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SURFACE CHANGE OF QUARTZ PARTICLE BY GRINDING AND ITS BIOLOGICAL EFFECT ON THE CELL

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In the previous paper[1] some of the authors have studied the toxicity of silica particles on the intraperitoneal monocytes of rats by endogenous respiraton, counting of cell number and morphological change, but we could not find out any remarkable high toxicity of crystalline silica particle demonstrated by Marks.[2] After the above mentioned study, tridymite No. 5691 was kindly supplied to us from Dr. G. Nagelschmidt, and this sample showed a very high toxicity to monocytes in experimental method.

A lower toxicity of our tridymite comparing to tridymite No. 5691 may by explained by the difference of preparation method, but we could not understand the difference of toxicity of quartz between ours and Marks's.

When we were studying to clarify this problem, we have noticed the change of quartz toxicity by dust preparing method, especially by the grinding time. In this paper we should like to report the effect of grinding for preparing quartz powder on the shape, surface feature, dissolution, structure and toxicity of quartz.

Table 1. Quartz used in this work.

Specimen	Original mineral	Locality	Mode of occurence	Content of metals in original minerals (detected by emission spectrography)※									
				Ni	Ca	Ti	Cu	B	Fe	Mn	Mg	Al	Si
Q — T	Quartz	Takekoma (Japan)	vein	—	+	—	—	+	tr.	—	##	##	###
Q — Y	Quartz	Yamanoo (Japan)	pegmatite	—	tr.	tr.	—	+	tr.	+	##	+	###
Q — B	Quartz	Brazil	vein	tr.	—	—	—	+	+	—	##	##	###
Q — I	Quartz	Ishikawayama (Japan)	pegmatite	—	—	—	—	+	tr.	—	+	##	###
Q — S	Quartz	Sado (Japan)	vein	—	+	—	##	—	tr.	+	###	##	###

※ Determined by N. Hara.

Note: — none tr. trace + small amount
medium ### large amount

In this study, various samples were prepared by Hamada, dissolution was studied by Hamada and Hayashi, electronmicrography, X-ray and electron diffraction by Shimazu, infrared absorption spectrum by Soda, toxicity by Koshi and Kawai, and the studies were directed and summarized by Sakabe.

I. PREPARATION OF SAMPLES

In this study we used five sorts of quartz, quartz from Takekoma(Q-T), Yamanoo (Q-Y), Ishikawayama(Q-I), Sado(Q-S) in Japan and Brazilian quartz(Q-B), considering that any different toxic action by natural producing condition of quartz may exist. Locality, mode of occurrence, and content of metal impurities are shown in Table 1. These silica samples contained free silica over 99%, and showed a typical quartz by X-ray diffraction pattern. Besides these quartz samples, vitreous silica prepared from Q-I and a few kinds of amorphous silica were used.

Small blocks of each quartz were wrapped in a gauge, and crushed by a small hammer on an anvil. Small particles of the size under 18 mesh separated from crushed particles were ground in a mechanical agate mortar for a required time. After grinding, particles of about 0.5μ in mean diameter were collected by sedimentation and centrifugal separation in distilled water.

1) *Quartz particles with different grinding time*:

Mainly we used the specimens of grinding time of 2 minutes or 6 hours. These were designated as 2M or 6H, so, for example, quartz from Ishikawayama ground for 2 minutes was designated as Q-I-2M. But in some cases, quartz particles ground for 1.25, 2.55, 20 and 40 minutes, 24, 100 and 280 hours were used.

2) *Leached quartz particles*:

Ground quartz particles were leached with 10% NaOH solution by the method which will be described in the next chapter. These leached quartz specimens were designated as -L, for exsample, quartz from Ishikawayama ground for 2 minutes and then leached with alkali as Q-I-2M-L.

Mean particle sizes of various quartz specimens are shown in Table 2, and size distribution curves of two quartz specimens are shown as examples in Figs. 1 and 2. As seen in Table 2, mean particle sizes of eight specimens were 0.35~

Table 2. Mean particle sizes of various quartz specimens

Specimens	D(μ)	Number of particle counted
Q-B-2M	0.49	248
Q-B-6H	0.44	195
Q-I-2M	0.52	143
Q-I-6H	0.41	249
Q-T-2M	0.50	208
Q-T-6H	0.35	240
Q-Y-2M	0.49	211
Q-Y-6H	0.41	178

Particle size was determined by electronmicrograph

0.52μ. The other quartz particles were also prepared in the same size range. These sizes were measured electronmicroscopically.

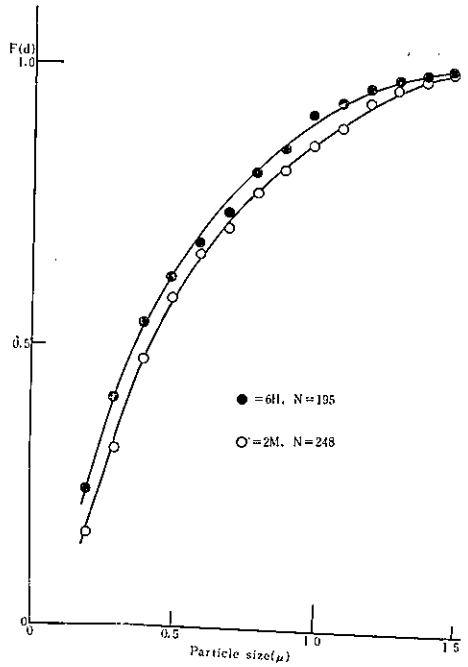

Fig. 1. Cumulative distribution curve of particle size of Q-I

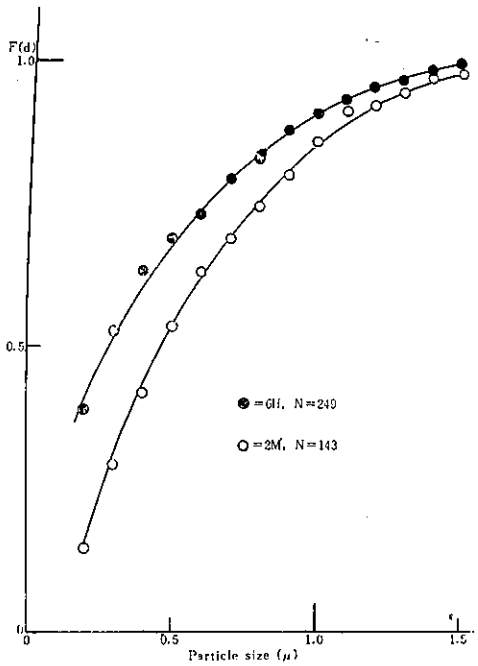

Fig. 2. Cumulative distribution curves of particle size of Q-B

Fig. 3. Electron micrograph of Q-I-2M particles

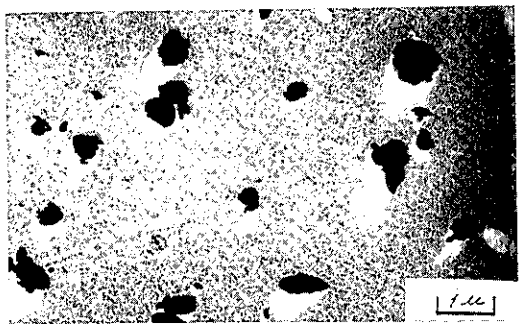

Fig. 4. Electron micrograph of Q-I-24H particles

Fig. 5. Electron micrograph of Q-I-6H-L particles

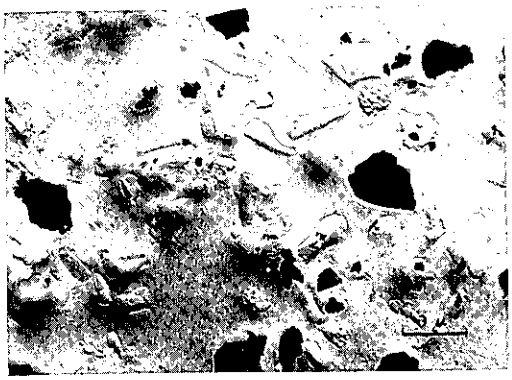

Fig. 6. Replica image of Q-I-2M particles

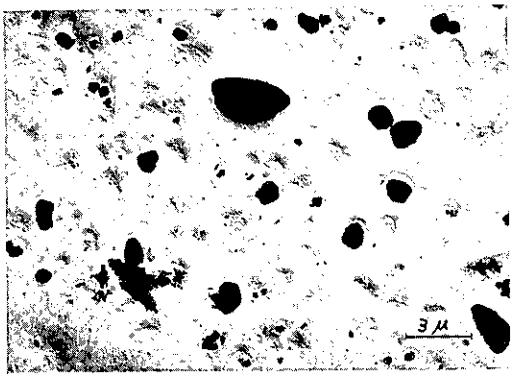

Fig. 7. Replica image of Q-I-24H particles

Ⅱ. ELECTRONMICROGRAPHIC STUDY

The change of shape and surface feature of quartz particles by grinding of various times were studied electronmicroscopically. As shown in Figs. 3 and 4, the shape of Q-2M particles was sharp and edgy, but it was changed to rather spherical or oval form with the increase of grinding time, and very fine particles adhered to the surface were seen. After quartz specimens ground for various times were leached with 10 % NaOH solution, they showed a more sharp and edgy shape than 2 M specimens of these quartz samples and very fine particles disappeared as shown in Fig. 5.

To study the surface feature, replica image of quartz particles was examined by "low pressure moulding method". Figs. 6 and 7 show the replica image of Q-I-2M and Q-I-24H respectively. As seen in the figures the former has a comparatively flat face but the latter a granular. It is not yet clear whether this granular face is the true face or due to the very fine particles coagulated on the flat face.

Ⅲ. DISSOLUTION OF QUARTZ PARTICLES IN 10 % NaOH SOLUTION

EXPERIMENTAL PROCEDURE AND RESULTS

In this experiment, we used Q-I-2M, Q-I-6H, Q-B-2M and Q-B-6H as test particles. One gram of each quartz particles was added to 25 ml. of 10 % NaOH solution, and agitated for 30 minutes in polyethylene vial. Then the dissolved silicic acid in the supernatant obtained by centrifugal separation for 30 minutes at 3,000 r. p. m. was measured colorimetrically. Precipitated quartz particles were again dissolved in 25 ml. of 10 % NaOH solution, and the amount of dissolved silicic acid was determined in the same way as in the first time. The same procedure was repeated until the amount of dissolved silicic acid in the supernatant reached the constant value.

For the silicic acid determination, molybdenum-blue method[3] was used. Ten ml. of the supernatant was pipetted into a 100 ml. volumetric flask, and 40 ml. of distilled water was added. After the addition of one drop of phenolphthalein solution and two drops of 0.5 N KOH solution, the solution coloured pink. Then 0.1 N HCl solution was added till the pink colour disappeared. At 8 to 12 minutes after the succesive addition of 1.40 ml. of hydrochloric acid solution and 8 ml. of 10% ammonium molybdate solution, 8 ml. of 20% tartaric acid solution and 2 ml. of aminonaphtol sulfonic acid solution were added, and then the solution was made up to 100 ml. with distilled water. The mixture was stirred for 30 minutes. The intensity of fully developed colour was measured at 815 mμ with spectrophotometer.

Data of these dissolution experiments are shown in Figs. 8 and 9. Remarkable difference in dissolution velocity was found between 2 M and 6 H specimens of each quartz, but not between Q-I and Q-B of the same grinding time. The amount of dissolved silicic acid from 6 H was about six times as much as that from 2 M in the first time

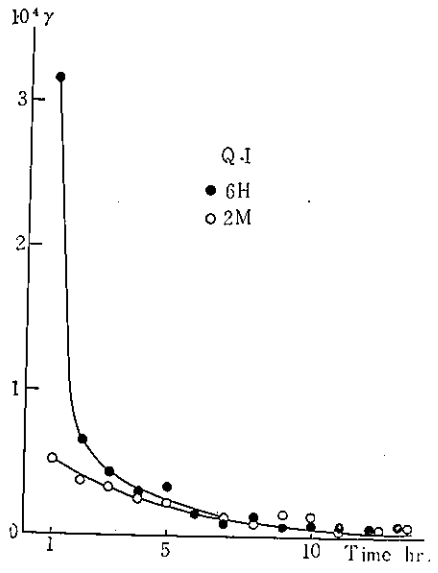

Fig. 8. Dissolution of quartz particles in 10% NaOH solution

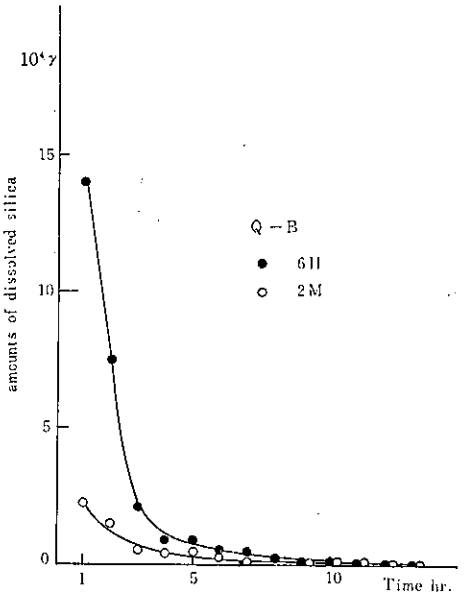

Fig. 9. Dissolution of quartz particles in 10% NaOH solution

dissolution. This initial high solubility of 6H decreased promptly and became to show the similar solubility as 2M. After about ten times dissolution all specimens were difficult to dissolve, and seemed to reach equilibrium.

Quartz particles washed with water repeatedly after these treatments were used as leached quartz (Q-L) in this experiment.

DISSCUSSION

The existence of a highly soluble surface layer on quartz particles was foreshadowed by the work of Briscoe et al.[4] and King.[5] King stated "all size of quartz particles behahed as if a soluble fraction of silicic was being leached from their surfaces, leaving a relatively insoluble residue, or core, which seems to be resistant to the dissolving action of water." In this experiment, also, solubility of quartz particles decreased gradually, and seemed to reach the equilibrium. But, initial solubilities of quartz particles were quite differnt with the grinding time. High solubilty of quartz particles prepared after a more longer grinding time may be explained by high soluble layer, but we cannot neglect the possibility of high solubility of very fine particles adhered to the quartz particles.

IV. DISSOLUTION OF QUARTZ PARTICLES IN PHOSPHORIC ACID SOLUTION

EXPERIMENTAL PROCECURE AND RESULTS

The analytical techniques used in this study were those described by Talvitie[6] and Schmidt.[7]

To 100 mg. of quartz particles in a conical beaker was added 6ml. of 85% phosphoric acid, and heated in a cylindrical hole of a heating apparatus. This heating apparatus was a copper cylinder with 100 mm in diameter and 120 mm in height, and a cylindrical hole with 40 mm in diameter and 40 mm in depth in the center of upper face. This copper cylinder was kept at 250°C during the dissolution experiment.

When the sample was heated for a long time, the beaker was agitated for 3 seconds at each one minute. After the sample was heated for a required time, the beaker was took out and cooled at room temperature, and then 125 ml. of hot water and 10ml. of fluoboric acid were added. After standing for one hour, the contents were filtered through a filter paper which ash was known. The residue was washed with cold 1 : 9 hydrochloric acid solution five times, with the same hot solution five times, and then with distilled water repeatedly. The residue was ignited repeatedly to constant weight, and then weighted.

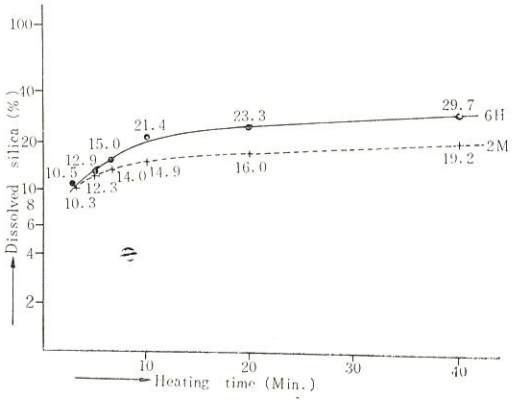

Fig. 10. Dissolution of Q-I by phosphoric acid
(copper mantle temperature : 280°C)

Table 3. The amounts of silicic acid dissolved by phosphoric acid solution

Specimens	% of dissolved silicic acid	
	-2M	-6H
Q-T	14.7	28.0
Q-Y	15.0	24.8
Q-B	25.4	29.8
Q-I	15.3	24.9
Q-I-L	6.9	5.0
Q-S	15.4	26.2
Vitreous silica	50.0	80.0

Experimental results are shown in Fig. 10 and Table 3. As seen in Fig. 10, dissolution of quartz particles by phosphoric acid at 280°C increased with heating time, but the

dissolution velocity was very small over 10 minutes. And the clear difference in solubility between Q-I-2M and Q-I-6H was seen. Q-I-6H was more soluble with phosphoric acid than Q-I-2M. Table 3 shows the amounts of silica dissolved from various quartz particle specimens by phosphoric acid at 280°C for 14 minutes.

Q-B showed the highest solubility among these quartz samples tested. It may be noticed that the vitreous silica produced by melting Q-I had a very high solubility. Concerning the grinding effect on the solubility, 6H showed a higher solubility than 2M. But, Q-B and Q-I-L did not show remarkable difference between 2M and 6H. Leached specimens Q-I-2M and Q-I-6H had the lowest solubility among these specimens.

DISCUSSION

Phosphoric acid method for the determination of free silica introduced by Talvitie has been used widely, but we have some doubt on its reproducibility. In this report, the modified method by Schmidt was used, and was very satisfactory. Discussion on the determination of free silica by phosphoric acid method will be published later in this bulletin.

In this study, it was clearly demonstrated that quartz particles of 6 hours grinding were more soluble than those of 2 minutes grinding, and quartz particles leached with alkaline solution had the lowest solubility among the quartz specimens used in this experiment. Quartz particles behaved similarly in phosphoric acid solution as in alkaline solution, and they seemed to have core which was difficult to dissolve. Increase of solubility of quartz particles by grinding may be explained by some change of surface structure, as vitreous silica showed a remarkable high solubility, but the effect of high solubility of very fine particles attached to the ground quartz particles can not be neglected.

Finally, it must be noticed that no marked difference of solubility was found between 2M and 6H specimens of Brazilian quartz, despite the fact that 6H specimens showed nearly double solubility of 2M in Japanese quartz.

V X-RAY DIFFRACTION AND ELECTRON DIFFRACTION OF QUARTZ PARTICLES

X-RAY DIFFRACTION STUDY

On the X-ray diffraction of powdered specimens the following items were examined : the intensity of X-ray diffraction, aspects on the separation of X-ray diffracted lines, vanishing of any particular line or appearance of new line.

(1) Intensity of X-ray diffraction

Each quartz specimens (0.5μ in mean size) was mixed homogeneously with fluorite (2μ in mean size) which was used as internal standard material. The diffraction

intensity of quartz particles was expressed by the linear (not integral★) intensity-ratio of quartz to fluorite as seen in Fig.11. The ratio was obtained from the line profiles on chart after re-mixing and re-setting the specimen in every time.

The data in Table 4 are the mean values of five times measurements.

(2) Aspects of the separation of X-ray diffracted lines.

This would be estimated by observing the line profiles of α_1 and α_2 of an identical index (hkl) reflection, or of the adjacent lines of different indices reflection, but for convenience we used so-called "fivefold lines of quartz".(see Fig. 12)

(3) Disappearance of any particular line or appearance of new lines

The diffracted patterns within $2\theta=2°\sim90°$ (Cu Kα/Ni) were examined.

Table 4: The relative values of the intensity of (101) reflection of various quartz specimens prepared by dry mechanical grinding, by leaching with 10% NaOH solution at room temperature, and by heating at 800° C in air for 7 days.

Specimens	Rerativ value of intensity of (101) ※ reflection in the case of assuming	
	2M=100% error : about 5 %	Q-B-2M=100%
Q-I 2M	100.0	94.4
2M-L	116.0	109.5
6H	82,1	77.5
6H-L	120.6	113.3
6H-H	92.0	86.8
24H	72.6	68 6
100H	68.0	64.2
209H	23.1	21.8
280H	5.4	5.1
300H	tr	tr
Q-B- 2M	100.0	100.0
6H	80.0	80.0
Q-T- 2M	100.0	98.4
6H	85.4	84.0
Q-Y- 2M	100.0	96.8
6H	86.0	84.0
Q-S- 2M	100.0	91.2
6H	91.2	83.2

Notice : ※Cu/K,Ni, primary voltage=40V, tube current=15mA,scanning speed=(1/8)°/min, chart driving speed=10 mm/min, time constant=5 sec., divergence slit=1.5mm(1°), inter slit=1.0mm, receiving slit=0.2mm, full scale=500C.P.S.

★ Among specimens the apparent half value breadth of (101) were equal within measuring error, therefore each linear intensity is proportional to each integral intensity, and the difference of linear intensity would mean that there are difference in integral intensity among specimens.

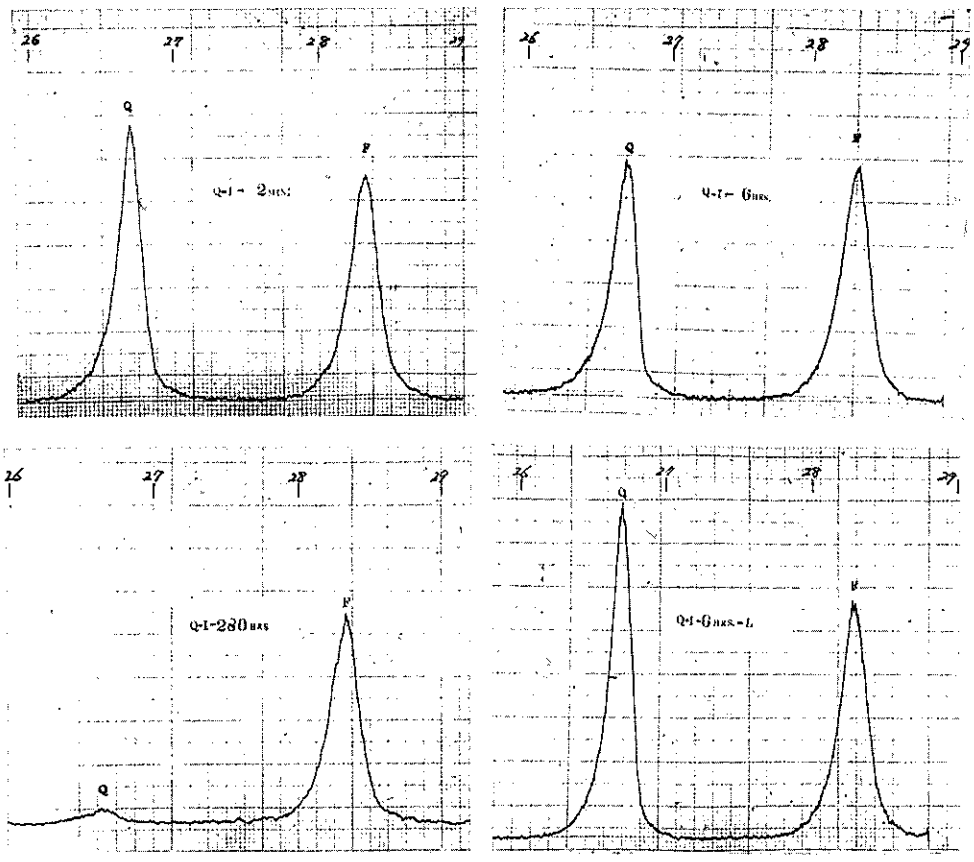

Fig. 11. Intensities of x-ray diffracted lines of (101) - reflection in quartz samples, Q-I-2M, Q-I-6H, Q-I-280H, and Q-I-6H-L. In the figure, Q shows the diffracton line of quartz and F shows that of fluorite as reference material.

