For organic vapors	CCl ₄	5 ppm	0.5%	100 min	0.3%	30 min	0.03%	50min.
For carbon monoxide	CO	50 ppm	1%	180 min				
For fire fighting	CCl ₄	5 ppm	0.5%	30 min				
	CO	50 ppm	2%	60 min		---		
	Cigaret smoke	5%	***	***				---
For metal fume	CCl ₄	5 ppm	0.5%	60 min	0.1%	30 min	0.03%	30min.
	Cigaret smoke	5%	***	***	****	****	*****	*****
For ammonia	NH ₃	50 ppm	2%	40 min	1%	10 min	0.1%	40 min.
For sulfur dioxide and sulfur	SO ₂	5 ppm	0.5%	50 min	0.3%	15 min	0.03%	35min.
	Cigaret smoke	5%	***	***	****	****	*****	*****
For hydro-cyanic acid gas	HCN	10 ppm	0.5%	50 min	0.3%	20 min	---	
For hydrogen sulfide	H ₂ S	10 ppm	0.5%	50 min	0.3%	20 min	0.02%	35 min

* The maximum allowable penetration limit is defined as the maximum allowable limit of unadsorbed test gas.

** The minimum service life is defined as the time for the unadsorbed gas to reach the maximum allowable penetration limit..

*** Smoke-removing efficiency should be more than 95% when measured against cigaret smoke at 100-200 mg/m³ concentration by light scattering method. Smoke removing efficiencies of direct connection type canisters (****) and chemical cartridges (*****) should be more than 80% and 60% respectively when measured at the same condition as for separate type canisters.

PRACTICAL APPLICATION OF GAS MASKS

When gas masks are used by the workers, the canisters and cartridges need to be estimated about their service lives in the environmental condition. Every canister and cartridge commercially available in Japan is attached with a card showing the breakthrough time of the canister or the cartridge for the test gas as shown in Fig. 1, i.e., the curve of breakthrough time vs. the concentration of the test gas. The users of gas masks can estimate the service life of a canister or a cartridge by referring the card. Fig. 2 shows the observed breakthrough time curves of cartridges for organic vapors.

Those breakthrough time curves attached to the commercial canisters and cartridges show that they can serve for longer periods than the minimum required service lives designated in JIS.

Figure 3 shows the results of gas removing tests of a kind of canister. The service lives of the canisters are determined as the time when the penetration gas concentration reaches to the maximum allowable concentration of the test gas. The measured service lives of some kinds of canisters, their averages and standard deviations are shown in Fig. 4.

GAS ADSORPTION PROPERTIES OF SOLID ADSORBENTS USED IN GAS MASKS

The predominant kinds of adsorbents used in gas masks in Japan are presented in Table III. Those adsorbents are classified into three categories, i.e., adsorbents which adsorb gases by physical adsorption (active carbon), ones which adsorb gases by chemical adsorption (soda lime, cupramint, acid-impregnated solid adsorbents, acidic alumina, amine-impregnated active carbon and metal oxides) and catalyst (hopcalite). Dust filter is packed in all kinds of canisters and cartridges and fine filter with specially high efficiency in some.

Active carbon has versatile uses to adsorb various kinds of gases and most of organic vapors. However, the adsorption capacity of active carbon varies according to the kind and concentration of the applied gas and vapor ². It also changes by the temperature and humidity of the air in which it is used. It should be noticed that the service life of a canister packed with active carbon would be shorter for the light-molecular weight-organic compounds than that for carbon tetrachloride. Fig. 5 shows the breakthrough times of small adsorption column packed with active carbon for some kinds of test flows containing organic vapors with or without humidity.

Canisters and cartridges packed with chemical adsorbents can be applied to limited kinds of gases which can chemically react with the solids. For instance, soda lime can adsorb any acidic gases, and metal oxides can be used to adsorb such gases that react with the metal ions to form complex ions. Cupramite is prepared by immersing a porous solid into cupric sulfate solution and it adsorbs ammonia and amines.

Hopcalite is an oxidizing catalyst for carbon monoxide and the service life of the canister of hopcalite is not the time for the saturation of the catalyst by adsorbed CO but the time for the catalyst poisoning due to moisture.

SOME EFFORTS TO DEVELOP NEW ADSORBENTS

The kinds of canisters and cartridges designated in JIS do not satisfy all needs of the workers to obtain clean inhalation air. So, canisters and cartridges which are not shown in JIS are manufactured and used for some gases, the examples of which are presented in the lower part of Table III. We have no standard for such canisters and cartridges, but the user should be informed about their breakthrough time curves when he purchases such canisters and cartridges.