Experimental results

The results are listed in Table 4.

(1) The intensities of (101) reflection of quartz specimens from different localities were nearly equal within measuring error, when the specimens were prepared under the equal size distribution and with equal grinding time, for example, the intensity of Q-I-2M was 94.9, Q-T-2M 98.4 etc., assuming the intensity of Q-B-2M as standard and taking it as 100%.

(2) The more the grinding time increased, the more the intensity of diffraction line decreased, namely, on the Q-I specimens the intensity of 2M was 100, 6H 82.1, 24H 72.6, 100H 68.0, if we took the intensity of Q-I-2M as 100.

(3) The intensity of diffraction line of leachd quartz particles was stronger than that of non-leached particles.

(4) When the specimen Q-I-6H was heated at 800°C in air for 7 days (designated as H), its intensity more increased than that of unheated specimen.

(5) Disappearance or appearance of particular diffracted line was not found except the halo pattern of amorphous silica which showed a very broad and diffused band with apex at about 4 A as seen in the pattern of silica-gel. To the Q-I-300H specimen showed only this amorphous pattern and did not show the diffraction lines of crystalline quartz.

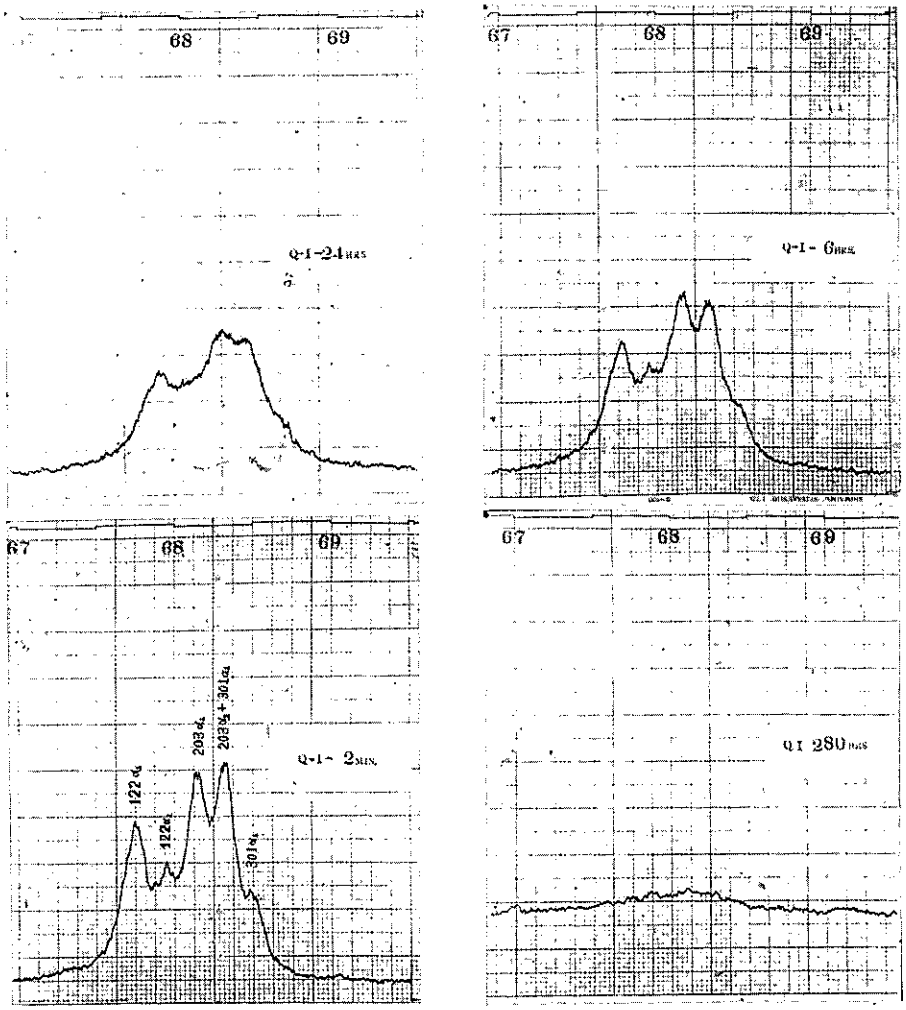

Fig 12. Aspect of the separation of x-ray diffracted lines of quartz samples, Q-I-2M, Q-I-6H,Q-I-24H, and Q-I-280H. X-ray radiation : Cuk_{α}/Ni

ELECTROMICRODIFFRACTION STUDY

For the electromicrodiffraction study of ground quartz particles, two kinds of particle size on each quartz were used. The one was 0.5 micron size which was used generally in this study, and the other was very fine particles which was collected from the supernatant after sedimentation of 0.5 micron particles. These fine particles were designated by the notation of F, for instance, as Q-I-2M-F.

Both the diffraction of a number of particles in one visual field under electron

microscope and the electromicrodiffraction of one particle by selected area diffraction method were studied.

From these studies it was observed that the intensity of diffraction of quartz particles decreased with the increase of grinding time in general.

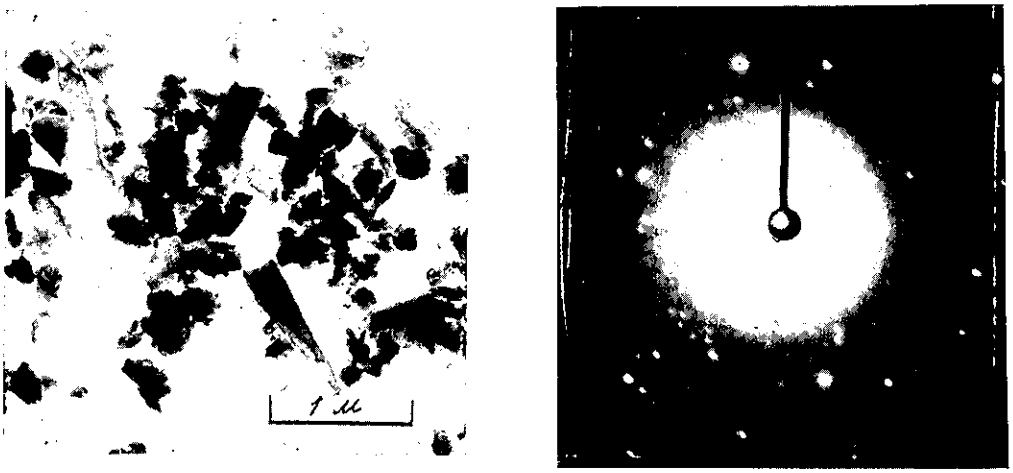

Fig. 13. Electron micrograph amd electron diffraction pattern of Q-I-2M-F particles

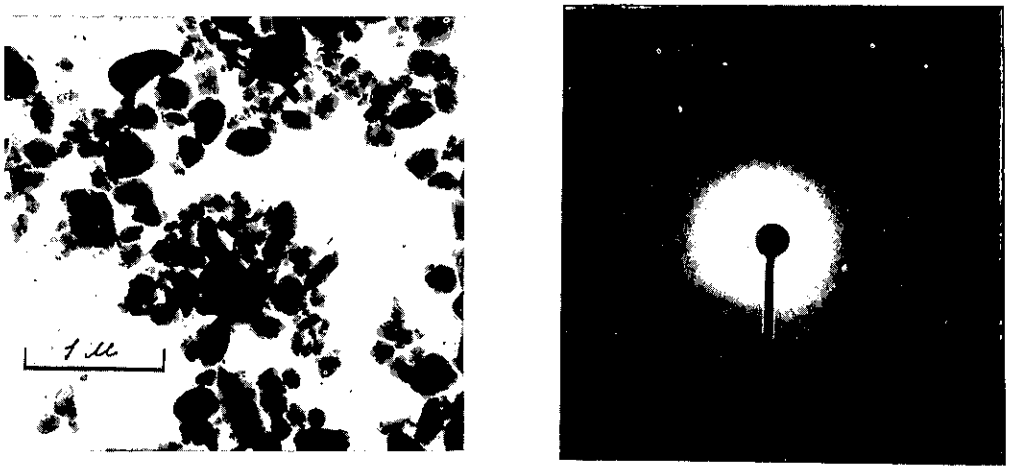

Fig. 14. Electron micrograph and electron diffraction pattern of Q-I-24H-F particles

Figs. 13 and 14 show the electromicrodiffraction patterns of Q-I-2M-F and Q-I-24H-F. In both figures left side shows the electromicrograph and right side the electromicrodiffraction of particles in left side. As seen in the figure many clear diffraction spots of quartz were observed in Q-I-2M-F, but less clear in Q-I-24-H-F. And these diffraction spots were hardly appreciable in Q-I-100H, 209H and 280H. Namely, the tendency was found that the intensity of electromicrodiffraction of quartz particles decreased with increase of grinding time. This tendency was more clear in F group than in 0.5

micron group. The case was the same in the result of study on the electromicrodiffraction patterns of one quartz particle, and the decrease of intensity and number of diffraction spots with grinding was recognized more definitely on such a fine quartz particles as 0.1 micron or less in size.

Finally, in Figs. 13 and 14 the change of shape of quartz particles by grinding is clearly shown as in 0.5 micron specimens. Quartz particles below 0.5 micron also lost their initial spiculate form and were transformed to the spherical or oval form with the increase of grinding time.

DISCUSSION

From these results it may be assumed that the quartz particles are disturbed in structure to change into something like amorphous state on the surface part by grinding for many hours, and this change is strengthened with the increase of grinding time. The changing process to amorphous, however, is not clear in details.

Ⅵ INFRARED ABSORPTION SPECTRUM OF QUARTZ PARTICLES

It was assumed that the surface structure may be changed by grinding of quartz. It was possibly considered to detect such a change of surface structure by means of the molecular spectroscopy, because the spectrum was one of the reflection of molecular structure, in other words, properties of chemical bond, geometrical structure of compound, and electronic properties.

MATERIAL

Silica:

In this study, Q-I-2M, Q-I-6H, Q-I-24H, Q-I-2M-L, Q-I-6H-L, Q-B-2M, Q-B-6H, Q-T-2M, Q-T-6H, Q-Y-2M, and Q-Y-6H were used as quartz particles. Besides these, tridymite, vitreous silica, and two kinds of amorphous silica were tested.

Tridymite was tridymite No. 5691 supplied from Dr. G. Nagelschmidt. One of the amorphous silica was Carplex which was very fine silica powder supplied from Shionogi Co. Ltd., and another was prepared from sodium silicate and CO_2 gas.

Chemicals:

KBr of c.p. grade was pulverized in agate mortar and sieved to the size of 200 to 300 mesh. Then the sieved powder was heated over 200° C for about one day and stocked in desiccated dried by calcium chloride anhydride.

Nujol oil (fluid paraffin) was ordinary c.p. grade.

MEASUREMENT

Potassium bromide pellet preparation:

1) Suspending fine dust particles in the supernatant which was obtained after the centrifugal separation in the last step of preparation of particles of 0.5 μ in mean

size were freeze dried after addition of adequate amount of pure potassium bromide. This method was the same as those in the article which will be published in this bulletin by Soda.

2) The quartz particles described in chapter 1 were mixed with an adequate amount of potassium bromide powder in agate mortar.

3) Mixed powder samples obtained with these procedure were dried by heating over 150°C for about 2 hours and powdered again in agate mortar moderately. Then the samples were put into the die for briquetting and pressed in vacuo to shape the suitable pellet of 10 to 13 mm. in diameter and of 1 to 2 mm. in thickness under the pressure of 10 tons per square centimeter by oil press.

Nujol mull method :

Silica samples were mixed with an adequate amount of nujol oil in agate mortar. This is called nujol mulling method. For using this method silica particles should be well dispersed.

Spectrum :

The pellet mounted with a suitable cell for the measurement of infrared spectrum. The nujol suspension sample was sandwitched between two rocksalt windows and mounted with a demountable cell for the measurement of solid samples.

Infrared spectra were observed by Perkin Elmer Model 137 Infracord Spectrophotometer. Spectrum was recorded in the wavelength range of 2.5 to 15 μ. The calibration of polystyrene film spectrum.

The wave number in cm.$^{-1}$ was obtained by dividing 10^4 by wavelength in μ.

RESULTS

The orientation effect of spectrum was tested comparing the spectra obtained with the nujol mulling method and with the potassium bromide pellet method, and those spectra were approximately same. Therefore, there was no orientation effect.

The hydration of potassium bromide which is hygroscopic substance was observed in the range of 3 μ of spectrum which was attributed to the stretching vibration of OH bond, but this effect was not so intense that the band did not interfere spectrum of silica. The reproducibility of spectrum especially due to the mixing of samples with matrix substance (potassium bromide or nujol oil) was examined in a few cases. When the mixing was carried out carefully the reproducibility (the shape of spectrum and the band intensity) was obtained almost satisfactorilly.

Spectra of quartz, and amorphous silica are observed as illustrated in Fig. 15 to 18. Spectra quartz particles were changed with grinding time. The longer the grinding time, the more intense the OH vibration bands near 3300 cm.$^{-1}$ and near 950 cm.$^{-1}$ were. Furthermore the difference of the aspect of the band group in the range of 1200 to 1000 cm.$^{-1}$ was clear compared with those of the other regions of wavelength. The band 1060

cm.$^{-1}$ became stronger and broader with the grindig time, and the band 1100 cm.$^{-1}$ was appeared as like as shoulder of the band 1060 cm.$^{-1}$. The band 1180 cm.$^{-1}$. also became the shoulder of the 1060 cm.$^{-1}$ and the 1150 cm.$^{-1}$ disappeared when the

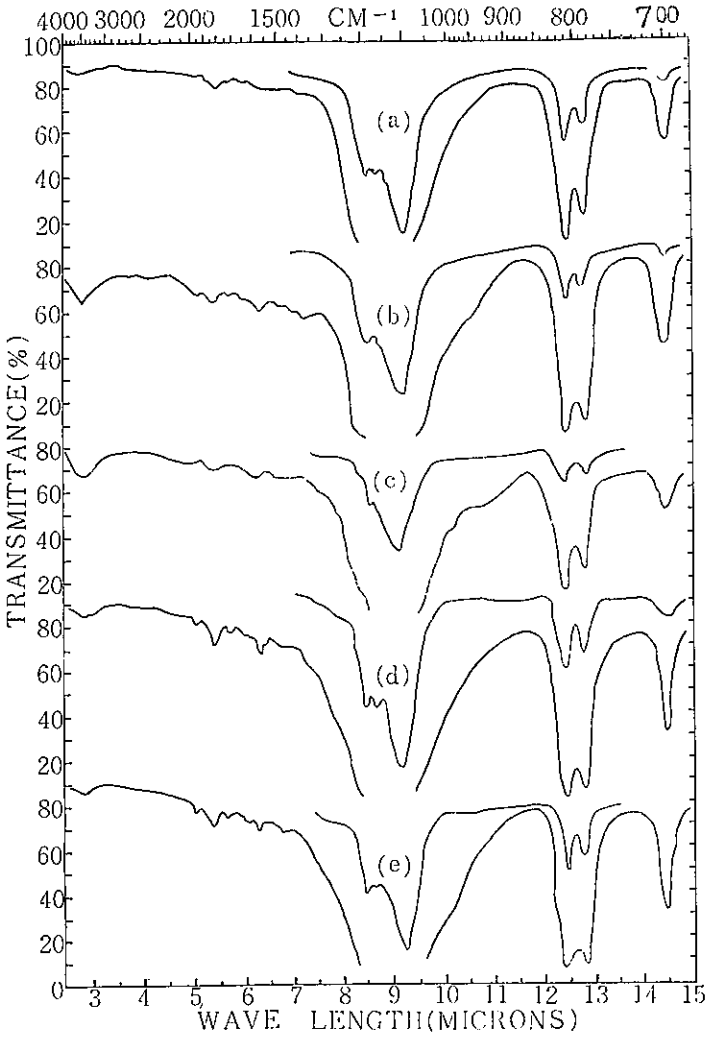

Fig. 15. Spectra of quartz particles (1) (a) Q-I-2M (b) Q-I-6H (c) Q-I-24H (d) Q-I-2M-L (e) Q-I-6H-L

grinding time was over 20 hours. But the bands near 800, 780 and 690 cm.$^{-1}$ were scarecely changed. These aspects were same even in the different particle sizes except slightly small change observed in the band near 1150 cm.$^{-1}$.

When the quartz particle was leached with NaOH, the spectrum approached to that of quartz particle with shortest grinding time. The bands 1170, 1150 and 1070 cm.$^{-1}$ became sharp and were separated each other.

The relationship between the grinding time and aspects of spectral bands were summarized in Table 5.

In order to understand these changes with grinding time the spectra of a few kinds of amorphous silica were observed. Amorphous silica showed the bands near 1100 cm.$^{-1}$ similar to that of quartz sample which was ground for long time. The band 950 cm.$^{-1}$

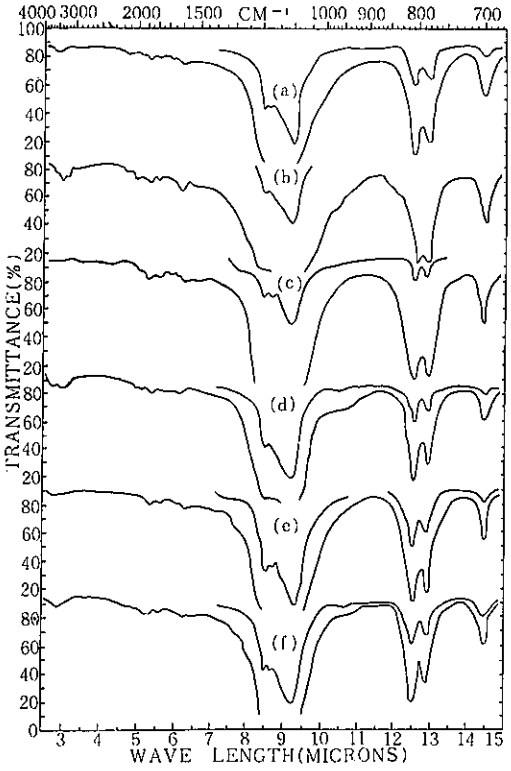

Fig. 16. Spectra of quartz particles (2)
(a) Q-B-2M
(b) Q-B-6H
(c) Q-T-2M
(d) Q-T-6H
(e) Q-Y-2M
(f) Q-Y-6H

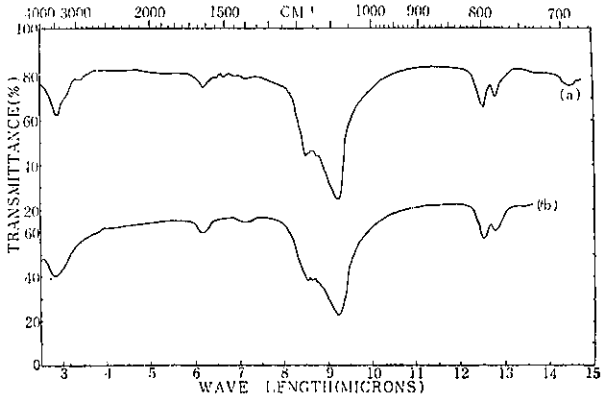

Fig. 17. Spectra of qnartz particles (3) Fine particles in supernatant portion from (a) Q-Y-2M and (b) Q-Y-6H

was observed only in the spectrum of carplex which showed the strong band in region of OH stretching vibration bands, but vitreous silica and another amorphous silica showed no band near 950 cm.$^{-1}$ and no strong band in the region of OH stretching vibration. These three non-crystalline silica showed the weak and broad band near 750 cm.$^{-1}$

The spectrum of trydymite was observed to know the relationship between the

molecular structure of silica crystal and the origin of spectral band. The spectrum showed the two significant aspects. The aspect of spectrum near 1100 cm.$^{-1}$ was

Table 5. The relationship between infrared absorption bands and various kinds of dust particle

Kinds of silica	Band aspects			
	1100cm^{-1} regin	950 cm^{-1}	800 to 600 cm^{-1}	near 3400cm^{-1}
Q-I-2M and Q-B-2M etc.	relative sharp three bands at 1180, 1150 and 1070 cm^{-1}	no band	three sharp bands at 800, 780 and 694 cmi^{-1}	very weak
Q-I-6H and Q-B-6H etc.	three bands at 1,180 1150 and 1070 cm.$^{-1}$, 1070 cm.$^{-1}$ masked 1050 cm,$^{-1}$	very weak band	similar as above	weaker
Q-I-24H	very broad intense band 1070 cm.$^{-1}$ masked 1180 and 1050 cm.$^{-1}$, the latter band was scarecely observed.	no band	similar as above	apparent band
Q-I-2M-L and Q-I-6H-L	sharp three bands 1180 1150 and 1070 cm,$^{-1}$ separated each other	no band	similar as above	not observed
Tridymite	single broad band at 1100 cm.$^{-1}$ and two shoulders at 1160 and 1070 cm.$^{-1}$	no band	single sharp band at 780 cm.$^{-1}$	not observed
Carplex	very broad two bands at 1090 and 1160 cm.$^{-1}$	medium intense band	weak and very broad band near 800 cm.$^{-1}$	relatively intense band
Vitreous silica	broad band at 1090 cm.$^{-1}$ and shoulder at 1170 cm.$^{-1}$	not observed	very broad and weak band near 810 cm.$^{-1}$	not observed

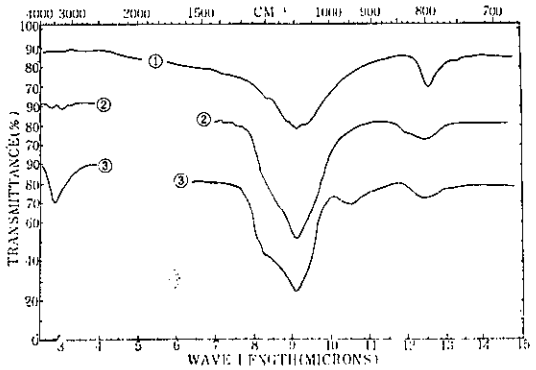

Fig. 18. Spectra of non-crystalline silica.
Curve 1. Prepared by sodium silicate and CO_2
Curve 2. Vitreous silica.
Curve 3. Carplex.

similar to that of amorphous silica and single strong band was observed near 780 cm.$^{-1}$

DISCUSSION

From the experimental results cited, following suggestion is obtained concerned with the band assignment, that is, which mode of vibration of the silica structure will give rise to which infrared absorption band.

(1) A band near 3300 cm.$^{-1}$ is generally accepted to assign to the stretching vibration of O-H bond, or that of N-H bond. C-H stretching vibration gives rise to band near 3000 cm.$^{-1}$. In this experiment all samples did not containe the bond N-H and C-H. If there were some samples containing the bond N-H or C-H, other vibration mode due to these bonds would be appeared in other regions, but all spectra showed no such aspects. Therefore the band near 3300 cm.$^{-1}$ is decidedly assigned to OH stretching vibration. It is assumed reasonably that O-H bond is constructed around the surface or the end of the silica structure and the structure may be written as Si-O-H (silanol group structure).

(2) A band group near 1100 cm.$^{-1}$ is assigned to the stretching vibration of a Si-O band and this band resembles each other even if the structure of silica is changed. In this region shapes and positions of the absorption bands are not so different among amorphous silica, quartz and tridymite etc., that this band group indicates silica structure. But in detail this band group differs according to the kind of the structure of silica (i.e. the bond length of Si-O valence, bond angle of oxygen atom, accordingly electronic structure of silica) as illustrated in Fig. 15, 16 and 18, and as summarized in Table 5 and 6.

Table 6 Tentative assignment of infrared absorption bands of quartz

Observed positions of bands	Assigment
near 3300 cm^{-1}	Stretching vibration of O-H bond around surface of particles (silanol group and adsorbed water).
2280, 2250 and 2070cm.^{1}	Stretching vibration of Si-O bond, this couples weakly with the deformation and torsional vibration or lattice vibration of silica skeletal structure (Antisymmetric stretching vibiation).
800, 780 and 695 cm^{-1}	Stretching vibration of Si-O bond, this couples strongly with the lower vibration modes such as deformation, torsional and lattice vibrations, and is very sensitve to structure. (Symmetric stretching vibration).
950 cm.$^{-1}$	Deformation vibration of Si-O-H bond (or Overtone or Combination vib ation of lower skeletal vibration modes).

(3) A band group near 800 to 600 cm.$^{-1}$ shows a various aspect with the kind of silica. Quartz gives rise to three bands at 800, 780 and 690 cm.$^{-1}$, tridymite one band at 780

cm.$^{-1}$ and cristobalite two bands at 800 and 620 cm^{-1}. These bands are sharp and depend obviously upon the skeletal structure of silica. Amorphous silica gives rise to broad and relatively weak band near 800 cm.$^{-1}$. All these bands are very sensitive with the silica skeletal structure. The assignment of the band in the region is not determined decidedly, but it will be generally accepted to assign all three bands to the other mode of the stretching vibration of Si-O bond than that of the bands near 1100 cm.$^{-1}$. The former may be attributed to the symmetric stretching vibration of Si-O bond and the latter to the antisymmetric stretching vibration. Frequency of the latter is higher than that of the former and the former is easily coupled with bending vibration and torsional vibration which are sensitive to the molecular structure. In general the dependence of the absorption band of stretching vibration upon the structure became when the coupling with other lower vibration such as particularly the bending vibration of the neighbour bonds is large.

(4) The broad weak band is given rise to near 950 cm.$^{-1}$. in carplex and in quartz ground for long time. This band assignment is not seen in the literature. From the rough consideration of mass of atoms constructing the silica structure and the order of restoring force of each bond(the force constant), it may be suggested that the deformation vibration of the O-H bond of the silanol group gives rise to the band near 950 cm.$^{-1}$.

From the study of grinding effect on the spectrum of silica the followings may be suggested.

A part of the structure of crystal silica deforms during the grinding but the original body structure does not, as the change of the spectrum, the aspect of the band group near 1100 cm.$^{-1}$, the intensity of the band near 3300 cm.$^{-1}$ and the appearance of a new band near 950 cm.$^{-1}$, is intensitied with the grinding time and this change of spectrum recovers after leaching of ground silica particles. In addition the bands 800 to 600 cm.$^{-1}$ are not influenced by grinding and leaching. Therefore it could be considered that the structure change means the deformation or modification of some part of crystal structure of silica and it is very natural to assume that the ground quartz particles has both character of crystal structure and modified or deformed (destroyed) structure. This phenomenon is explained in two ways. One explanation is that the fine particles produced during the grinding, coagulates to the larger partcles and this fine particle has a deformed structure. (Coagulation of fine particles was observed electron micoscopically as mentioned already). The other explanation is that during the grinding the surface structure of silica crystal is destroyed to take the modified structure. If the spectrum of the deformed structure is produced by the fine particle aggregated around the larger particle, it must be expected that the spectrum of finer particles in supernatant shows a less intense band characterizing the crystal structure and a more diffuse band characterizing the deformed structure than that of particles in precipitant. But the spectrum of the fine particle obtained from the supernatant by the centrifugal separation is nearly the same as that of the larger quartz particles obtained by the centrifugal

precipitation, as shown in Fig. 17. Therefore from the experiment, it is logical to conclude that the layer of the modified structure exists around the surface of the quartz particle itself after the grinding. Above argument is further developed by following consider-ation. As shown in Fig. 19, spectrum of ground quartz particle can be schem-

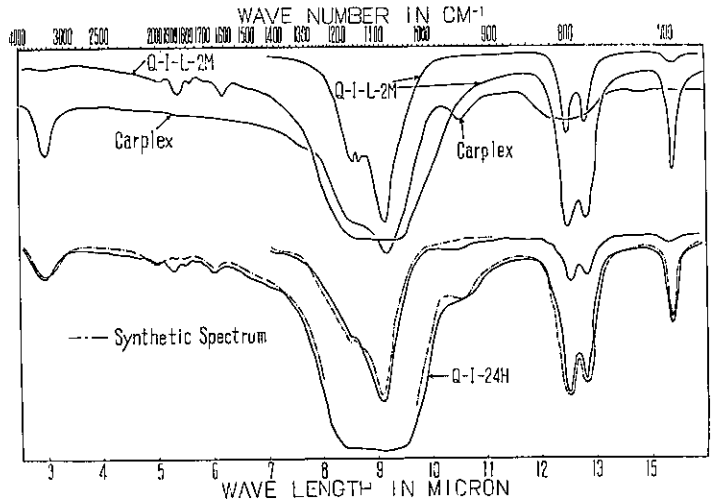

Fig. 19. Schematic diagram synthesized spectrum of ground quartz.

atically drawn as the result of combination of two spectra of leached quartz and carplex obtained by taking into account the intensity of band near 950 cm.$^{-1}$. First, the intensity of the spectrum of carplex is reduced at all wavelength to make the intensity of band 950 cm.$^{-1}$ of carplex equal to that of ground quartz particle. Then the spectrum of leached quartz particle is drawn to make the intensities of bands 695 and 800 cm.$^{-1}$ of leached quartz equal to those of ground quartz particle. These two spectra are combined to get the absorbance $\log_{10}(T_0/T)$ at each wavelength equal to the sum of those of two spectrum at same wavelengths, where T_0 and T are the transmittance of blank and sample spectra respectively. In this synthesized spectrum the spectrum of ground quartz particle is qualitatively the same as sum of the spectra of carplex and leached quartz. This means obviously that the ground particle is constructed from large portion of pure quartz and small portion of deformed silica structure.

From above discussion, a speculative concept may be obtained as regards to the structural change of the quartz particle during the grinding and leaching. When the particles of quartz crystal are ground in agate mortar, the crystal is divided into two or more particles and the surface of the particle is scrubbed and pushed. The ground surface suffers under strong pressure locally and its structure is destroyed at the weak point of crystal lattice such as dislocation of crystal lattice, lattice defect and vacancy of atoms in the crystal lattice. The deformed structure expands with the grinding and the surface of particles ground for longer time is covered with different deformed

structure from the essential crystal structure. But bulk of the particle has the same structure as the original crystal structure of quartz. With grinding the surface area increases, the amorphous structure is built up around the surface of the particle and the silanol group increases.

SUMMARY

Quartz particle showed the various infrared absorption spectra by the preparation of dust particle, particularly grinding time and leaching. These changes of the spectra indicate obviously the fact that the particle surface and not in the bulk, suffers the mechanical pressure and changes its original structure into the modified and perhaps random structure and the silanol group increases (perhaps the surface area also).*

VII EFFECT OF QUARTZ PARTICLES ON THE PHAGOCYTIC CELLS IN VITRO

From preceding studies, it was assumed that the surface of quartz particles was changed by grinding. In this section we have studied on the effect of quartz particles ground for various time to the cultured phagocytic cells.

EXPERIMENTAL METHOD

1 Cells:

Exsudate were induced in peritoneal cavity of male rats of Wistar strain by intraperitoneal injection of 5 ml. of sterile Tyrode's solution containing 0.01 % glycogen. The exsudate obtained 2 days after the injection was washed out with steril Tyrode's solution containing 12 units of heparin per ml., and then the cells were separated from this heparinized solution by centrifugal separation at 1,000 r.p.m. for 5 minutes and washed twice with sterile Tyrode's solution. The cells were suspended in the culture medium.

2 Medium :

Tyrode's solution containing 30 % of rat serum was used as culture medium. Streptomycin and penicillin were added to the medium at final concentration of 50μg and 50 units per ml. respectively.

3 Culture procedure and estimation of cell activity :

1). *Deiermination of dehydrogenase activity:*

A test tube with double rubber cap was used as culture chamber, and it was 150 mm. in length and 22 mm. in diameter, and had a capacity of approximately 20 ml..

Quartz dusts were added to 2 ml. of medium containing 4 million cells, and the

*The author expresses his hearty thanks to Mr. S. Masuda in Laboratory of Chemistry, Faculty of Science, Unversity of Tokyo, for the measurement of the infrared absorption spectrum of almost all of this work.

culture was incubated for 48 hours at 37° C in a incubator. After incubation, dehydrogenase activity was determnid with tetrazolium reducing method by Marks and James.[8]

2). *Morphological examination:*

As culture chamber a square tube with a capacity of 10 ml. in which a small piece of cover glass was placed was used.

After incubation at 37° C for 48 hours, cover glass on which cells adhered was taken out from culture tube. And then the cells on the glass plate were fixed with methanol and with Giemsa solution.

EXPERIMENTAL RESULTS

1) Grinding time and toxicity of quartz:

Q-I specimens with various grinding times, 1.25, 2.5, 5, 20 and 40 minutes, 6 and 100 hours, were used as quartz particle specimens.

Dehydrogenase activity of the cells was decreased by addition of quartz particles, but the longer the grinding time of quartz, the more the effect on dehydrogenase activity was reduced, and the activity of cells added with quartz particles ground for 100 hours was nearly the same to that of the control cells to which no quartz was added. These are shown in Fig. 20.

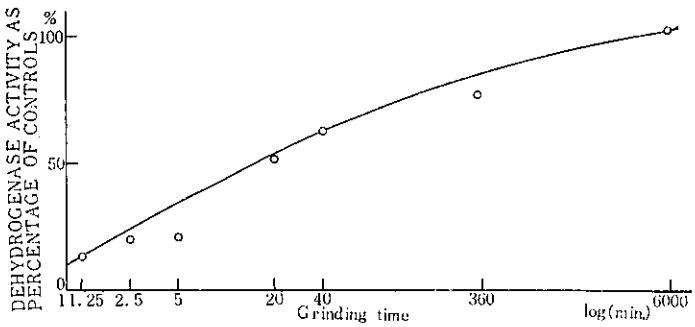

Fig. 20. The relationship between toxicities and grinding time of quartz particles.

2) The variation of toxic dosis of quartz by grinding or locality:

Marks showed that the toxicity of Madacascar quartz was about thirty times as great as that of Belgian quartz. Therefore, toxicities of Q-T, Q-Y, Q-I and Q-I-L were examined on the two speciemens ground for 2 minutes and 6 hours of each quartz.

The dehydrogenase activities of cell cultures were determined after the incubation with 30, 60, 120 and 240μ g of each dust for 48 hours, and control cultures were made without dust. The average degree of the dehydrogenase activity was plotted against

the logarithm of the dose of dust and from the curve was read off the amount of dust per culture required to depress activity to 50 % of control level. This amount was termed the toxic dosis. The data are summerized in Table 7. Among 2M specimens,

Table 7. Dust dosis of 50 % depression of dehydrogenase activity.

Specimens	-2M	-6H
Q-Y	55μg	220μg
Q-T	52	240
Q-B	96	230
Q-I	44	290
Q-I-L	38	56

Condition of culture : incubation time, 48 hours
cell number, 4.0×10^6
temperature, 37° C
gas phase, air

Q–B showed the lowest toxic effect, Q–I–L the highest, and the other three almost similar. On 6H specimens, noticeable difference was found among four samples non-treated with alkali solution, but Q–I–L exhibited very high toxicity comparing the other four samples. Concerning the grinding effect, remarkable difference of toxicity was found between 2M and 6H specimens except the leached. And 2M and 6H speciemens of Q–I showed the similar toxicity if they were leached with alkali solution.

3 Morphological change of phagocytic cells :

The phagocytic cells cultured for 48 hours without quartz particles are shown in Fig. 21a. Fig. 21b shows the cells which phagocytosed the particles of Q–I–6H, and no noticeable changes of the cells were seen notwithstanding that the cells were laden with a lot of particles. The cells cultured with Q–I–2M and Q-I-6H-L are shown in Fig. 21c and d. In these, the cells were severely damaged.

DISCUSSION

1) In the previous paper we had studied on the effect of silica dust on the cultured phagocytic cells, and it was noticed that the activities of dust laden cells were not different from that of control cells. But Marks showed the high toxicity of quartz particles. At first we could not understand why this marked difference of quartz toxicity was produced, but from this study it may be assumed that this is in part due to the condition of grinding for preparing dust particles, as the quartz particles used in the previous experiment were ground for long time. It was clearly demonstrated that the toxicity of quartz particles is controlled by the condition of grinding for preparing particles specimens.

Marks demonstrated the difference of toxicity between Madagascar and Belgian quartz, but there was not found any noticeable difference among quartz particles from

Fig. 21. Morphological changes of intraperitoneal monocytes cultured with quartz particles. 200 μg of each quartz particles were added to 2 ml. of medium containing 4 million cells, and then the culture was incubated for 48 house at 37° C.

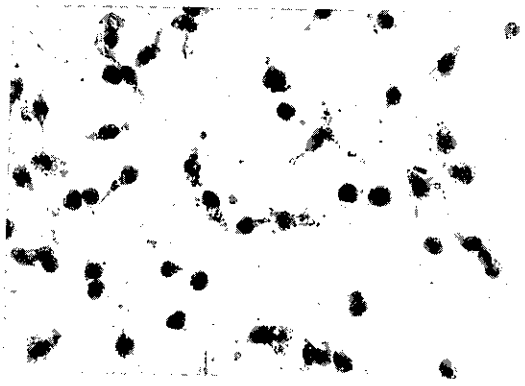

Fig. 21. a. Control culture.

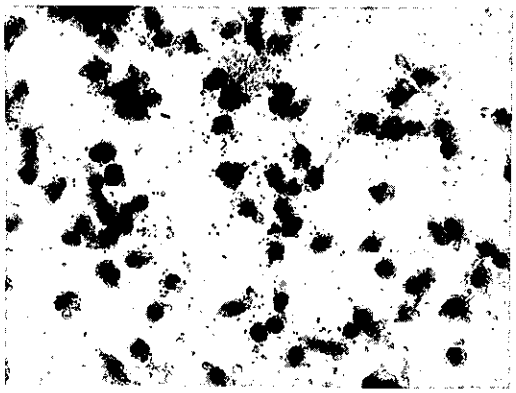

Fig. 21. b. Monocytes cultured with Q-I-6H.

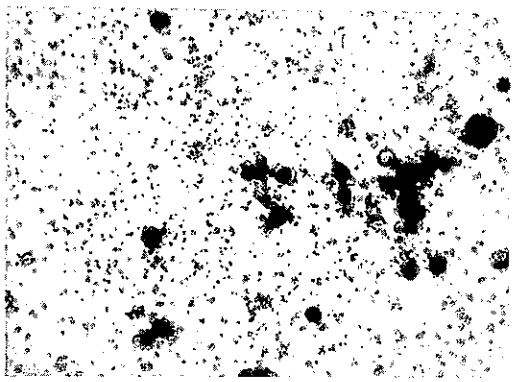

Fig. 21. c. Monocytes cultured with Q-I-2M. Cells are severely damaged and very scanty.

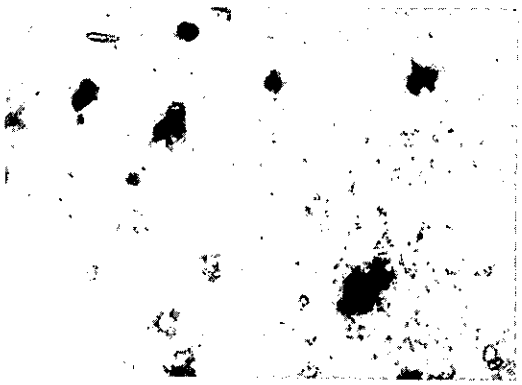

Fig. 21. d. Monocytes cultured with Q-I-6H-L. Severely damaged and very scanty celles.

four different localities in our studies.

2) It was observed that the toxicity of quartz particles decreased with grinding, and was recovered after leaching with alkali solution. It is difficult to assume that the toxic effect of quartz is due to the dissolved silica from quartz particles, as far as quartz does not dissolve in a quite different way in the cells from in the simple solution, since the quartz particles ground for a long time has low toxicity in spite of their high solubility. The decrease of quartz toxicity with grinding may be explained by the change of surface.

SUMMARY

Intraperitoneal monocytes of rat were incubated with quartz particles from various

localities and of different grinding time, and their capacity to reduce tetrazolium (dehydrogenase activity) was measured. If we assumed the decrease of this reducing capacity as toxicity to the cells, no significant difference of toxicity was found among quartz samples from different localities used in this experiment, but the longer the grinding time of quartz particles was, the lower its toxicity was. And the toxicity of quartz particles lowered by grinding was recovered after the leaching with alkali solution.

Ⅷ GENERAL DISCUSSION

1) Many theories have been proposed to explain pathogenesis of silicosis, and recently Nagelschmidt[9] and Schepers[10] reviewed silicosis theories. It is reasonable to assume that there are many succesive biological reactions such as chains before the formation of silicotic nodule. Perhaps, the first step of these biological reactions is that the particle is phagocytosed by phagocytic cells. Therefore it is a very interesting and important problem to understand the effect of quartz particles on these cells.

Marks showed the remarkable decrease of tetrazolium reducing power of the intraperitoneal monocytes of guinea pigs by crystalline silica particles. We also have studied the influence of silica on the monocytes from the intraperitoneal cavity of rat, but we could not find out any noticeable impairment of cell activity by quartz as reported in the previous paper.

In the study planned to clarify this discrepancy, we found out the grinding condition have an effect on quartz toxicity. Therefore, very low toxicity of our quartz may be explained in part by rather long grinding time, although there remains the problem of different locality.

As reported in this paper, it must be noticed that the toxicity of quartz decreases with increase of grinding time, for instance quartz particles ground for 100 hours almost lose its toxicity, and these decreased toxicity is recovered by alkali leaching. Accordingly we must be very careful in preparing dust particles in the study of pneumoconiosis.

Formerly, Sakabe and Koshi[11][12] studied on the dissolution of quartz dust and reported the possibillity of dissolution of silicic acid in colloidal form from parent quartz particles, but Paterson and Wheatley[13] could not find colloidal polymerized silicic acid in the quartz extracts. This conflict may be caused by the grinding condition of quartz together with the difference of locality.

Tissue reactions by quartz particles with various grinding times introduced intratracheally will be reported in next number of this bulletin.

It may be interesting to rediscuss the inertness[14] of sand in Sahara desert from the standpoint of grinding effect.

2) The toxicity of quartz decreases with increase of grinding time, and at the same time various changes take place in quartz particle itself. These are summarized in Table 8. In the Table, only quartz ground for 6 hours is listed as example of long

Table 8 Changes of shape, solubility, structure and toxicity of quartz particles by grinding and leaching

Specimens	Shape	Dissolution		X-ray diffraction		Electron micro-diffraction	Infrared absorption spectrum				Toxicity
		Dissolution velocity in 10%NaOH solution	Dissolved amounts in heated phosphoric acid solution (15min. at 280° C)	Diffraction intensity (arbitrary unit)	Separaton of diffraction-lines	Diffraction intensity	Absorption band assigned to antisymmetric stretching vibration of Si-O		950cm^{-1}	Stretching vibration of O-H (3300cm^{-1})	Dust dosis of 50 % depression of dehydro-genase activity
							1150cm.$^{-1}$	1080cm.$^{-1}$			
Quartz ground for 2 min.	Spiculate	low	17.6%	100	Sharp	Strong and clear	s	Relatively Sharp	None	Less intense	44 γ
Quartz ground for 6 hr.	Rather spherical or oval	High	26.6%	80	Diffuse	Weak and obscure	1 peak	Broad band	Appear	More intense and broad	190 γ
Quartz leached by alkali	Spiculate	Difficult to dissolve	5.0%	120	Sharp	Strong and clear	Similar pattern to quartz ground for 2 min. and more clear.				38 γ (for 2min.) 46 γ (for 6hr.)

time ground quartz.

i) After long time grinding, quartz particles lose its initial sharp edges transformed into a spherical or oval form. And often very fine particles adhere to its surface. After leaching with alkali solution, ground quartz particles take a more sharp and edgy form and very fine particles disappear.

ii) Initial dissolution velocity of quartz in alkali or hot phosphoric acid solution increases with grinding.

iii) From the study with X-ray diffraction, electron diffraction and infrared spectrum, it is assumed that the original surface structure of quartz is changed to take a disturbed and perhaps a random structure by grinding. These changes are intensified with increase of grinding time. But, if the ground quartz particles are leached with alkali solution, changes attributable to grinding disappear. Therefore, how short a grinding time may be, quartz surface suffers the structural change.