Those canisters and cartridges have become to be manufactured because the vapors such as methyl bromide, vinyl chloride and mercury were not much adsorbed by the ordinary adsorbents. For instance, a canister for metal fume had been used for the filtration of mercury vapor, but the vapor can not be adsorbed on active carbon to a large amount. In addition, the adsorption capacity of active carbon for mercury vapor decreases in the presence of humidity.^{4,5)}

Adsorption capacity of active carbon for methyl bromide and vinyl chloride is not large, but it is promoted by the impregnation of amines and metal ions respectively.

For adsorption of ammonia, a few kinds of adsorbents are applicable such as cupramite, acidic active carbon and acidic alumina. The author reported that acidic active carbon impregnated with transitional metal ions is an effective adsorbent for ammonia⁶⁾.

The more variety of adsorbents would be necessary to fulfill the requirements of workers who handle various kinds of toxic chemicals.

THE NEW FUNCTIONS OF GAS MASKS

Such functions as a breakthrough time detector inlaid in a canister, a voice transmission and microphone attached to a facepiece are not designated in JIS but can be found in some kinds of gas masks.

Any criteria for protection factor or fitness and the methods to measure the factors are not included in the current JIS T8152.

INTERNATIONAL COOPERATION FOR THE DEVELOPMENT OF GAS MASKS (PERSONAL OPINION)

When a chemical becomes to be noticed for its toxic effect in any countries over the world, it is taken as a problem in Japan at the same time. The development of respirators for such substances and precise technical information for the application of the respirators are necessary for which international communication would be valuable.

TABLE III The kinds of adsorbents used in canisters and cartridges and applicable gases.

Kinds of canisters and cartridge	Adsorbents (including dust filter)	Examples of applicable gases
For halogen gases	Active carbon Soda lime	Fluorine, chlorine, bromine, phosgene
For acidic gases	Alkaline active carbon Soda lime*	Hydrohalogenic acid, nitric acid, sulfuric acid, sulfur dioxide, nitric oxide
For organic vapors	Active carbon	Organic solvent vapors (acetone, MEK, MIBK, toluene, xylene, methyl acetate, ethyl acetate) tetraethyl lead, acrylonitrile, styrene, benzene
For carbon monoxide	Hopcalite Dessicant	Carbon monoxide
For fire fighting	Active carbon Hopcalite Dessicant Dust filter	Gases, vapors and smoke generating in fire
For metal fume	Active carbon Soda lime Dust filter	Fumes of zinc, antimony and phosphor
For ammonia	Acidic active carbon Acidic alumina* Cupramite*	Ammonia
For sulfur dioxide and sulfur	Active carbon Soda lime Dust filter	Sulfurous acid, fume of sulfur
For hydrocyanic acid gas	Metal oxide Soda lime	Hydrocyanic acid gas, gases from cyanic compounds
For hydrogen sulfide	Metal oxide Soda lime Active carbon	Hydrogen sulfide
For methyl bromide**	Impregnated active carbon	Methyl bromide
For vinyl chloride**	Impregnated active carbon	Vinyl chloride
For mercury**	Impregnated active carbon	Mercury vapor
For phosphine**	Hopcalite Active carbon	Phosphine

* The adsorbents with * sign are used instead of the adsorbents without the sign in some canisters and cartridges.

** The canisters and cartridges with this sign are not designated in JIS T-8152 but manufactured.

The testing methods and apparatus to assess the quality of gas masks would be better developed by the international exchange of information, though the standards for the respirators are left different in different countries.

References

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3. R. Soda, Industrial Health_4, 45 (1966)
4. Y. Matsumura, Atmosph. Environ._8, 1321 (1974)
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Fig. 1

Breakthrough time curves presented on a card attached to a cartridge for organic vapors.