From these data it may be assumed that the toxicity of quartz to the monocytes is not caused by the dissolved silicic acid from quartz, but by the activity of surface. It is not yet clear what kind of surface property of quartz is responsible for the toxicity. Silanol group of silica surface may be considered, but it is not a sole cause of toxicity, as the silanol group increases with grinding.

Many works[15)~18)] on the surface of quartz have been reported, and the thickness of disturbed surface layer is estimated to be approximately 300A. It is obscure whether the decrease of structural disbarance by grinding is due to the progress of change of each particles or to the spreading of disturbed surface.

Ⅸ SUMMARY

Change of quartz particles by grinding and its toxicity to monocytes was studied. The former was examined by electronmicroscope, dissolution, X-ray diffraction, electron diffraction, and infrared absorption spectrum, and the latter by the tetrazolium reducing capacity and morphological change. With the increase of grinding time quartz particles of the same size showed a more spherical shape, more granular surface, higher initial solubility, more disturbed structure of surface, and less toxicity.

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要　旨

磨砕による石英粉末の変化とその単核細胞に及ぼす影響

坂部弘之　河合清巳　興貴美子　左右田礼典
浜田　晃　島津正司　林久人

著者等はけい肺病因に関する研究を進めて来たが，遊離けい酸じんが肺内に侵入して，けい肺結節を形成する迄には，いうまでもなく，いくつかの生物学的反応が継起するであろうが，肺内にとりこまれた粉じんに対する最初の生体反応は喰細胞に摂取されることにあると考えられる。従つて，各種粉じんが喰細胞に対して，どのような影響を及ぼすかという問題は興味あるところであり，著者等は前報に報告したようにラット腹腔内からとり出した単核細胞に対する，石英粉末その他の影響を観察して来たが，石英粉末による著しい細胞障害を見出すことは出来なかつた。しかし，その後石英粉末の細胞障害性は石英粉末の作製方法，すなわちその磨砕の方法により，著しく変化するものであることを見出した。本報においては，石英が磨砕により，その物理化学的性質をどのように変化さすかを，アルカリ及び熱りん酸に対する溶解性，電子顕微鏡による粒子の形態，X線回折及び電子顕微回折による結晶構造の変化，赤外吸収スペクトルによる分子構造等の面から研究し，更に石英を磨砕することによりどのように単核細胞に対する障害性が変化するかを細胞のテトラゾリウム還元能からしらべた。その結果を要約すると，磨砕時間の長くなる程，石英の粒子の形は尖鋭さが失われて球状に近くなり，アルカリ又は熱りん酸に対する溶解速度は増加し，結晶構造は乱れて来，その細胞毒性は低下する。しかし磨砕したものをアルカリ溶液で溶解さすと当初は溶解速度は大きいが，次第に溶け難くなる。この溶け難くなつた石英粒子では，その物理化学的性質において，又細胞毒性において，磨砕による影響と考えられるものは見られなくなる。すなわち磨砕により石英粒子表面には結晶構造の乱れが生じ且つ又石英粒子の細胞障害性は，その表面構面により，きびしく支配されるものであることが判つた。

Bull. Nat. Inst. Indust. Health, 4, 29~43 (1960).

DETERMINATION OF QUARTZ DUST IN THE ATMOSPHERE BY MEANS OF INFRARED SPECTROSCOPY

Reisuke SODA

Until recently, the amount of atmospheric quartz dust has been determined by two methods, that is, the X-ray analysis and chemical analysis with phosphoric acid. These methods have been improved in some points but are not satisfactory. An X-ray analysis needs ordinarily the sample size of the order of 100 mg or more and the particle size of above 10 microns. Phosphoric acid method which dissolves the other components than free silica, determines chemically the quantity of quartz after dissolving the other components. (1) It is not yet decided clearly, whether the various silica crystals other than quartz are not dissolved by heated phosphoric acid, and whether the other minerals are dissolved completely. (2) The dissolution rate is finite, so the quantity of the free silica determined by phosphoric acid method may be changed with dissolution time. (3) As dissolution is influenced strongly by the surface area of dust, particle size may affect the amount of free silica determined with this method. (4) Solubility also may depend on the other conditions such as the concentration of sample in phosphoric acid, stirring and the temperature.

New method for determination of quartz with an infrared spectrum in the mine air was reported by M. F. Gade and K. F. Luft.[1] They determined the amount of quartz after the elimination of absorption band due to clay minerals by heating the samples above 800°C.

Each infrared absorption band is attributable to the vibrations of the special functional group and of the characteristic structure of the compound. Therefore when the particle contains the structure of quartz as component, the infrared spectrum gives rise to the band due to the quartz structure and would not be influenced by the particle size and the absorption intensity would be proportional to the amount of the portion of quartz structure. The other structure than quartz gives rise to each characteristic absorption bands[2]. By this method the ambiguity and the difficulties in the above stated method of the determination of the quartz dust would be overcome. In this report the author states a few experimental results obtained by the infrared analytical method of quartz dust collected in impinger with water.

EXPERIMENTALS

The dust was collected in the impinger with about 10 cc. of water for a proper time. This aqueous dust suspension was freeze dried after the addition of 100 to 150 mg. Potassium bromide powder. This process may influence the spectrum from a

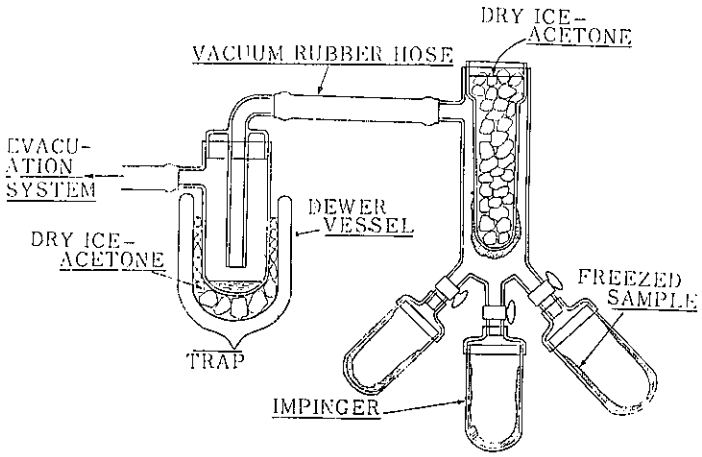


Fig. 1. Schematic figure of freezing-drying apparatus (all-joint system)

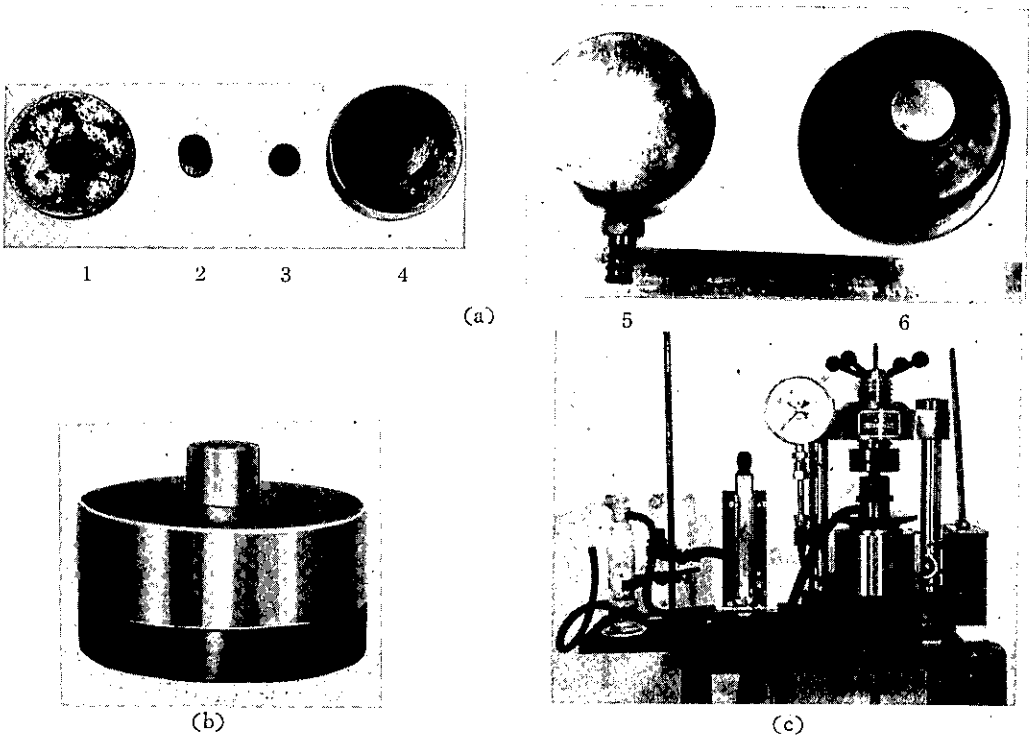
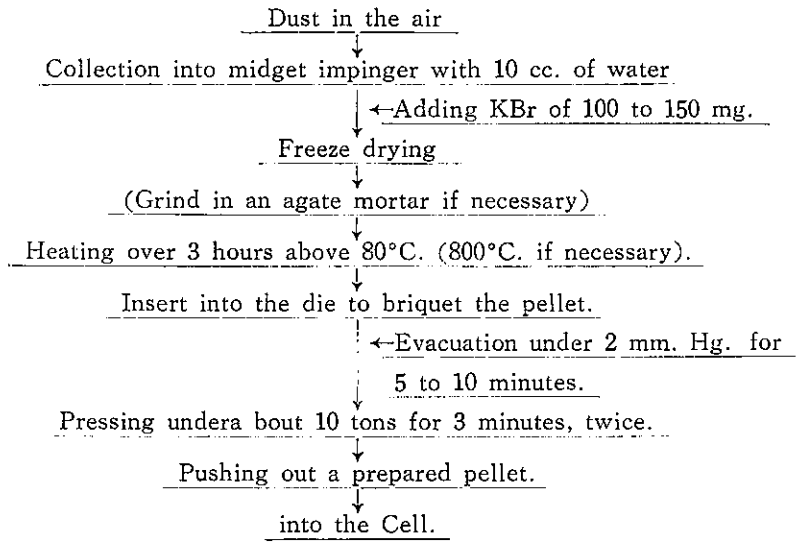


Fig. 2 Die for preparaion of KBr pelllt and briquetting press. (Maekawa shikenki seisakusho).
(a). Parts of die: (1). Bottom steel disk (magnetized), (2). Top plunger (12mm. diameter and 19mm. long), (3). Bottom plungr (12mm. diameter and 4mm. thickness), (4). Enclosing steel chase with a hole at center (12mm. diameter and 16mm. depth), (5). Steel base with a little hole and a hose connection outlet for evacuation and (6). Rubber wall with steel guide.
(b). Setting of assembly.

(c). Pressing by oil (briquetting) press.

procedure: (1). The chase is put on the bottom steel disk. (2) The bottom plunger is inserted into the hole of the chase. (3). The sample powder is poured into the hole and piled up to the center of the hole by a spatula as far as possible. (4). The top plunger is inserted and rotated several times to make the powder flat. (5). Then this assembly is put on the base steel. (6). The rubber wall is capped on and the total assembly is pressed by the oil press as (c). (7). The pressed assembly is discharged and the pellet is pushed out smoothly using the oil press.

potossium bromide disk obtained with the following method. The freezed sample was prevented from melting during the drying. Apparatus as shown in Fig. 1 is suitable for this process. The freeze dried powder was heated up over 180°C * for about three hours to dry and to evaporate the organic substances which may interfere the measurement of spectrum. To make the pellet the dried powder was inserted into the die as illustrated in Fig. 2. The charged die was evacuated under the pressure of 2 mm. Hg for 5 to 10 minutes and then pressed at 10 ton per square centimeter for about 3 minutes. The die was pressed twice by turning it with the briquetting oil press, in order to minimize the influence of unbalance of the press. The pressed disk would be pushed out smoothly, as the disk will be broken when this procedure is carried out violently. The thickness of this disk was about 1 mm. Prepared disks were transparent but in sometimes slightly opaque pellets were shaped. The infrared transmittance of the latter was not so weakened that there was no need to be careful to produce the quite transparent disk. But when the mixing was not sufficient or the powder size was rather large for the sake of unsuccessful treatment of the freeze drying



The thickness of pellet is about 1 mm. and diameter about 10 mm.

Figure 3. Schematic diagram of the procedure of dust collection, freezing drying and preparation of KBr pellet.

1)

* If necessary the sample would be heated up about 800° C.

operation, the shaped disk was completely opaque and the white spots were seen. Such a disk was not suitable for measurement of an infrared absorption spectrum and the obtained spectrum showed a very poor figure and analysis of the spectrum could not be carried out satisfactorily. Therefore, it was desirable to obtain the transparent disk as far as possible. The process of this operation is schematically illustrated in Fig. 3.

In order to make the calibration curve, leached quartz of particle size of about 1 micron obtained by the method reported in this bulletin by H. Sakabe et al.[4] was used. This quartz particles were mixed with purified potassium bromide powder in agate mortar and dried by heating at about 200°C. for 3 hours. The dried sample was shaped into disk by the same method as mentioned above.

Potassium bromide powder was made as follows. Potassium bromide of special grade was heated above 150°C. for an hour. It was not necessary to use potassium bromide recrystallized from its aqueous solution by adding concentrated hydrobromic acid. Dried potassium bromide was ground in agate mortar and then the powder of partilce size of 200 to 300 mesh was separated by the stainless steel sieve. This sieved powder was dried above 200°C. for about 3 hours. This powder was stocked in the desiccator with phosphorous pentoxide and used for calibration. The potassium bromide powder of the other size was used for the above mentioned freeze drying method.

Samples used were quartz from Ishikawayama (Q-I), from Yamanoo (Q-Y), from Takekoma (Q-T), from Yamanashi-ken (Q-Yn) and Brazilian quartz (Q-B). Samples were ground mechanically for 2 minutes (-2M), 6 hours (-6H), 24 hours (-24H) and 100 hours (-100H). Some sample was ground by hand without shearing effect in agate mortar (-O) and some was leaching with 10 % of NaOH aqueous solution (-L). As non-crystalline silica, three kinds of silica were used. They were (1) carplex supplied from Shionogi Co. Ltd., (2) vitreous silica and (3), amorphous silica prepared from silicate. H. Sakabe et al.[4] report in this bulletin more precisely about these silica symbols such as Q-I-L etc. and preparation of sample. For the comparison of spectrum kaolin and talc were also used.

The prepared disk was inserted in special cells for the measurement of an infrared spectrum. The cell is illustrated in Fig. 4. One cell held the sample disk and the other the reference disk which contained potassium bromide alone. The spectrum was recorded with Perkin Elmer Model 137 Infracord Spectrophotmeter and Perkin Elmer Model 221 Spectrophotometer.

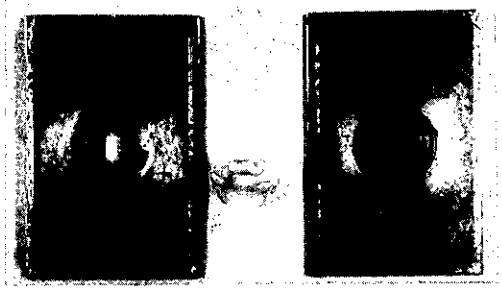


Fig. 4. Cell for KBr pellet.
Left to right: pellet holder cell made brass, polyethylene stopper (screwed) and set cell for measurement.

An absorbance of the absorption band was expressed as $\log_{10}(T_{100}/T)$, where T_{100} was the transmittance (% transmission) of 100 % line obtained with the sample beam

passed through the potssium bromide disk which contained no sample and T was the transmittance of the sample, as illustrated in Fig. 5. Absorbance per milligram of quartz powder was designated as absorption coefficient E' and so

$$E' = (1/w)\ log_{10}(T_{100}/T),$$

where w was the amount of quartz in milligram. If more precise determination is required, the band area must be measured but practically it is not necessary to use band area because the area is approximately proportional to absorbance. Value of position of absorption band is written as the wave number in $cm.^{-1}$. ν, which is the reciprocal of wave length in micron, λ, as follows.

$$\nu = 10^4 / \lambda$$

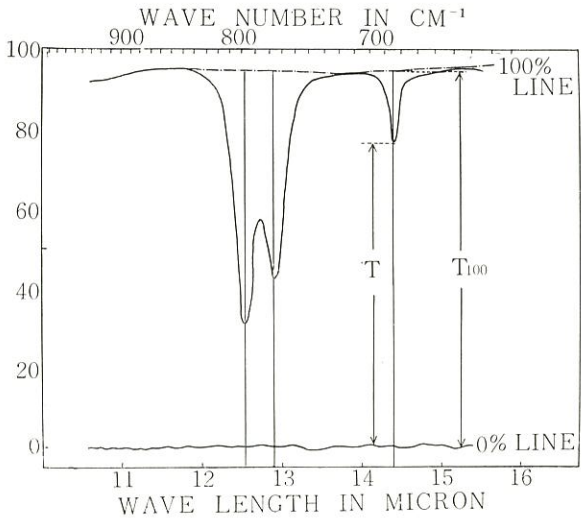


Fig. 5. The base line method (the conventional method) to obtain the absorbance of the absorption band.
The base line is the same as 100 % line which is the tangent line at the maximum transmittarce points of both sides of the absorption band. 0 % line is a back ground which is obtained by a 'shut-out' of the sample beam. (complete shut-out).

RESULTS

Typical infrared absorption spectrum of quartz for the calibration is illustrated in Fig. 6. Spectra of the other crystalline modification of silica are shown in Fig. 7

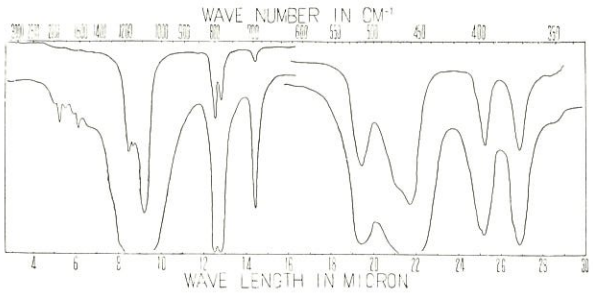


Fig. 6. A typical infrared absorption spectrum of quartz (Q-I-L). Particle Size is about 1 micron. Upper spectral curve is obtained by diluting the sample which presents lower curve.

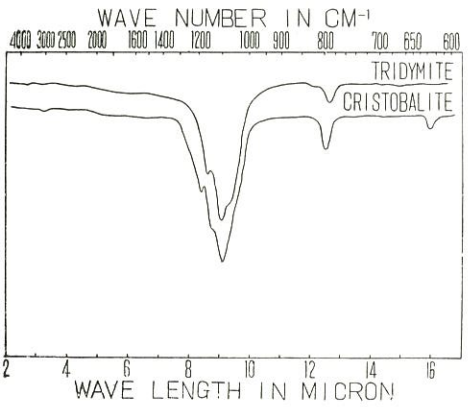
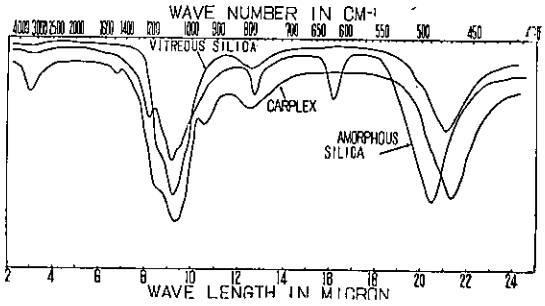


Fig. 7. Infrared absorption spectra of tridymite and cristobalite [2].



Fif. 8. Infrared absorption spectra of non-crystalline silica modifications.

and those of the non-crystalline silica in Fig. 8. In the region of the wave length of 8 to 9 microns all the compounds gave rise to the strong absorption band groups but in the region of 12 to 15 microns each compound showed the characteristic bands of the medium intensities respectively. The positions of absorption bands of each compound are summarized in Table 1. Quartz gave rise to three characteristic bands at 800, 780 and 694 cm.$^{-1}$, tridymite single band at 792 cm.$^{-1}$, cristobalite two bands at 798 and 620 cm.$^{-1}$. Carplex gave rise to single weak and broad band at 798 cm.$^{-1}$, vitreous silica at 801 cm.$^{-1}$ and amorsphous silica at 791 cm.$^{-1}$. All of these arose similar and strong band at 1080 to 1100 cm.$^{-1}$ with followers of one or two bands of medium intensities near 1200 and 1150 cm.$^{-1}$. Kaolin and talc showed similar band groups as above stated samples in the region of wave lengths of 8 to 9 microns but showed five characteristic bands in the region of 800 to 600 cm.$^{-1}$ respectively.

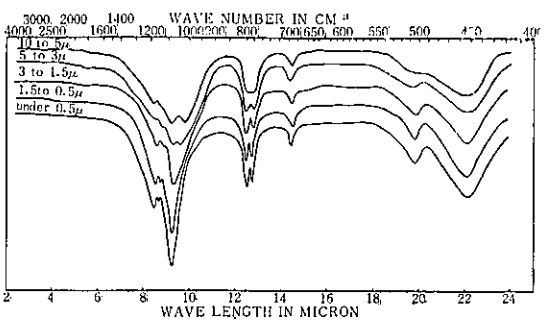


Fig. 9. The effect of the particle size on the infrared absorption spectrum of quartz (1), (Q-I-L).

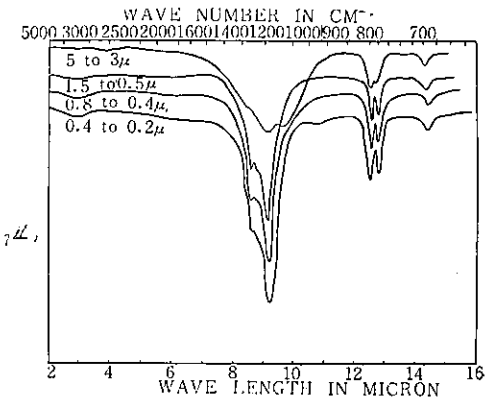


Fig. 10. The effect of the particle size on the infrared absorption spectrum of quartz (2), (Q-1-100H)

The particle size had some influence on the spectrum as shown in Fig. 9 and 10. Spectra in Fig. 9 were obtained using the quartz particle ground mechanically and leached with 10 % aqueous solution of sodium hydroxide and in Fig. 10 were obtained with quartz dust ground mechanically for about 100 hours. As shown in next chapter, bands at 800, 780 and 694 cm.$^{-1}$ were suitable to obtain the relation between the absorbance and the weight of sample. Table 2 shows the weight of quartz and

Table 1. The absorption band position (in cm^{-1}) of various kind of quartz and silica

Sample	Band positions (4000 to 600 $cm.^{-1}$)						
Q-I-L							
10 to 5 μ		1160(w) 1130(sh) 1086(m) 1030(m)			795(m) 777(m)	694(w)	
5 to 3		1166(m) 1135(sh) 1081(s) 1046(m)			796)m) 777(m)	694(w)	
3 to 1.5		1166(m) 1139(m) 1081(s) (1054)			796(m) 777(m)	694(w)	
1.5 to 0.5		1170(m) 1145(m) 1079(s)			798(m) 779(m)	694(w)	
0.5 under		1174(m) 1148(m) 1079(s)			798(m) 779(m)	694(w)	
Q-I-100H							
5 to 3 μ	3300(w)	1161(m)	1087(s) 1037(s) (948)?		796(m) 776(m)	694(w)	
1.5 to 0.5	3300(w)	1164(m) (1142)?	1088(s)	(948)	799(m) 779(m)	694(w)	
0.8 to 0.4	3300(w)	1166(m) 1142(w)	1088(s)	(948)	799(m) 779(m)	694(w)	
0.4 to 0.2	3300(w)	1167(m) 1142(w)	1088(s)	948(w)	799(m) 780(m)	694(w)	
Q-I-24H	3400(w)	1170(m) (1145)	1080(s)	950(w)	800(m) 780(m)	694(w)	
Q-I-6H	3300(w)	1168(m) ?	1082(s)	948?	799(m) 779(m)	694(w)	
Q-I-2M		1171(m) 1145(m)	1074(s)		799(m) 779(m)	694(w)	
Q-I-O		1175(m) 1145(m)	1074(s)		799(m) 779(m)	694(w)	
Q-I-		1175(m) 1145(m)	1075(s)		800(m) 780(m)	694(w)	
Q-I-		1175(m) 1145(m)	1075(s)		800(m) 780(m)	694(w)	
Q-B-O	3400?	1170(m) 1140(m)	1080(s)		799(m) 778(m)	694(w)	
Q-B-2M	3400(w)	1180(m) 1150(m)	1080(s)		800(m) 780(m)	695(w)	
Q-B-6H	3400(w)	1175(m) (1140)	1085(s)	950(w)	799(m) 778(m)	694(w)	
Q-T-2M		1180(m) 1150(m)	1080(s)		800(m) 780(m)	694(w)	
Q-T-6H	3400(w)	1180(m)	1080(s)	950(w)	800(m) 780(m)	695(w)	
Q-Y-2M	(3400)	1180(m) 1150(m)	1080(s)		799(m) 779(m)	694(w)	
Q-Y-6H	3400(w)	1170(m) 1140(sh)	1070(s)		799(m) 780(m)	694(w)	
Tridymite*		1175(m)	1109(s) 1090(s)		792(m)		620(w)
Cristobalite*		1204(m) 1160(sh)	1104(s)		798(m)		
Carplex**	3400(m)	1175(sh) 1149(sh)	1085(s)	948(mw)	798(w)		
Amorphous silica	3400?	1196(m)	1093(s) 1056(m)		791(m)		620(m)
Vitreous Ailica	(3400)	1175(sh)	1098(s)		801(w)		
Quartz from Yamanashi	(3390)	1164(m) ?	1082(s) (1063)	948?	799(m) 779(m)	694(w)	
Kaolin	3690(m) 3509(w) 3636(sh)	1105(m) 1034(s) 1007(s) 934(m)			912(m) 795(w) 787(w) 754(m) 696(m) 644(m)		
Talc	3676(m) 3460(w)	1173(w) 1168(w)	1079(m) 1014(s)	985(s)	797(w) 778(w) 668(m) 641(m) 620(m)		

* Tridymite was supplied from Dr. Nagelschmidt, Cristobalite was not observed and it takes from reference (2).

** Carplex is the trade name of amorphous fine silica particle (Shionogi Co. Ltd.,).

Band intensity,

s, strong; m, medium; mw. medium weak; w, weak;

sh, shoulder band of neighbour (strong) band:

Table 2. The weight of quartz and absorbance at 800, 780 and 694 cm.$^{-1}$

Kind \ Band / Weight(mg.)		Absorbance $\log_{10}$ (T_{100}/T).		
		800cm.$^{-1}$	700cm.$^{-1}$	694cm.$^{-1}$
Q-I-100H below 1 μ particle size	0.854mg.	1.317	0.859	0.230
	0.431	0.789	0.554	0.137
	0.358	0.695	0.493	0.121
	0.204	0.305	0.220	0.057
	0.087	0.138	0.093	0.019
	0.076	0.116	0.079	0.017
Q-I-L 10 ~5 μ	2.330	—	—	0.721
1.5~0.5μ	1.65	—	—	0.572
5 ~3 μ	1.160	—	—	0.382
3 ~1.5μ	1.05	—	—	0.398
0.5μ~	0.75	1.534	1.190	0.288
10 ~5 μ	0.482	—	—	0.142
5 ~3 μ	0.410	—	—	0.132
0.5μ~	0.357	0.648	0.486	0.134
1.5~0.5μ	0.320	0.505	0.368	0.096_5
3 ~1.5μ	0.204	0.321	0.243	0.073_5
10 ~5 μ	0.104	—	—	0.032
1.5~0.5μ	0.087	0.157	0.113	0.029
0.5μ~	0.084	0.164	0.110	0.027
3 ~1.5μ	0.056	0.096_5	0.069	0.025

absorbances, and particle size of sample Q-I-100H was about one micron but Q-I-L sample had various sizes. At 800 and 780 cm.$^{-1}$ the spectrum was saturated with quartz of over 1 mg., therefore in such a spectrum, absorbances of these bands could not be obtained accurately. Samples Q-I-L which contained quartz about 0.48, 0.41 and 0.10 mg. were those of particle sizes of 5 to 10 mirons. When particle size was larger than 3 microns doublet band at 800 and 780 cm.$^{-1}$ lost its sharpness as shown in Fig. 9 and 10, and so absorbarce was not suitable to measure the amount of quartz with such a particle size. But band at 694 cm.$^{-1}$ was not influenced by this particle size range. Therefore the amount of quartz of various sample sizes and particle sizes could be measured by the use of band at 694 cm.$^{-1}$.

Spectra in Fig. 11 were obtained by the freeze drying method. Blank curve obtained by potassium bromide alone gave rise to bands in two regions, 3,300 to 3,400 cm.$^{-1}$ and near 1,600 cm.$^{-1}$, attributable to water contaminant and another broad weak band near 9 microns due to impurities. But no appreciable absorption band was observed in the region of 12 to 15 microns. Spectra obtained with freeze dried sample of Q-Y and Q-B had nearly the same pattern as those obtained by other methods. If freeze dried sample was not heated up 180°C. for 3 hours, the spectrum decreased its transmittance

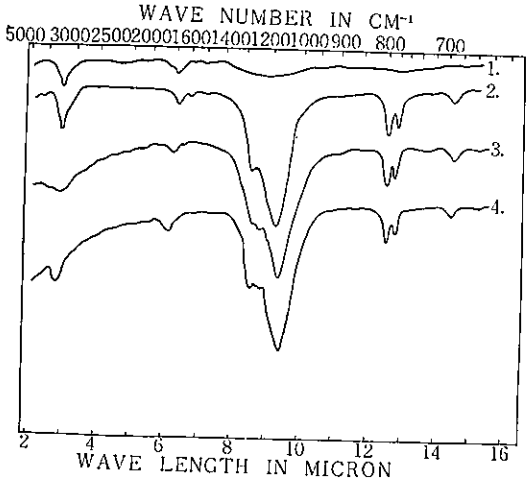


Fig. 11. Infrared absorption spectra of the fine particle suspended in water.
Spectrum No. 1 is the blank curve (KBr alone).
Spectrum No. 2 is the Q-Y-2M sample dried over 180° C for 3 hours.
Spectrum No. 3 is Q-B-6H sample non-treated.
Spectrum No. 4 is Q-Y-2M sample non-treated.

steeply at shorter wave length but in the longer wave length region the decrement was not so large that analysis of quartz from this spectrum was able to be carried out without difficulty. Therefore, if freeze dried sample did not contained any impurities, the heating the dried sample over 180°C. for 3 hours would be unnecessary. From the spectra illustrated in Fig. 11, and in Fig. 6, 9 or 10, it would be clear that the spectrum obtained with freeze dried sample was the same as those of sample prepared by other process such as mixing of dry particle with potassium bromide powder in agate mortar or nujol mulling method. The latter method is used easily and generally but was not reported in this paper. H. Sakabe et al.[4] will report that the spectrum

Table 3 The kind of quartz and the value of E' at 800, 780 and 694 cm.$^{-1}$

Kind \ Band	Absorbance per milligram E'		
	800cm.$^{-1}$	780cm.$^{-1}$	694cm.$^{-1}$
Q-I-0	1.45	1.05	0.27
Q-I-2M	1.50	1.07	0.29
Q-I-6H*	1.30	0.90	0.22
Q-I-24H	1.45	1.05	0.24
Q-I-100H	1.55	1.03	0.28
Q-I-L-2M	1.75	ca. 1.2	ca. 0.3
Q-I-L-6H	1.65	1.21	ca. 0.3
Q-I-L	1.82	1.33	0.35
Q-B-0	0.8	0.5	0.2
Q-B-2M*	0.5	0.35	0.1
Q-B-6H*	0.9	0.6	0.15
Q-T-2M	1.17	0.65	0.21
Q-T-6H	0.96	0.63	0.16
Q-Y-2M	1.24	0.91	0.24
Q-Y-6H	1.00	0.65	0.19

* The weight of quartz sample may be not so correct. E' has an unit, mg.$^{-1}$

with nujol mulling method is essentially the same as that by potassium bromide pellet method. Therefore, it is suitable for analysis of quartz to use the spectrum obtained from freeze dried sample. In Table 3, the absorption coefficients of various quartz samples with different preparation methods and localities are summarized.

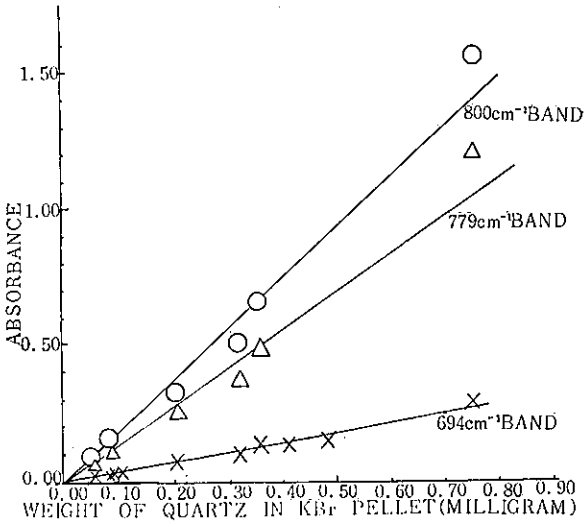


Fig. 12. Calibration curve of quartz sample at the absorption bands, 800, 780 and 694 cm^{-1}. The standard sample is Q-I-L which has particle size under 3 microns.

Calibration curve was obtained with Q-I-L sample and illustrated in Fig. 12. Absorbance of band 800 $cm.^{-1}$ or 780 $cm.^{-1}$ was higher than that of band at 694 $cm.^{-1}$. From the inclination of these calibration curves, the absorption coefficient was also obtainable as the mean value. As shown in Fig. 12, linear relation between absorbance and weight of quartz was obtained. Values in Table 3 and 4 were calculated by this method. From these tables and figures, it was obvious that value E' of well leached quartz had the highest and this value decreased with grinding time. Relation between

Table 4. The particle size of quartz and the value of E' at 800, 780 and 694 $cm.^{-1}$.

Kind and Particle Size	Absorbance per milligram E'		
	800$cm.^{-1}$	780$cm.^{-1}$	694$cm.^{-1}$
Q-I-L 10 to 5 microns	0.989	0.880	0.301
5 to 3 microns	1.37	1.057	0.353
3 to 1.5 microns	1.659	1.228	0.422
1.5 to 0.5 microns	1.68	1.219	0.308
under 0.5 microns	1.89	1.259	0.334
Q-I-100H 5 to 3 microns	1.25	0.716	0.305
1.5 to 0.5 microns	1.75	1.21	0.281
0.8 to 0.4 microns	1.78	1.22	0.31
0.4 to 0.2 microns*	1.41	0.98	0.257

* The weight of quartz sample may be not so correct. "E'" has an unit, $mg.^{-1}$

particle size and absorption coefficient E' is illustrated in Fig. 13 and Table 4. The figure shows evidently that absorption coefficient of band at 694 cm^{-1} is not influenced by particle size but other two bands are apparently influenced.

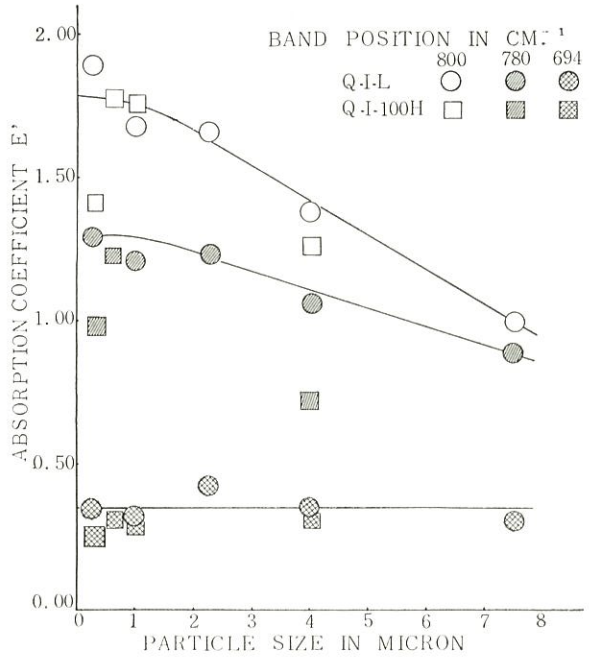


Fig. 13. Particle size of quartz sample and the absorbance E' at 800, 780 and 694 $cm.^{-1}$.

In this report value 0.35 $mg.^{-1}$ was used as the absorption coefficient of band at 694 $cm.^{-1}$, 1.33 $mg.^{-1}$ as that at 780$cm.^{-1}$ and 1.82 $mg.^{-1}$ as that at 800 $cm.^{-1}$. If the value 0.35 $mg.^{-1}$ was used, detectable amount of quartz was 30 γ or less, and if the other values were used for absorption coefficient, the amount was about 10 γ.

DISCUSSION

An infrared absorption spectrum is a representative of structural character of compound. An absorption band arises from a characteristic structural factor and a chemical functional group, hence it can be inferred from the properties of bands that what functional group or what kind of structure is found in the compound. Furthermore it is possible in principle to guess an appearance of a spectrum from the chemical and geometerical structure of the compound, more precisely, the structural factor which expresses physical properties of the structure of the compound. Silica has the unit of the structure SiO_4^{4-} and a Si atom combines four oxygen atoms and the directions of these valence bonds take an angle of 109° 28′ each other, i.e., the angle of tetrahedral structure. The bond angle of Si–O–Si takes several values according to the species of silica modifications. Silica gel and sol take the angle at about 110° to 120°, quartz

approximately 140° and tridymite or cristobalite near 180°. The bond length of Si–O linkage also is different according to silica modifications[5]. Therefore infrared spectra of silica modifications show similar appearances but there appear some bands which differ partly each other caused by fine strutural factors of modifications. The region of wave length of 8 to 9 microns represents the former and the other regions the latter.[2,3] The analysis, particularly quantitative, utilizes the characteristics of a compound. Therefore, the region of 12 to 15 microns is suitable for a quantitative analysis and furthermore this region is measured easily by the ordinary spectrophotometer. If longer wave length is able to be observed, the region of 25 to 30 microns and further longer wave length region are more suitable for an analysis. But these region can be measured only with special spectrophotometer at present. In this paper, the discussion is limited to the former spectral region for general use.

An infrared absorption spectra of co-polymers are similar in spite of different degree of polymerization if the co-polymers are relativily large molecule (co-polymers are composed of above hundred monomer molecules). The particle of 0.1 microns of quartz in diameter has about 24×10^6 of SiO_4^{4-} unit structures. Therefore, as far as the unit structure of quartz is the same, the spectrum would show the same pattern even if the particle size is different. This is the case of Fig. 9 and 10. The spectral region of the wave length of 8 to 9 microns show the different appearance according to the particle size on the quartz particle above 3 mirons but below 3 mirons spectra are not so different with the particle size. The changes of absorption bands with the particle sizes will be discussed in other paper**and here only the result of the observation of the infrared absorption spectrum is shown. The band 694 $cm.^{-1}$ (14.4 microns) has the same aspect and same absorbance even if the particle size is different. Therefore this band can be used for quantitative analysis of quartz. When the particle size is 3 microns or less the band at 780 $cm.^{-1}$ or 800 $cm.^{-1}$ is able to be used for the analysis. In general the band at 694 $cm.^{-1}$ is most suitable for this purpose.

From Fig. 11, Table 3 and above stated results it may be concluded that this freeze drying method is very suitable for the determination of amount of quartz dust in atmosphere. By this method fine spectrum is obtained and the interference due to organic substance and clay etc. may be removed out with heating up sample.

X–ray analysis of the free silica generally requires the content of quartz of 10 to 100 mg. and it is convenient to examine the rather large particles such as above 10 microns. The phosphoric acid method uses in it chemical reaction, so the method may be expected to give high accuracy but has several questions as mentioned previously. In this respect the freeze drying method with the infrared absorption spectrum is an excellent method for the analysis of quartz in atmospheric dust. If it is combined with above two methods the result obtained may be quite accurate.

** Presented partly in "The 9th meeting for infrared and Raman spectrum" held at Osaka University, October 12th, 1960.

The detectable amount of quartz with this method is the order of 10 γ and if the other components do not interfere the absorption band of quartz, the order of 1 % of quartz is detectable in the dust of 1 mg. The accuracy is about 5 % of the amount of quartz obtained by this method.

Clays and other several minerals show the absorption bands near 690 cm.$^{-1}$ (14.5 microns) and 800 cm.$^{-1}$ (12.5 microns) which interfere the bands of quartz, 800, 780, and 694 cm.$^{-1}$ [1,3] but these interfering bands are eliminated when the compounds are heated up to 800°C.[1] Some silicate and silica compouds show weak broad bands near 800 cm.$^{-1}$ but no bands near 690 cm.$^{-1}$ The case in which all three bands are interfered by other components is very rare and even in such a case, one or two bands may be used for the determination of quartz amount. Particularly the band at 694 cm.$^{-1}$ is the most reliable characteristic one which is scarecely interfered.

The bands in the region about 1100 cm.$^{-1}$ exhibit the characteristic aspects by the different preparation method of the particle sample, i.e., the grinding time or the treatment of the surface layer. This phenomenon is illustrated in Fig. 14. The bands at 800, 780 and 694 cm.$^{-1}$ did not show such a phenomenon. But the intensities of these bands vary with above stated treatment as illustrated in Table 3. This means that the some part of quartz particle changes to the disturbed structure different from the parent quartz structure[4]. Therefore the leached sample must be adopted for calibration.

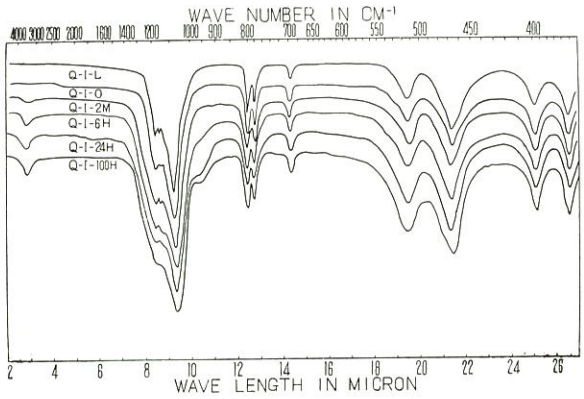


Fig. 14. Infrared absorption spectra of mechanically ground quartz and leached quartz.

In this study, as the cell is so small that the infrared beam is partly cut off, the loss of incident beam to sample disk and to the photometer is large. Therefore the S/N ratio is small. If the improvement of this method such as the reduction of disk size and prevention of loss of infrared beam is made, the order of 0.1 γ or less of quartz may be detectable. In the next report, the author will show the results which will be carried out as the field work.

SUMMARY

The content of quartz in the suspended dust in the atmosphere can be determined by means of an infrared absorption spectroscopy to the order of 10 γ with the method reported in this paper, i.e., the freeze drying method. The particle size has no influence on the sensitivity and accuracy. The absorption band at 694 $cm.^{-1}$ (14.4 microns) is the most reliable and characteristic one for the analysis of quartz. Absorbance per milligram of quartz with this band was 0.35 $mg.^{-1}$ For the determination of quartz by this method, leached quartz must be used as the standard sample for the calibration.

ACKNOWLEDGEMENT

The author expresses his hearty thanks to Mr. M. Hamada for his kind help and supply of the dust particles of distinct sizes.

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The author wishes to express his gratitude to Mr. M. Kawano of Railway Technical Research Institute for the measurement of the infrared absorption spectrum in the cesium bromide region (16 to 34 microns).

Finally the author wishes to express his gratitude to assist. prof. T. Miyazawa and collabrators in the laboratory for use of Perkin Elmer Model 221 spectrophotometer at Institute for Protein Research, Osaka University.

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(4) Sakabe, H., et al.,: This bulletin No. 4, (1960).

(5) For example,
Fisher, R. E., and Ring, C. E.,: Anal. Chem., 29, 431 (1957).

ADDENDUM

The author has just read the report by Tuddenham and Lyon* who state the similar argument as this report. The author has great interest to their work and is glad to see the same result.

* Tuddenham, W. M., and Lyon, R. J. P., Anal. Chem., 32, 1630 (1960).