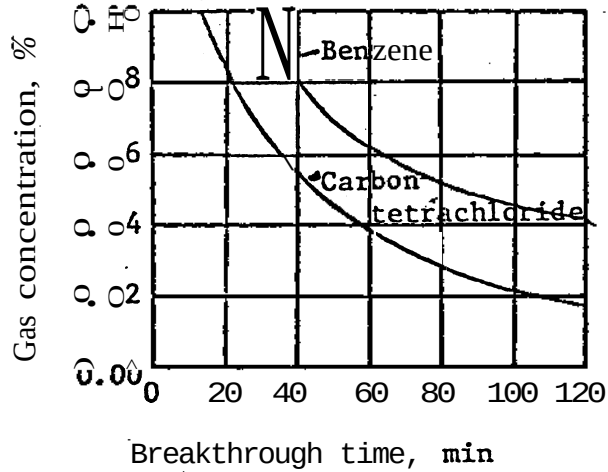
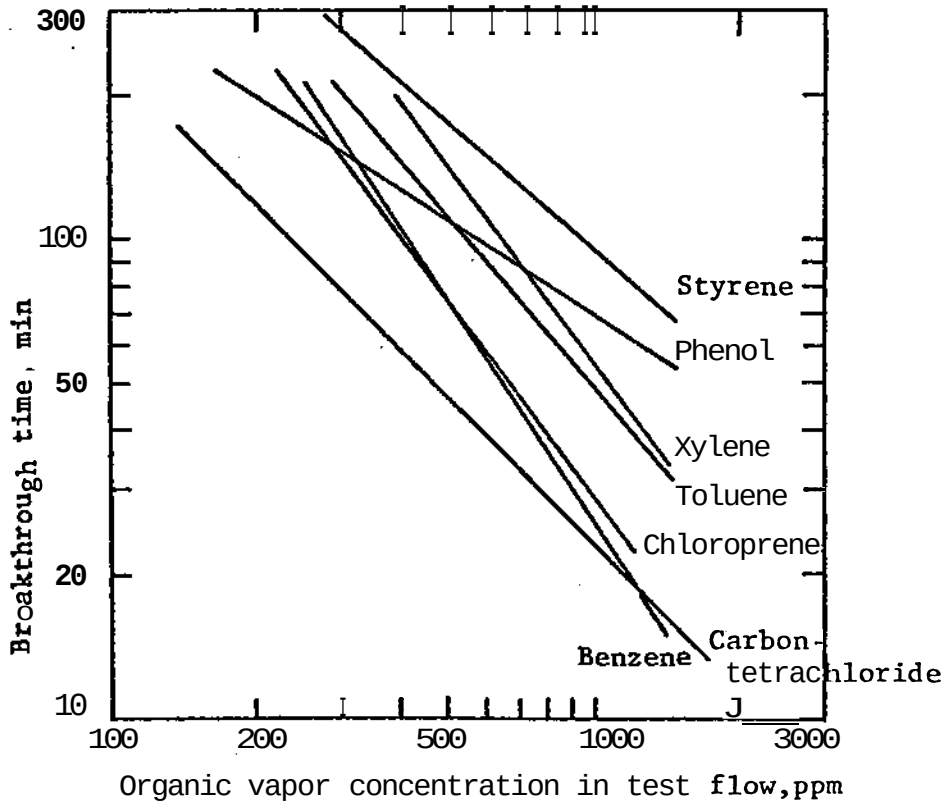


Fig. 2 Breakthrough times of cartridges for organic vapors against the test air flow containing various kinds of organic vapors. The test flow is conditioned at 30 l/min, 20°C and 50% of relative humidity. (Observed by Shigematsu Works Co. Ltd.)