QUARTZ DUST BY INFRARED SPECTROSCOPY

要　　旨

大気中浮游粉塵中の石英の赤外分光法による定量

左右田　礼　典

従来の石英の分析法はX-線廻析によるものと燐酸法とであつたが前者は石英の粒度に左右され，又その量も余り少い場合は分析が困難である。後者は燐酸による溶解の条件により測定値がバラつき，且不溶解の物質を free silica として一括してしまうというあいまいさがある。赤外吸収スペクトルは物質の基本構造が不変であれば粒度に左右されないと予想される。この事は本報に於て実証された。スペクトルの一部は変化するが定量に利用する吸収帯は影響を受けず検量線によく乗る。方法は粉塵をインピンジャー（水約 10cc. を入れて）に捕集し，これに臭化カリ約100mg. を加えてから凍結乾燥する，この過程が一応この方法の成功のきめ手である。上手に出来れば乾燥粉末は細かく臭化カリと試料との混合が充分で後述の成型した錠剤はスペクトル測定に適したものになる。凍結乾燥した粉末を約 180°C で 3 時間位乾燥する。この際 800°C に加熱すると有機物は勿論の事，妨害をする粘土鉱物の妨害吸収帯が消去される。（文献 1 参照）次にこれを錠剤成型器（第 2 図）に入れて先ず 2mmHg以下で 5 分乃至10分排気する。それから 1 平方糎当り約 10 トンの圧力をかける。大体 3 分間かける。プレスの不均衡を考慮して錠剤成型器を一度まわして再び加圧をする。終つたら錠剤をこの成型器から静かに押し出す。本報の場合厚さ約 1mm，直径約10mm の錠剤をつくつて測定したが一般的なものではない。これを第 3 図に図式的に示した。

出来た錠剤を臭化カリ錠剤用のセルに入れてスペクトルを測定する。吸光度は第 5 図に示すように T_{100} と T を求め $\log_{10}(T_{100}/T)$ として求めた。この方法はベースライン法と云われる簡便法であるが通常の分析にはかえつて余計な誤差に気をつかわずに手軽に出来る便利さがある。吸光度から便宜上の吸光係数 E' を出したがこれはこの測定に用いた分光器及び方法によつて得られる 1mg の石英当りの吸光度である。以上の実験法に基いて得られたスペクトルの結果等を第六図から第十四図に亘つて示してある。又第一表から第四表にそれをまとめた。吸収帯の位置は最近波数という値で示されるがそれは波長（ミクロン）の逆数で，$\nu=10^4/\lambda$（νが波数cm^{-1}，λが波長である。）第六図から第八図にいろいろの種類のシリカの代表的なスペクトルを示したが 12から 15 ミクロンの波長域が特長のある吸収帯でそれぞれの化合物の判別に用いられるし，定量の特性吸収帯となる。石英の場合 694cm^{-1} の吸収帯が最もよいがそれについで780と 800 cm^{-1} の二本の吸収帯が用いられる。第九図と第十図は粒子の大いさによる影響であるが殆ど粒子の大いさに影響されず 3 ミクロン以下では全く影響がない。特に 694cm^{-1} はその影響を全く受けない。ただその強度は磨砕の長い試料で弱くなるから標準試料は leach したものを用いるべきである。粒度との関係は第三表と第十三図に示されている。今回の未だ条件に不完全さの残る方法によつても粒度の影響が殆どないことと比較的少量の試料が測定出来ることはこの方法の利点であり燐酸法とX-線法とを組み合せれば略完全に石英の分析が出来ると思われる。この方法の限界量は石英10γの桁迄であり（694cm^{-1} の吸収帯による）780cm^{-1} か800cm^{-1}が使えれば 1γ は可能である。誤差は大体 5％と見られる。この測定に用いた分光器は米国製パーキンエルマー社の137型インフラコード分光器と221型分光器である。

Bull. Nat. Inst. Indust. Health, 4, 44~53 (1960)

GAS CHROMATOGRAPHIC ANALYSIS OF ATMOSPHERIC POLLUTANTS IN INDUSTRIES

Yoshimi MATSUMURA and Reisuke SODA

Gas chromatographic technique is useful to analyse the multicomponent mixtures of gases or liquids simultaneously in one process and it has been conveniently applied to the measurement of the atmospheric pollutants by many investigators. Levadie et al.[1] and Mansur et al.[2]investigated the analytical methods of organic vapors in industrial atmospheres by gas chromatographic methods. In their methods, the vapors were collected in a sampling bottle with an adequate solvent and then the samlped solution was quantitatively analysed by gas chromatography. In another method, the vapors were collected in a cooled column packed with a suitable adsorbent in it. For the satisfactory measurements in field reseaches, a sampling apparatus having high sampling efficiency as well as a property not greatly influenced by slight structural irregularities of the apparatus has been required.

The present paper reports on sampling efficiency of organic vapors by absorbing method which employs an organic solvent with several sampling bottles, and the method of quantitative analysis of the sampling solution by gas chromatography. As a quantitative determination method, the authors discussed the relationship between concentration and the peak area ratio of the solute against solvent on the gas chromatograph chart.

EXPERIMENTALS

Sampling of vapors:

Six kinds of sampling bottles were examined for their sampling efficiencies and the distribution ranges of the efficiencies. The types of bottles are shown in Fig. 1 and their detailed structures and test conditions are summarized in Table 1. In this experiment, toluene was used as a sampling solvent and benzene as a test vapor.

A certain amount of benzene was vaporized by heating in a closed cubic chamber of volume of 27 m^3 to prepare the atmosphere of suitable benzene vapor concentration and the inside air was stirred with a fan set on the ceiling of the chamber during the entire period of experiment. Ten minutes after the start of fan, the test air was led out of the chamber through glass tubes with their openings at the center of the chamber. Sampling apparatus was composed of two sampling bottles of the same type, one flow rate meter, one dry gas meter for total air volume and one suction pump in series. From one to four such series were set and driven to collect the test vapor into the bottles at the same time.

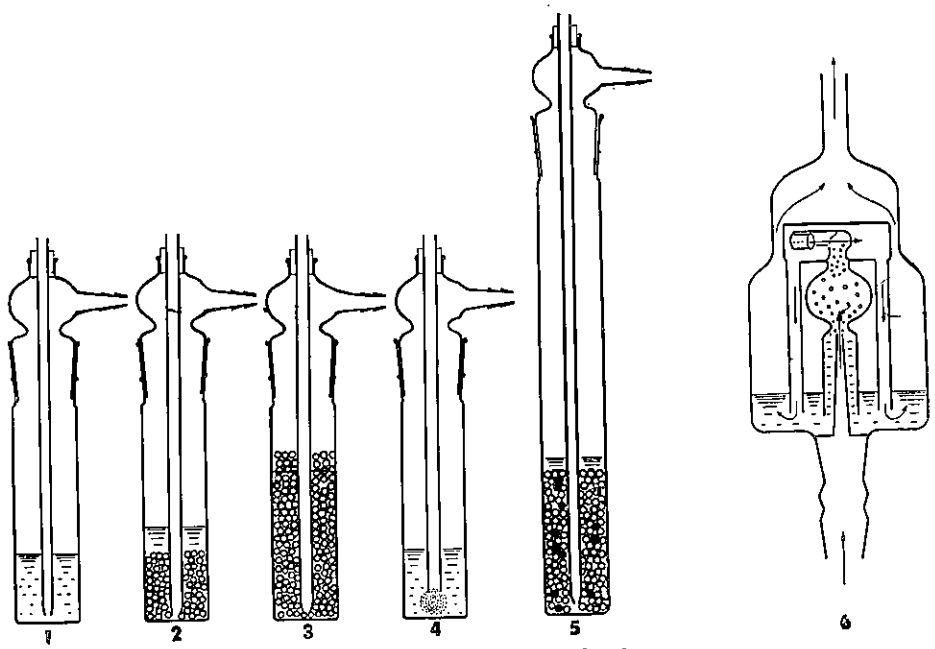

Fig. 1 Types of sampling bottles

Table 1 Characteristics of bottles and conditions of gas collection.

Test No.	Type No.	Structure description	Solvent volume (cc.)	Air flow rate (*l*/min)	Total air flow volume (*l*)	Test vapor concentration (ppm)	Note
1	1	Midget impinger	10	2	40	183	Originally devised as a dust sampler but often used for gas sampling.
2-1	2	Midget impinger with 10cc. glass beads	10	2	40	144	Glass beads used in No. 3, 2 and 5 are about 3 mm in diameter.
2-2					10	972	
3	3	Midget impinger with 25cc. glass beads	5	0.7	40	125	More than 5 cc. of solvent would overflow when bubbled
4	4	Midget impinger with a ball filter	10	2	15	178	Sintered glass ball filter at the nozzle, producing fine bubbles of 1 to 2 mm. in diameter
5	5	Midget impinger with 20cc. glass beads	10	11	40	244	The same structure as No. 3, but there is no afraid that the solvent should overflow.
6-1	6	Dautreband impinger	50	16	75	144	Highly effective for dust sampling.
6-1					200	244	

Quantitative determination of the sample solutions by gas chromatography:

The gas chromatographic apparatus used in this experiment had been constructed in this institute by one of the anthors. A katharometer was used as the sensing element of the detector. And its out-put was connected through the attenuator to in-put of the

recorder of 3 mV full scale. The response of the recorder was changeable from $^1/_1$ to $^1/_{1000}$ times by changing attenuation.

Chromatographic column was a copper coiled tubing of 2 m long and 4.5 mm. inside diameter, packed with Celite of 30 to 65 mesh coated by dioctyl phthalate (weight ratio 3 to 1). The temperature of column and detector was 110 ± 1°C and helium was used for the carrier gas, the flow rate of which was about 40 cc./min.. Bridge current was about 150 mA..

0.05 cc. of a sample solution was inleted with a syringe into the gas chromatograph through a serum cap. On the chromatogram, benzene peak was recorded at the highest sensitivity ($^1/_1$) and toluene peak at lower sensitivity ($^1/_{50}$). The peak areas of benzene and toluene were measured with a planimeter and the benzene concentration was determined from the ratio of these two peak areas using the calibratin curve. The procedures are shown in Fig. 2 and the calibration curve is illustrated in Fig. 3.

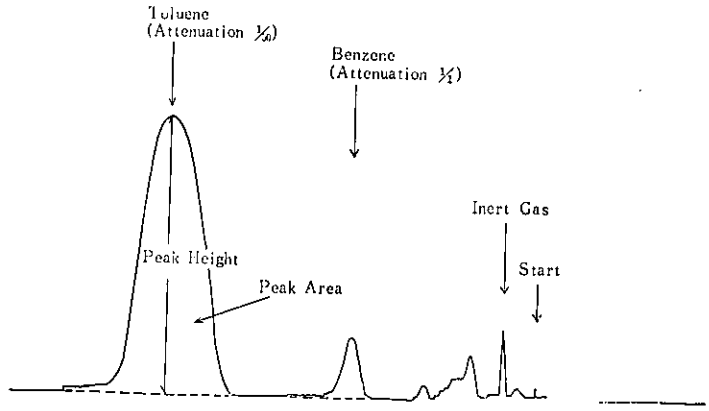

Fig. 2 Gas chromatogram of benzene in toluene.

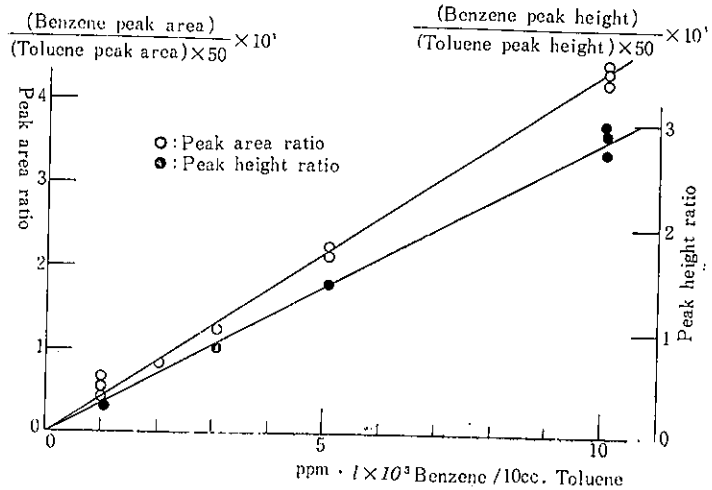

Fig. 3 Calibration curve for the determination of benzene concentration in toluene. Curves of concentration against peak area ratio and peak height ratio.

Benzene concentration in toluene solution was written as the product of the vapor concentration (ppm.) and the total volume of collected air(l).

Benzene sampling efficiencies of the bottles were determined as follows. If the efficiencies of the two bottles set in a series are the same, the efficiency E is expressed as

$$E=\frac{C_1-C_2}{C_1}$$

where C_1 is the benzene concentration in the first bottle and C_2 in the second bottle.

The vapor concentration in the sampled air, C_0, was obtained as follows.

$$C_0=\frac{(C_1/E)\times(v/10)\times(273+t)}{V\times 273}\times 10^6\, ppm.$$

where C_1 is the concentration of the sampled vapor in the first bottle (ppm$\times l/10$ cc. toluene): E, the efficiency of the bottle: v, the volume of the solvent present in the first bottle at the end of the air sampling (cc.): V, the total aspirated air volume (l): t, the temperature of the air (°C).

A dust chamber was used for the experiment. It was enclosed with cement wall and glass windows and the duct was set at the one side of the walls to exhaust the inner air. Benzene vapor for the test was dispersed by evaporation in this chamber and the fan was driven. The vapor concentration decreased slowly and almost linearly with time, although the test air was not pumped out. In this experiment, one running time of sampling was short, about twenty minutes, hence the change of the concentration could be neglected.

RESULTS AND DISCUSSIONS

Table 2 Gas sampling efficiencies of various types of bottles.

Test No.	Type No.	Efficiencies (%)
1	1	60, 68, 70, 82
2-1	2	72, 72, 69
2-2		100, 90, 87
3	3	59, 50, 51
4	4	88, 88
5	5	95, 95
6-1	6	70
6-2		54

From the experimental results shown in Table 2, it is able to select the most suitable type of bottle for the purpose of this work. For a bubbler to show high efficiency,

enough gas-liquid contact time and contact surface are needed so as to reach equilibrium. Among the six types of sampling bottles, the bottle No. 5 is the most suitable one for this requirement. The bottle No. 1 can not be properly used, as it showed the low efficiency and large fluctuation. This may be caused by the irregularity of the structure of its nozzle, and by the short contact time as well as small contact surfaces as a result of large bubbles. The efficiencies of the bottles No. 2 and 5 are better than those of No. 1 as illustrated in Table 2. In these bottles, the irregularity of the structure and the generation mechanism of bubbles are improved with the small glass beads packed in the bottom of the bottles. Perhaps the glass beads and the solvent are used with a most satisfactory amount in the bottle No. 5, therefore its efficiency is the highest of the three types with glass beads. In No. 3 bottle, the solvent volume was too small. The solvent volume influences on the efficiency. When a small amount of solvent exists as a thin film among glass beads, the diffusion of the solute once dissolved in the solvent into the inner part of the solution may not occur smoothly and the re-evaporation of the solute from the solution may not be neglected. Therefore, the solute captured in the solvent is necessary to diffuse rapidly into the inner part of the solution to obtain the high sampling efficiency and its concentration must not become high partly, particularly at the bubble surfaces. Dautreband impinger is made for dust sampling and its characteristics are the generation of the solvent mist and the impingement of the dust with the mist. This impinger shows high efficiency for dust collection but in this experiment it shows lower efficiency for gas sampling. The mist is well generated when the air velocity is high, but it rather affects negatively for gas sampling, because for absorption of the gas, slower air velocity is advantageous to approach to the equiliblium state. The ball filter used in the bottle No. 4 makes fine bubbles but it has too large flow resistance to obtain a sufficient air flow by ordinary pumps. It may show comparatively higher efficiency if only the contact time of bubbles in the solvent is increased.

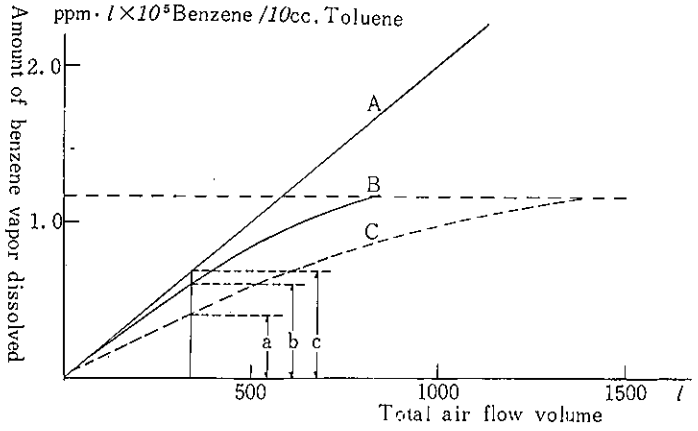

Fig. 4. Schematic diagram for illustration of sampling efficiency against air flow volume.

The total sampled air volume had some influence on the efficiency as shown in Table 2. That is, the efficiency is apparently higher with the volume of 10 *l* than with 40 *l* at the bottle No. 2. In the course of sampling of vapors, the concentration of solutes in a solution increased as the air continues to flow. According to the theory of gas-liquid equilibrium, the rate of dissolution of vapor component from gas phase to liquid phase will be lowered as the solute concentration in the solution increases. This may be the reason of the efficiency drop with the increase of aspirated air volume. Such an influence of sampled air volume on the sampling efficiency is illutrated in Fig. 4. Curve A gives the relation between the solute concentration in the solution and the total air flow volume, when the vapor is completely trapped in the solvent. However, even if the sampling bottle is the most suitable one, that is, the equilibrium is established between the gas phase and the liquid phase in that bottle, the air passed through the sampling solution contains the amount of vapor at the pressure responsible to the concentration of the solute in the liquid phase. Then the curve is shown as Curve B in this case which reaches a saturated state if the total air flow is very large. Practically, bottles never have such ideal characters as to reach gas-liquid equilibrium in the course of bubbling and then the concentration accumulated should be smaller than Curve B. This is the case of Curve C. (From another experiment and consideration, the fact has been cleared that only about half of gas-liquid equiliblium was reached with No. 2 bottle.) Sampling efficiency is given by c/a. Many structural improvements will approach its value to b/a, and in addition b/a will be approach to 1 by the the control of the sampling temperature. As shown in Fig. 4 these three curves approximately coincide when total air flow volume is relatively small, and in this region of small air flow volume, it is not necessary to consider the amount of gas or vapor in the passed air undissolved into the liquid in the impinger or re-evaporated from the solution. Therefore, if the sensitivity of detection is very high, the sampling time can be sufficiently shortened and the analysis becomes more precise.

Generally, organic solvents used in industries, for example, thinner, gasoline and even industrially pure solvents, are mixtures of many components, each of which has various partial pressures. Then, even if they are sampled in one bottle, the efficiencies are different for each component. Hence, it is necessary to determine the efficiency for each component, case by case. Such consideration can be neglected for rough estimation of vapor concentrations but it is necessary when the precise determination is required. By the gas chromatographic measurement, both peak area ratio and peak height ratio show sufficient linearity aganist benzene concentration in toluene, so each can be used for the determination of benzene. Peak height ratio is obtained more easily than peak area ratio and hence it is more practical to be used, but it deviates easily from the calibration curve by little fluctuation of the conditions of operation, such as a rate of carrier gas flow, sample size and the temperature etc.. From this reason, the peak area ratio was used in these experiments. The peak height ratio can be used

practically if operations were performed with enough cautions.

In selection of the solvent, it is necessary to consider the solubility of the object vapors into the solvent, volatility of the solvent and relative retention times of vapors and solvent on the gas chromatogram. It is desirable that the retention times of solvent differs as far as possible from those of vapors for the purpose to avoid the overlapping of tails each other. The more the both peaks overlap, the less the precision of the results becomes. When the components of object vapor mixture are unknown, it is necessary to use two kinds of organic solvents, whose retention times are different, because the peaks of the vapors are, sometimes, masked by a solvent peak. From comparison of the two gas chromtograms of different solvent, it is able to analyse all components, even if some of them are masked by solvent peaks.

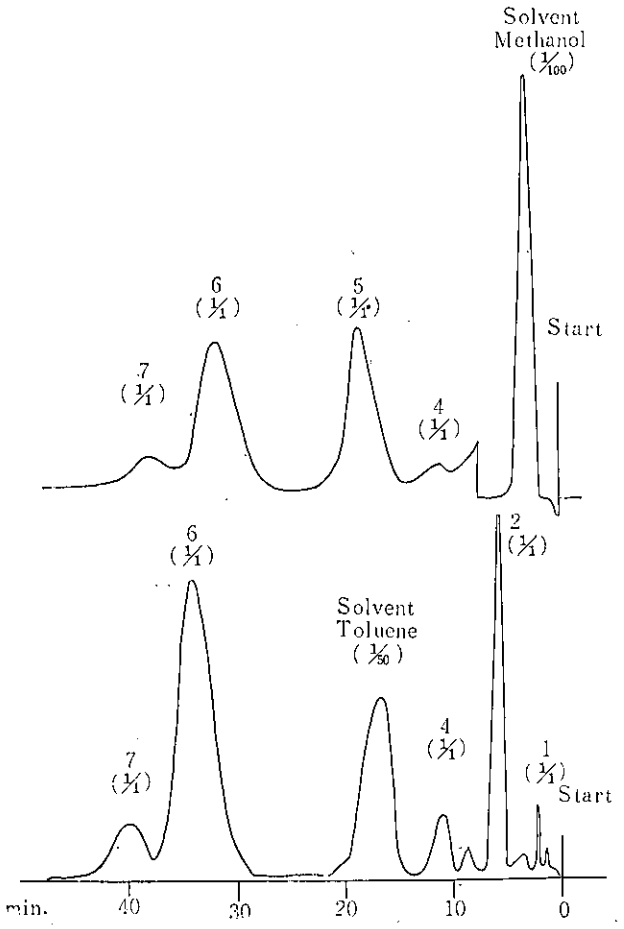

Fig. 5. Analysis of the vapors in a dyeing factory.

Gas chromatograms of the samples in the first bottle of two pairs of apparatus. Total air flow volumes are 17.4*l* for methanol solvent and 61.8*l* for toluene solvent.

FIELD TEST OF THIS METHOD

One of the authors determined the concentrations of organic vapors in some dyeing factory. Toluene and methanol were used as solvents in sampling bottle No. 5. Results at the position where the highest concentration was expected were shown in Table 3. Each component was determined by observing the change of gas chromatogram after adding the known substance in the sample. If the peak of a component increased and the shape of the peak did not changed, then the component responsible for this peak on the chromatogram was the same as the added one.

Results were shown in Table 3.

Table 3 Results of measurements of organic vapors in a dyeing factory.

Peak No.	Component	Sampling efficiency(%)	Vapor concentration (ppm)
1	Methanol	53.2	102
2	Ethyl acetate	40.9	118
3	Benzene	38.7	81
4	Unknown	73.8	170
5	Unknown	75.6	276
6	m-, p-Xylene	86.5	730
7	o-Xylene		

SUMMARY

Using six kinds of sampling bottles and toluene as a solvent, benzene vapor was collected and the trapped concentration was determined by means of gas chromatography. From the experimental results about the sampling efficiencies of these bottles, long midget impingers with glass beads at the bottoms were found the best one. And the important factors for gas sampling were discussed.

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要　　旨

工場に於ける空気汚染物質のガスクロマトグラフイーによる分析

松　村　芳　美　　左右田　礼　典

最近，環境中のガスや蒸気を，適当な溶剤を用いて捕集瓶中に捕集し，又は，吸着剤を充填した，冷却したカラム中に濃縮して，これをガスクロマトで分析する方法がよく用いられている。本報に於ては，汚染蒸気を，一種類の溶剤と，第1図及び第1表に示した6種類の捕集瓶を用いて捕集する方法と，これをガスクロマト法で定量分析する方法を試み，その結果と，この方法に対して得た知見と適用性を論じた。

試験空気としては，一定量のベンゼンを，27m³ のチャンバー内に蒸発させ，ファンで充分攪拌しながら，これをガラス管で外に導いた。捕集装置は，同型の二つの捕集瓶に夫々溶剤としてトルエンを加えたもの，流速計，ガスメーター及び吸引ポンプを連結して一組とし，この様な装置を，第1表の条件で，1～4組同時に操作した。

各捕集瓶内の試料を，自家製の熱伝導度型ガスクロマト装置で分析した。記録計は3mVフルスケールで，感度は 1/1～1/1000 倍まで切り換えることが出来る。分離カラムは，dioctyl phthalate を被膜した Celite（30～60メツシュ）を，長さ2m，内径4.5mm の銅管に充填したものを，又キャリヤー・ガスはHeを流速約 40cc./min. で用いた。分析温度は110±1°C，検知部のブリッジ電流は約150mA，サンプル・サイズは 0.05cc. で注射器で注入した。

ベンゼンピークは最高感度で，トルエンピークは感度1/50で描き，夫々のピーク面積をプラニメーターで測定した。試料中のベンゼン濃度は，ピーク面積比と濃度との関係曲線から得た。第3図はピーク面積比又はピーク高比とトルエン10cc. 中のベンゼンの濃度の関係曲線である。両者ともよい直線性を示したが，ピーク高比は容易に求め得る為実用的であり，ピーク面積比は分析条件に影響され難い点でより精確である。濃度は，トルエン 10cc. 中のベンゼン量を，その空気中にあつた時の濃度（ppm.）と採気量（l）との積で現わした。各組の捕集瓶の効率は(1)式で，採気した空気中のベンゼン濃度は(2)式で与えられる。(1)，(2)式に於て，C_1，C_2は夫々一組の捕集装置内の二つの瓶中のベンゼン濃度，Eは捕集効率，V は採気の終点に於ける溶液量，　Vは全採気量，t は温度である。

結果は第2表に示した。

結果に示された様に，No. 5は，効率が高く，ばらつきが少い為，最も捕集瓶として適したものであつた。

捕集効率が高くなる為には，次の様な条件が考えられる。

(1)　空気中の蒸気が溶剤に溶解し，気液平衡に達するに充分な気液接触時間及び接触面積があること。No. 1に較べ，No. 2，3，5のガラス玉はこの点を改良したと云える。

(2)　一度溶解した蒸気が，気液界面に部分的に濃縮されず，速に液相内部に拡散すること。気液界面に濃縮されていると，再蒸発によつて逃げる部分が多くなるからである。

(3)　気泡の発生状態が安定していること。No. 1はこの点で良好でなく，構造的な不揃が効

率にも影響していると思われる。ガラス玉はこの点も改良している。

No. 4 は細い気泡を発生するが，通気抵抗が大きく，効率が低い為，実用に適さない。気液接触時間を更に大きくすれば改良されるであろう。

No. 6 は，粉塵捕集用として効率が高いが，高流速でミストを発生させる機構はガス捕集には適さなかつた。気液平衡に達するには流速が速すぎ接触時間が不足したと思われる。

全採気量が，捕集率に影響することも，No. 2 を用いた二つの結果から明らかである。この効果を第 4 図で説明した。曲線 A は蒸気が完全に溶液中に捕集された場合である。しかし，最も理想的な捕集瓶を用いても，液相濃度が高まるにつれて，その濃度に対応した量の蒸気が採気後の空気中に残るので，この量を差し引いた場合が曲線 B である。実際の捕集瓶は，更に低い量しか蓄積しないであろう。これが曲線 C である。効率は c/a で現わされる。もし分析感度が高く，換気量が小量でよければ，この範囲では三曲線はほぼ一致し捕集率は高い。又気液平衡に充分達する様な構造の瓶を用い，捕集温度を低下して平衡を移動すれば，c/a を 1 に近づけることが出来る。

この方法をテストする目的で，某染色工場の有機物蒸気を測定した。トルエンとメタノールを溶剤とし，No.5 の捕集瓶を用いた。二つのクロマトグラムの比較から，溶剤ピークに重さなる部分の成分についても分析を行つた。第 5 図にクロマトグラムを，第 3 表に結果を示した。

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NITROGLYCOL POISONING IN AN EXPLOSIVES PLANT

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In Japan, four fatal cases presumed as nitroglycol poisoning were reported for two years from 1959 to 1960. These are the first reported cases of nitroglycol poisoning in Japan, although if thorough investigation be carried out, there would be found more fatal cases. Until the occurence of these victims no preventive measures for nitroglycol poisoning were taken. Labor Standards Bureau, Ministry of Labour planned to take an administrative steps against nitroglycol poisoning, and by the request of the Bureau we have studied on the health of workers and environmental conditions in an explosives plant, though in very short period. In this plant, no fatal cases but three severe cases were experienced. Mixing rate of nitroglycol increased gradually from 30 % in 1955 to 50~60 % after 1958, and when we investigated the plant, it was 40 %. Small amount of nitroglycol was also used before 1955, but the exact mixing rate was not clear.

CASE HISTORIES

Case 1. T.S. a 36-year-old man. He had worked in this plant since 1953, and as dynamite extruder since 1956. For about ten days after he began to work in the extruding house, he felt headache, but soon was accustomed to it. And he had worked healthy till an attack in summer of 1960.

On the morning on Monday, July 11, 1960, before the breakfast, he felt a weakness of the arm and stiffness of the shoulder, then headache and tightness of the breast, and soon fell unconscious. He recovered after about 20 minutes and perspired profusely.

Case 2. G.S. a 44-year-old man. He had been engaged in explosives manufacture in this plant since 1937, and had worked as dynamite extruder since 1955. He had headache for about half a month after he began to work as extruder, and occasionally he felt weakness of the arm, oppression in the breast, and nausea on the morning in May and June of 1960.

On Monday morning, July 18, 1960, when he was reading a newspaper before the breakfast, he felt weakness of the arm, heaviness in the breast and nausea, and soon lost consciousness. After the injection of some medicament by physician, he recovered consciousness and sweated profusely. On the next morning he suffered again from the same symptoms as on the previous day, but consciousness was not lost. On the 20th July, he had same but slight symptoms, and he went to hospital.

Case 3. S. S. a 46-year-old man. He had worked in this plant since 1943, and as

dynamite extruder since 1956. He had worked healthy after accustomed to headache, and his only complaint was the lowering of tolerance to alcohol. He took a holiday on Monday August 22, 1960, and so he was free from the work for two days. In the early morning of Tuesday, August 23, 1960, when he had sat down for the breakfast, he felt cold in head, and lay down. But the symptoms were not improved and he felt nausea. Then he went to lavatory expecting the improvement of the symptoms after defecation, and there he felt a severe tight sensation in the breast and fell unconscious. Soon after, he recovered consciousness and sweated on the whole body. He had no attack on the 24th August, but on the 25th he suffered from the same symptoms except unconsciousness.

It may be noticed that these three cases occurred among the workers in dynamite extruding house. In this plant, extruding work seemed to be particularly prone to produce poisoning. This may be explained by the fact that the evaporation surface of gelatinous dynamite is great and nitroglycol and nitroglycerine are absorbed through the skin in addition to by inhalation, as the workers handled the gelatinous dynamite with the naked hand.

BLOOD PRESSURE AND SUBJECTIVE SYMPTOMS OF WORKERS

We had examined the blood pressure and subjective symptoms of the workers who seemed to be heavily exposed to nitroglycol. The blood pressure was measured before and after the work on Monday in consideration of the acute nitro-effect. Data are shown in Fig. 2 (P.63). As seen in the Figure 2, the systolic blood pressure was much lower than the mean value of Japanese, but the diastolic did not show any remarkable difference from normal value. It was not yet decided whether this low systolic pressure was produced by nitro-compounds or was the common symptom of the residents in this district. The changes of blood pressure before and after the work are shown inFig. 3 (P.64). After the work, systolic pressure was lowered, diastolic raised, and the pulse pressure lowered compared with each value before the work. It seems difficult to say that the nitro-effect is responsible to these changes, as normal workers also show such trend of changes in factories where nitro-compounds are not manufactured. And we could not find out any workers having the signs of chronic nitroglycol poisoningdescribed by Forssman et al.

Subjective symptoms of these workers are shown in Table 2. (P.65). Main symptoms were headache, fatigue, palpitation of the heart, pain in the breast, dizziness, nausea, sensory and motor disturbance of the hand, stiffness of the shoulder, menstrual disturbance, and the depression of the tolerance to alcohol. However, some of these symptoms might be caused by other factors.

Symptoms may be divided into two categories, that is, the one is the symptoms similar to abstinence symptoms which appear after the separation from the exposure to nitroglycol, and the other which is observed during exposure.

ATMOSPHERIC CONCENTRATIONS OF NITROGLYCOL VAPOR

For the determination of nitroglycol vapor concentration, the air containing nitroglycol and nitroglycerine vapors was sampled in ethanol and then the solution was quantitatively analysed by colorimetry using phenol disulfonic acid reagent. Concentrations of nitroglycol and nitroglycerine were not determind separately in this method. As vapor pressure of pure nitroglycol was considered by about 100 or more times greater than that of nitroglycerine, the concentration of the trapped nitrates vapors might be considered almost equal to that of nitroglycol.

SAMPLING AND ANALYTICAL PROCEDURE

The air was aspirated by a hand-worked suction pump and sampled in a midget impinger with 20 cc. glass beads of 3 mm. in the diameter and 10 cc. ethanol. The aspirating flow rate was 2*l*/min.. When 20*l* was aspirated, 5 cc. ethanol was newly added in the impinger and sampling was continued till the total aspirated volume was 50*l*. The sampling efficiency of this method proved to be 95±4 % by another experiment.

The sampling solution obtained as described above were poured through a glass wool filter into another impinger to remove glass beads. The glass beads and glass wool were washed with another 5 cc. ethanol and this washing liquid was also added to the sample solution. Clean air filtered by resine dust filter and active carbon was passed through the sampling solution and solvent ethanol was vaporized at room temperature till the total sample volume become 2 cc. Two cc. of phenol disulfonic acid reagent was added to this residue. Then immediately, cooling the solution in water, 20 cc. of 6N ammonium water was added to neutralize the liquid. The optical density of the colored solution was measured in 400 mμ within 30 min. after coloration and the nitroglycol concentration in the solution was determined from the calibration curve.

PREPARATION OF CALIBRATION CURVE

Pure nitroglycol was synthesized by nitration of ethylene glycol in mixed acid and purified by many time washing with water and sodium carbonate solution. Solutions of various nitroglycol concentration in ethanol were prepared as to correspond the concentrations of nitroglycol in the sample solution in which 50 *l*. of air containing from 0 to 1 ppm. nitroglycol was aspirated. They were colored in the same method as in the case of the sample solutions. Calibration curve was obtained from the relation of optical densities against nitroglycol concentrations of these solutions. The curve is described as a straight line in Fig. 4 (P.67).

DISCUSSIONS ON AN ANALYTICAL METHOD

(a) Phenol disulfonic acid reaction is generally sensitive for organic nitrate esters and

inorganic nitrates but insensitive for organic and inorganic nitrites, and nitrates vapors or dusts in the air except nitroglycol, for instance, nitrocellulose and ammonium nitrate, were expected to interfere if any were present at the sampled air. These effects could not be eliminated.

(b) General method of phenol disulfonic acid reaction was modified in some respects. In general, nitrate esters trapped in ethanol solution are hydrolyzed with concentrated potassium hydroxide solution and then the solvent is vaporized at room temperature almost to dryness. The produced nitrate ions are brought to the reaction with phenol disulfonic acid reagent. In this method, hydrolyzation factor must be determined and this factor is difficult to be fixed. In our method, similar to Goldman's method, the solvent was vaporized to 2 cc. at room temperature and the reagent was added. The sample volume after the evaporation influences on the sensitivity of coloration. The influence of the sample volume on the coloration is shown in Fig. 5 (P.68).

(c) During sampling procedure, water vapor is also trapped in ethanol with nitroglycol. To determine the influence of this trapped water on the nitroglycol analysis, the nitroglycol solutions containing from 0 to 50 % of water (0–1 cc. in 2 cc. solution.) were prepared. The optical densities were not influenced with the content of water in the solution.

(d) After the sample solution were colored, the optical density increased with time. Considering this time effect, measurement was performed within 30 min. after coloration. This time effect is shown in Fig. 4 (P.67).

(e) The optical densities of sodium nitrate solution and nitroglycol solution of the same concentration showed good agreement with each other. From this result, nitroglycol in ethanol solution seemed to react completely with phenol disulfonic acid reagent.

ATMOSPHERIC CONCENTRATION OF NITRO-COMPOUNDS

Concentration of nitro-compounds in the air was expressed as nitroglycol concentration. Data are shown in Table 3 (P.68).

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労 衛 研 報 第4号, 58～71 (1960)

某ダイナマイト製造工場のニトログリコール中毒調査

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橋爪　稔　松下 秀鶴　松村 芳美

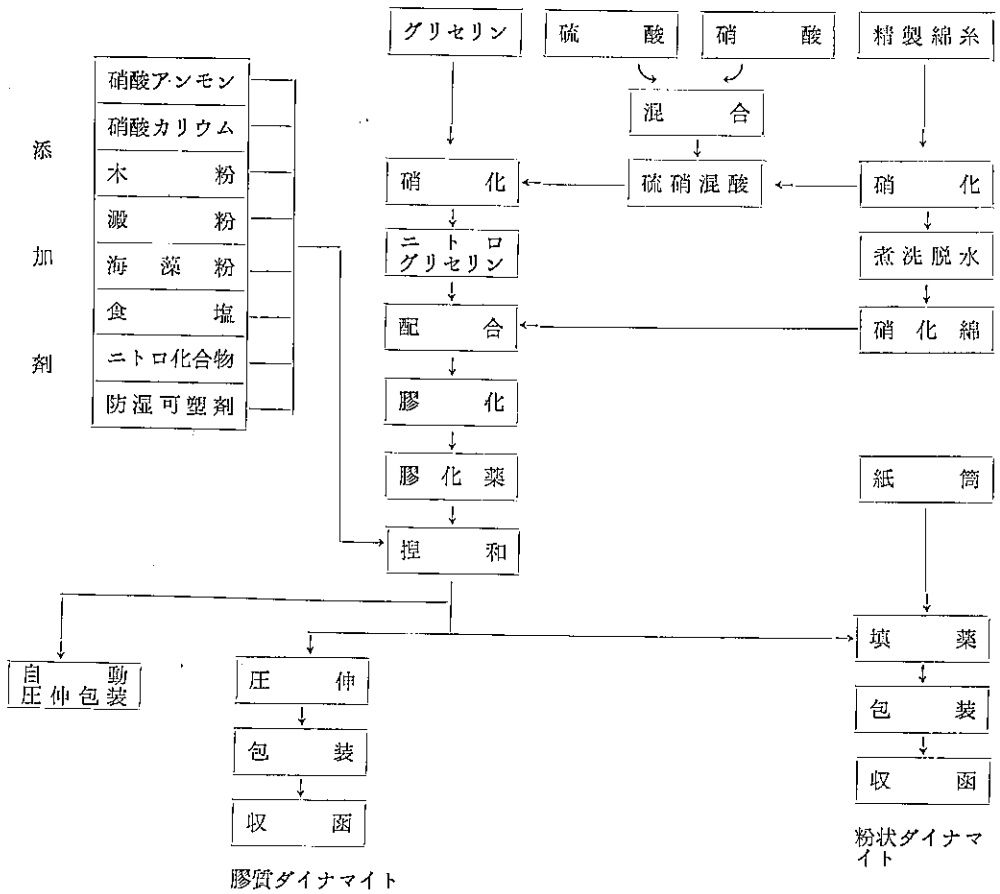
Ⅰ 緒　言

昭和35年，某火薬製造工場において，ニトログリコール中毒と考えられる患者が発生し，更に過去にさかのぼり調べると34年，35年の2年間の間に同工場に於てニトログリコール中毒らしい心臓疾患により4名の労働者が死亡しているので，ニトログリコール取扱工場の実態調査の依頼が労働省からあつた。

日本における主要火薬製造会社は3社であり，製造工場は4個所ある。これらの工場のうち，我々はT工場を選んで昭和35年10月10，11日の2日間緊急実態調査を行つた。

Ⅱ T工場の概略

第一表　ダイナマイト製造工程



工場は製薬工場と原料工場に分かれ，前者で火薬の製造が行われている。このダイナマイト製造工場に働く労働者数は調査時に於て男子 333 名，女子 330 名である。

製造工程の大略は第一表に示した。(第一表)

工場は多数の小工場からなり，それぞれの工場はその周辺を土壁により囲われ誘爆が防止されてある。

各小工場で働く人員は大体20名以下で数名のところが多い。

Ⅲ 現在迄の経過

1. 昭和26年ニトログリセリンで女子に薬疹の発生があり，新入女子工員のうち20～30％罹患した。その当時の会社の嘱託医師の工夫により，ラノリンにニトログリセリンを50％混和して patch test を行うことにより，ニトログリセリンに鋭敏な人を見出すことが出来るようになつたので爾来採用時必らず patch test を実施し patch test 陰性の人のみ採用するようにしたので，現在では薬疹の出るものは殆んどいないという。

2. ニトログリセリンの他にニトログリコールを採用するようになつたのはニトログリセリンの凍結予防のためであるが，ニトログリコールの混入率の比は次の如く逐年増加して来た。

年　次	ニトログリコール混入率
昭和30年	30％
31年	45％
32年	55％
33年以降	50～60％

(昭和30年以前は正確には不明)

これは一つにはニトログリコールの価格の低下にもよる。調査時に於けるニトログリコール混入率は 40％であつた。

3. 戦後工員の間に頭痛の訴えはあつたが，中毒として重要視することはなかつた。

昭和 34年末，労働組合三社協議会から他の火薬工場においてニトログリコールによると思われるような死亡者が出ているので本工場で検討して欲しいという申出があり，工場側でしらべたところニトログリコールはニトログリセリンより毒性が強く，頭痛，食欲不振等の症状をひきおこすことを知つた。

昭和35年夏，圧伸部門から狭心症様の症状を示す三名の患者が発生し，診察した医師より作業に関係があるのではないかと思うと言われた。

現在中毒防止対策を進めるため，薬害対策委員会を作るに至つた。

4. 昭和35年発生した療養を必要とするに至つた 3 症例について

第 1 例：　T．S．(36才)

昭和28年 11月入社し，最初原料工場の T．N．T．製造に従事したが，体がだるくなり，無煙火薬製造に移つた。ここで，28年—31年の間働いたが，体の調子は良かつた。31年以降圧伸に移つた。圧伸に移つてから始めの10日位，頭痛，殊に後頭部が痛く，歩くと頭にひびいて痛く，又頭を振ると痛かつた。朝は痛くないが昼食のため山を降りる時に痛くなつた。然しこの疼痛は辛抱出来ぬという程のものではなかつた。十日程働いているうちに頭痛が感じなくなつた。しかし休みあけの日の昼頃からは痛くなることもあつたが，その翌日は何ともなかつた。その他には異常はなく，元気で作業に従事していたが，本年 7 月に発作がおこつた。

7 月11日　月曜日　朝起床して顔を洗い，暑いのでパンツ一枚で一寸外に出，朝食を食べよ

うと思つて家に入つた時，両腕の力が抜け，肩が凝る感じがし，丁度重しをかけられたような感じであつた。そこで子供を呼んで肩を叩いて貰つたが，少しもよくならぬ。そのうち後頭部が痛くなり，胸がしまつて来て，間もなく失神した。医師が来訪して受診する前に気がついた。気がつくと頭痛もなく手もだるくなかつたが寒気がし冷汗が出て間もなく恢復した。恢復後は普通と全くかわらなかつた，夫人の話では失神の期間は20～30分位であつたという。その後42日間休んだ後，会社に出勤し，爆薬を取扱つたところ，その晩4～5回手がだるく，胸が苦しかつた(胸が少さくなるような感じ）が，失神はしなかつた。

第2例：　G．S．（44歳）

昭和12年5月入社，第一甲薬　圧伸，無煙で働き，昭和30年9月以降圧伸で作業した。

入社後最初は無煙火薬を取扱つたが始めての時は頭痛を覚えた。圧伸に移つてから始めのうちは作業は一日おきではあつたが，前頭並に後頭に疼痛を覚え，歩くとビンビン来た。然し半月位で大体馴れた。それでも夜とか朝に頭が痛かつたり，重かつたりすることもあつたが，会社に来て作業を始めると頭痛は覚えなかつた。先輩の言では圧伸では頭が痛くなるから，その時は外で休み，帰宅したら濃いお茶を呑めと言はれた。濃い茶を呑むと頭の痛みは少しはおさまつた。

昭和35年5月～6月頃に休のだるいことがあつた。これは主に朝感じ，特に休日の翌日というようなことはなかつた。5月と6月の間に1週間に1回又は2週間に3回位次のような症状があつた。即ち，朝座つている時，新聞をもつのも嫌になるくらい，手がだるくなり，手をうしろにつこうとしても手で体が支えられなくなり，胸が重苦しく，嘔気がして来る。この嘔気がおさまると気持がよくなり正常に帰る。朝食前にこうした症状はあらわれたが，又自転車で会社に来る途中，ペタルを踏むのが嫌になり，ものを言うのも嫌になることもあつた。それでも会社に入ると何とも感じなかつた。医師に診断をうけたところ寄生虫だといわれ，回虫，12指腸虫の駆除をうけた。