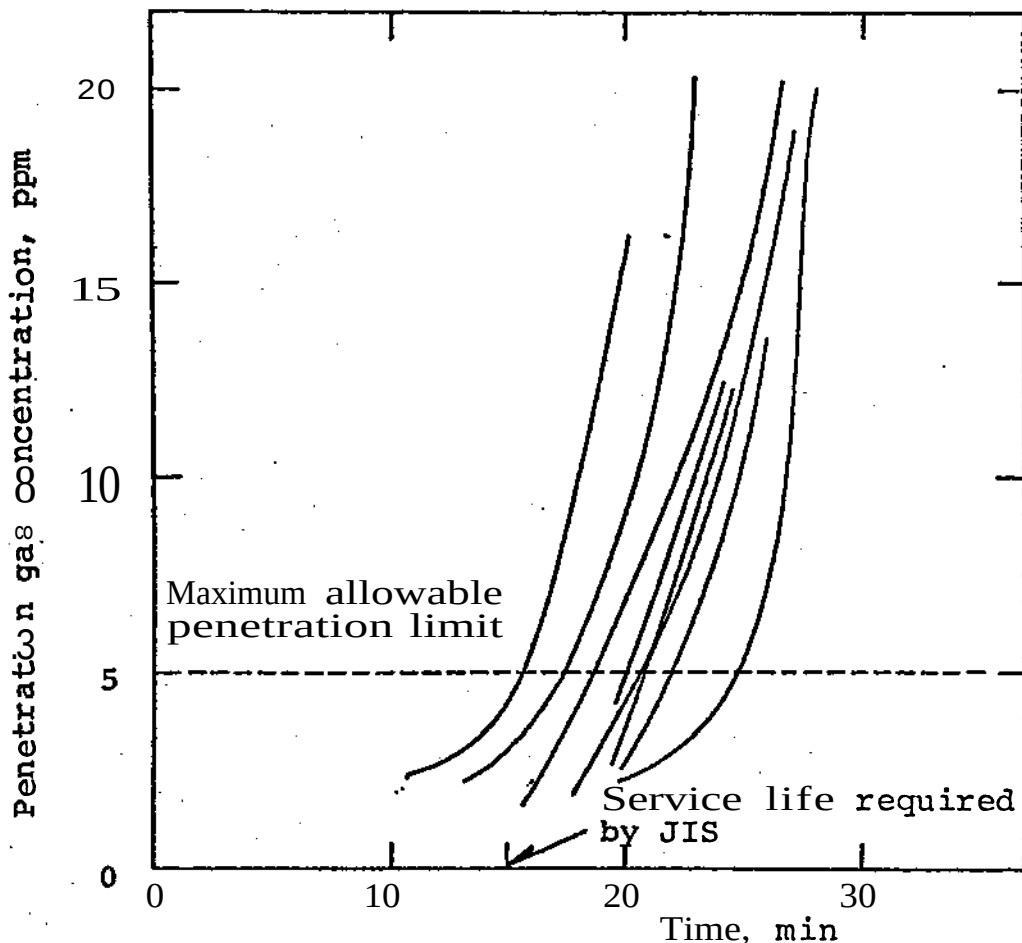


Fig. 3 Time course of the concentration change of SO_2 penetrating the direct connection type canisters.

Separate type canisters for organic vapors tested with CH_3Br 0.5 % (v/v)

(Average : 33.4min)

(S D : 1.85)

Direct connection type canisters for ammonia tested with NH_3 1 % (v/v)

(Average : 19.8min)

(S D : 1.69)

Direct connection type canisters for sulfur dioxide tested with SO_2 0.3 % (v/v)

(Average : 20.0min)

(S D : 2.85)

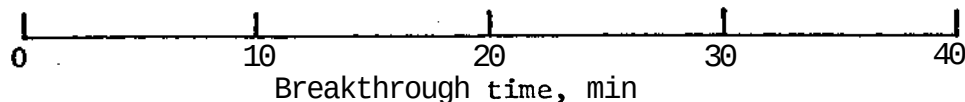


Fig. 4 Breakthrough times of some kinds of canisters.

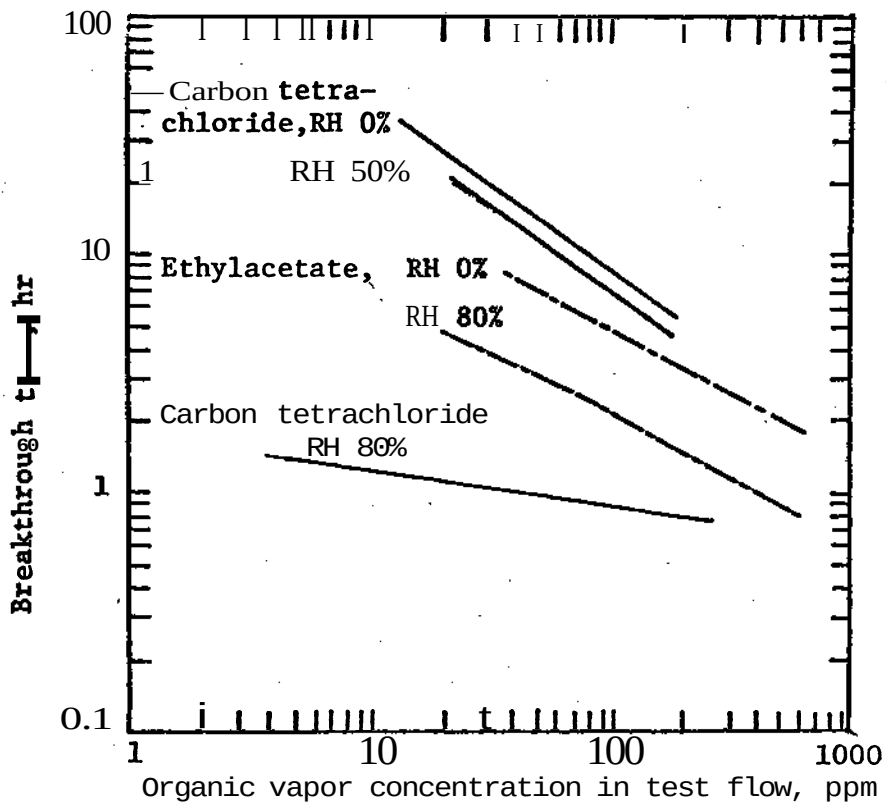


Fig.5 Breakthrough times of an active carbon column of small scale (0.1g) for organic vapor flows with or without humidity. The test flow is conditioned at 100 ml/min, 25°C and various relative humidity.