7月17日の日曜日，畑にリヤカーを引いて行つただけで仕事らしい仕事はせず，一日，テレビを見ていた。7月18日の月曜日の朝起きたときは何んともなかつたが，7時10分頃，食事前に新聞を読んでいると急に手がだるくなり，自分でもんでいた。そのうち胸が重苦しくなり，嘔気がして来たが吐かない。ますます胸がしめつけられ，苦しいなと思つているうちに失神した。医師が来て，注射を打つてから気がつき，全身に冷汗を出して，正常に帰つた。

7月19日(火）に出勤しようと思つたら朝食前再び前日と同じ症状が発現し，胸苦しく，嘔気があり，苦しいなと思つているうちに発汗して正常に帰つた。7月20日更に同様な症状があつたので入院した。

第3例：　S．S．（46歳）

昭和18年4月以来，無煙，圧伸，無煙と働き31年2月以降圧伸で作業して来た。

頭痛にも馴れてしまい元気に作業に従事していた。唯以前は2合位酒が飲めたのが，現在は盃3杯で真赤になり，胸がどきどきするのであまり呑めぬ。発作は今年8月におこつた。21日は日曜で22日は月曜なので月曜日は休暇をとつて2日の休みを在所の旧盆の墓掃除に行つた。月曜日の晩10時頃約5粁の距離を自転車で帰つた時，胸が重苦しかつた，しかしこういうことは前にもあつたので，すぐ治ると思い寝た。

8月23日(火)，6時50分起床，前夜と同様に胸苦しく，気分がさつぱりしない。食事のため坐つたところ頭頂が冷たく感じ貧血のような気がするなと思つた。この時子供から「顔色が真青だ」といわれた。床をのべてもらい休んだが胸がしめつけられるようになり，嘔気がした。

排便すれば良くなると思い便所に行つたが，そこで息の出来ぬ程胸がしめつけられ，ツクバンで終い夫人に連れ出され，立つと共に意識不明におちいつた。気がついた時はふとんの中に寝て居た，然し更に胸苦しいので医師を呼んだ。医師の着いた時はあぶら汗を全身にベツトリかいて恢復した後であつた。その後は正常。

8月24日は正常で，8月25日朝，再び朝食前に同様な発作があり，胸がしめつけられ，胸を切り開きたいような気持がした。しかしこの時は失神することなく，多量の発汗と共に正常に帰つた。

8月26日ＥＫＧ，X線でしらべたが異常はなかつた。

以上が，本人達の述べた症状であるが，発作時，これらの患者を往診した医師の言によると，狭心症の症状であつたという。そして本人達の述べた症状の他に顔面は蒼白であり，チアノーゼのあつたことを附加した。

Ⅳ　血圧並びに自覚症状

当工場の堀田医師が填薬，圧伸，包装の作業に従事する作業員の作業日における血圧を測定した結果は第1図に示した。図中の曲線は厚生省昭和33年度国民栄養調査成績の年令別全国平均である。図に見るように最高血圧は男女共に全国平均に比して著しく低い。最低血圧も又平均値より若干低いように考えられる。脈圧についても同様に男女共平均より低下している。次に我々はニトログリコールえのバロクの比較的多いと考えられる配合(2)，圧伸(18)，捏和(３)，包装(14)，填薬(11)から48名を選び，日曜日に１日休んで月曜日に出勤した時の作業前並びに作業後の血圧をしらべたがその成績は第２図に見るようである。最高血圧は男女共，明らかに低下している。然し最低血圧には全国平均との間に著しい相違がない。脈圧は作業前，作業後共著しく低下している。

そこで作業前と作業後を比較するため，（作業後の値―作業前の値）をプロツトしたのが第３図である。図から判るように作業前に比し，作業後最高血圧は一般に低下し，最低血圧は上昇し，脈圧は低下している。

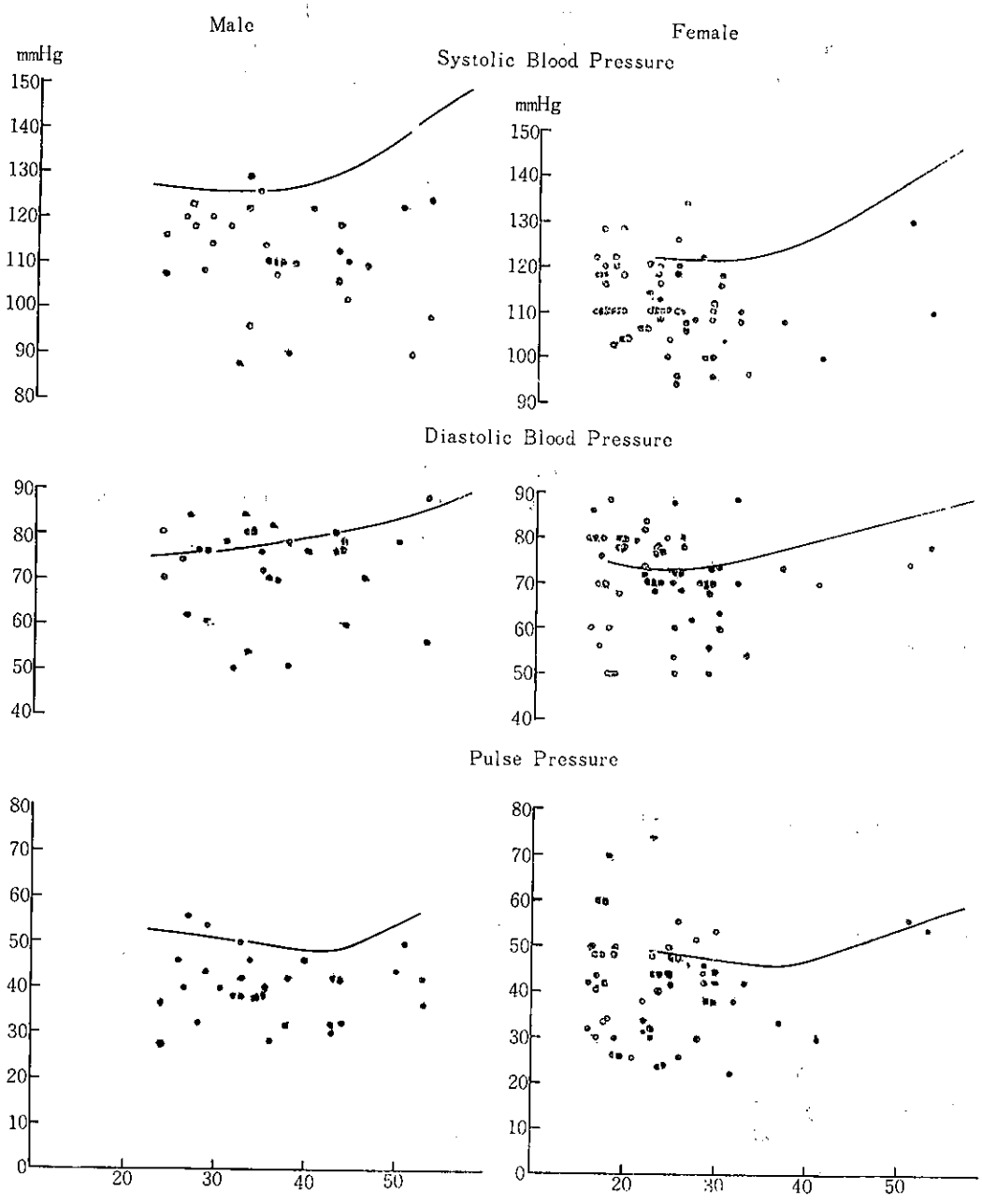
これらの変化が全年令にわたつて均等であるか又は歪があるかは興味ある問題であるが，これらの図からは，一見年令別に変化の様態を異にするのではないかということを示唆する点もあるが，正確にはそのための正しい調査計画にもとづいた資料について吟味すべきであると思う。

一般に昼間作業にあつては，最高最低，脈圧は時間的にW字型の経過曲線を画き，若し朝夕を比較すれば最高血圧はやや低下し，最低血圧は上昇し，脈圧は低下する。従つて，これらの結果から，厳密ではないが，一応高濃度のニトログリコールのバクロから一日離して，ニトログリコールの急性の効果を見ようとしたこころみは，これだけの資料から完全な結論は得がたく，尚詳細な検討が必要であると思う。

自覚症状については血圧検査を行つた上記48名についてしらべ，予め質問表を与えて記入して貰い，後で各人について記入事項についてチエツクした。自覚症状として見られたものは頭痛，倦怠感，心悸亢進，胸部圧迫感，めまい，嘔気，手足のしびれ，手足のいたみ，肩のこり，皮膚炎，生理時腹痛，生理不順，アルコール耐性の低下等である。調査結果は第２表のようである。

1)　頭　　痛

多くの人は休日あけに頭痛があるという。殊に２～３日休んだ後の作業日に強いとい

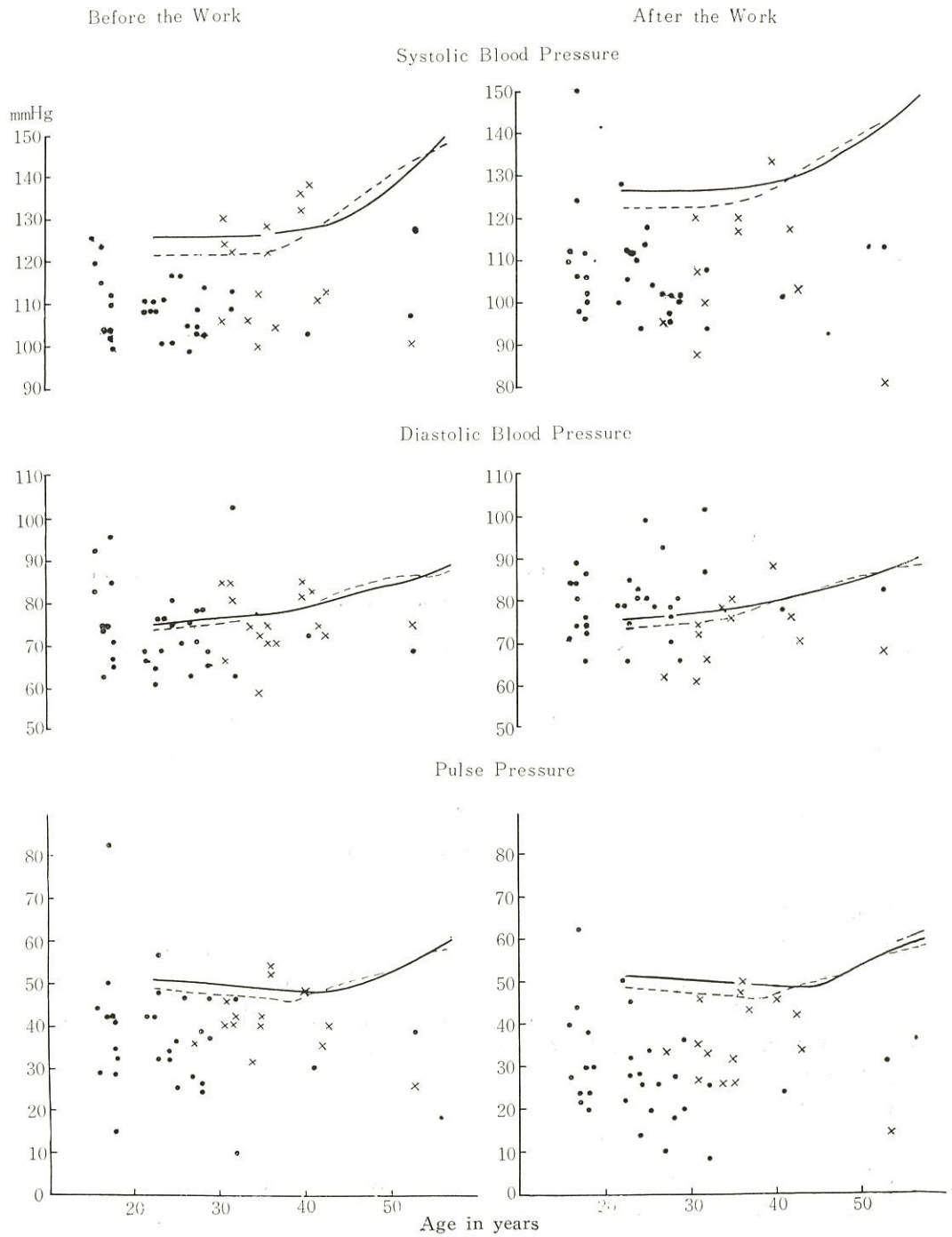


solid line: the mean value of Japanese

Fig. 1. Blood pressure of the workers in cartridging, extruding and packing houses.

う。この作業につき始めの頃に比べては軽くなつたという人が多いが，ひどくなつたり，よくなつたりという人もあるし，又絶えず頭が重いと訴える人もある。

2) 倦 怠 感



× : male worker　　solid line : mean value of male in Japanese
• : female worker　　dotted line : mean value of female in Japanese

Fig. 2. Blood pressure of the workers before and after the work on Monday in cartridging, extruding and packing houses.

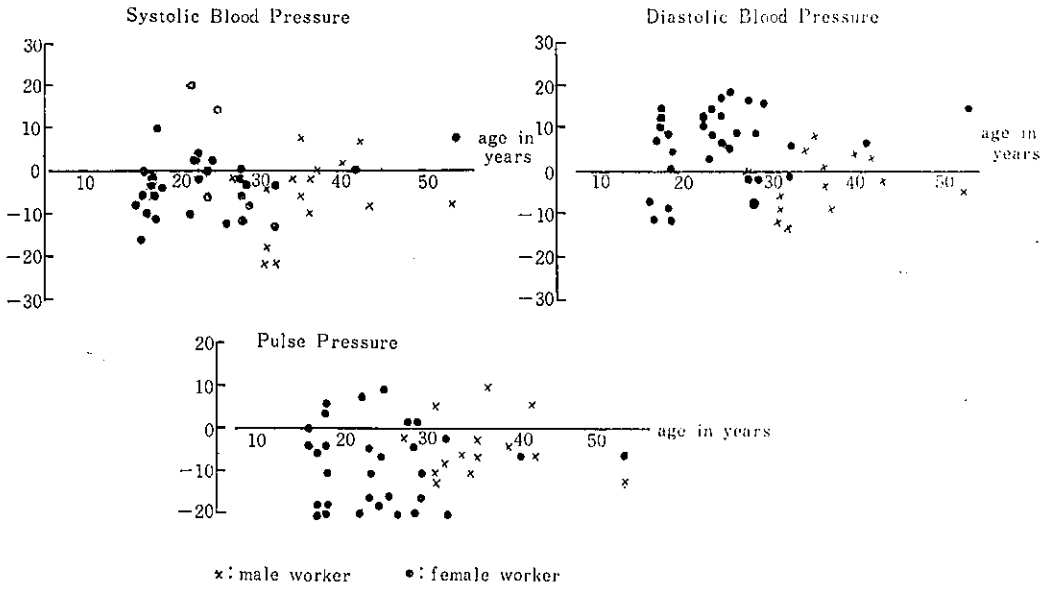


Fig. 3. The changes of blood pressure before and after the work.
The plotted values are the difference of blood pressure before and after the work (plotted values =values after the work − values before the work.)

休業あけの作業日に訴える人があるが，一般には休日あけに限らない。

3) 心悸亢進，胸部緊迫感，めまい，嘔気

作業中心臓がドキドキし，胸苦しく，嘔気があり，一寸休むと治るという人がある。又同時に体のあつつぽくなるという人もある。又時々心臓がドキドキするとか，作業中軽い胸苦しさを覚えるという人がある。又作業中でも家でも時々胸がしめつけられ，めまいがするようなことがあるという訴えもある。しかし，会社出勤の途中，胸が苦しく，心悸亢進があり息がつまるようになることがあり，少し休むと治るという訴えもある。又休日明けの朝，胸部緊迫感を訴える人もある。

4) 手足のしびれ，いたみ

四肢が夜しびれるという人(膠質)，冬両手を湯につけて温めないと自由に動かぬ（寒さのためのカジカムのとは異る）という人(圧伸)，夜就寝中両手がしびれ，そのため目が覚めるという人(圧伸)，手がしびれ折り口が折れなくなるという人（塡薬）等があり，手足のいたみでは，唯手足が痛いという人や節々が痛いという人がある。

5) 生理障害

腹痛又は不順が強くなつたという訴えが少くない。

V 環気中ニトログリコールの濃度

1. 環境中のニトログリコール及びニトログリセリン混合蒸気の定量法

労働環境中にあるニトログリコール及びニトログリセリン混合蒸気の定量方法として，これをエタノール中に捕集し，フエノールジスルフォン酸試薬を用いる硝酸イオンの一般的な定量法を若干改変して用いた。測定結果は，両者の混合総量として測定され，又環境中に他の硝酸塩又は硝酸エステルが存在する場合には，これらの量も測定値に含まれて来ることを

Table 2. Subjective symptoms.

		Number of workers	Number of workers who have had never symptom	Number of workers who have had symptom	Course of symptom from employment to explosives work				
					gradually decreased	constant severity	gradually increased	occasionally	severe after the holiday
headache	No.	48	10	38	7	5	9	6	15
	%		20.8	79.2	15.6		41.7		31.3
oppression in the chest	No.	48	23	25	0	0	6	14	4
	%		47.9	52.1			41.7		8.3
pain in the breast	No.	48	33	15	1	1	3	3	1
	%		68.6	31.4	2.1		14.6		2.1
palpitation of the heart	No.	48	28	20	0	0	7	10	3
	%		58.3	41.7			35.4		6.3
sensory and motor disturbance of the hand and leg.	No.	48	31	17	1	0	7	6	0
	%		64.6	35.4	2.1		27.1		
pain of the hand and leg.	No.	48	32	16	0	0	7	5	1
	%		66.7	33.3			25.0		2.1
fatigue	No.	48	16	32	3	2	13	8	6
	%		33.3	66.7	6.7		47.9		12.5
loss of body weight	No.	48	35	13	1	1	7	1	0
	%		82.9	17.1	2.1		18.8		
menorrhalgia	No.	31	18	13	1	0	6	4	0
	%		58.1	41.9	3.2		32.3		
menoxenia	No.	31	17	14	0	0	10	2	0
	%		54.8	45.2			38.7		

考慮する必要がある。（具体的には粉状ダイナマイト填薬工程に於ける硝酸アンモニア及び我々は測定しなかつたが，配合工程に於ける粉状ニトロセルローズ等）

A. 測　　定

(a) サンプリング

直径3mmのガラス玉を約20ccを入れたミゼット•インピンジャー，ロータ•メーター，手動式吸引ポンプを直列につなぎ，エタノール10ccを吸収溶剤として用いて，2 l/minの流速で，総量50 lの被検空気を捕集した。通気によるエタノールの蒸発減少による捕集効率の低下を防ぐ為，20 l 採気した後エタノール5ccを加えて，採気を継続した。(23°Cに於て50 l の空気をインピンジャー内でバツブルする間に，約5ccのエタノールが蒸発する。)捕集効率は，95±4%であるが，得られた測定値に対しては，捕集効率に関する補正を加えた。

(b) 比色定量法

上記の方法で採取した試料を次の操作によつて定量した。

ミゼット・インピンジャー内のガラス玉を除く為，グラス・ウールを敷いたロートの上から，インピンジャーの内容物を別のインピンジャーに移し，グラス・ウールとガラス玉を，更に5ccのエタノールで洗滌して，これも試料溶液に加えた。ダストフイルターと活性炭層を通して濾過した新鮮な空気を，この試料溶液に通し，バツブルさせて常温で，全体が2ccになるまで，エタノールを蒸発させ，試料を濃縮した。濃縮された試料の中に，フェノール・ジスルフォン酸試薬2ccを加え，直ちに冷却しながら6Nのアンモニア溶液20ccを加えて呈色させ，30分以内に400mμで吸光度を測定した。吸光度と試料濃度との検量線から，試料の濃度を決定した。（第4図）

(c) 検量線の作製

エチレングリコールの混酸による硝化によつて合成し，精製したニトログリコールのエタノール溶液に一定量の水を加えて検量用の試料とした。ニトログリコールの濃度は，上記サンプリング方法で10ccの溶剤中に0～1ppmの蒸気を捕集し，これを2cc中に濃縮した場合に相当する範囲に調整し，2cc中に0.5ccの水（空気中の水蒸気が同時に捕集されたものとして）が含まれる様にした。

B．測定法の検討

フェノール•ジスルフォン酸反応による呈色方法を採択したことについて

フェノール・ジスルフォン酸試薬は，硝酸エステルの定量に度々用いられる他の一方法——グリース試薬による，亜硝酸イオンとしての呈色反応——に較べ，無機硝酸塩の影響を受けるという欠点がある。しかし，他の硝酸エステルが混合している場合の妨害効果は，いづれの方法でも防ぐことが出来ない。唯現場の妨害物質についての状況が測定法を検討する際不明確であつたことと準備期間が短かかつたので取敢えず現場で定量出来る様に，簡単な分析方法として本法を選んだ。比色の感度は，グリース反応による亜硝酸イオンの方が良いが，フェノール・ジスルフォン酸反応に於て，我々は1サンプル中に採気する被検空気の量を多くすることにより，この点を充分補つた。

(d) 検量曲線の作製

濃度——吸光度曲線を作製するに当り，次の様な検討を行いその結果に基いて原法を若干修正した。

i）ニトログリコール又はニトログリセリンをフェノール・ジスルフォン酸で呈色する方法では，一般に，これら被検蒸気を含むエタノール溶液に，先ず苛性カリ水溶液を加え，エステル結合を加水分解して，硝酸イオンを生成させる為の前処理を行い，その後呈色試薬を加える様，指示している。Goldman[1]は，加水分解に際し，硝酸エステルが，ニトリルや亜硝酸イオンを同時に生成することを妨ぐ為，前処理をせずにエタノールを常温で蒸発し，これに呈色試薬を加えている。しかし，常温放置は長時間を要するため，ミゼット・インピンジャー内でバツブルにより常温で，一定量になるまでエタノールを蒸発させることにした。

ii）同一量のニトログリコールを含むエタノール溶液について，エタノールの量を変えてサンプルサイズを変化し，これに呈色試薬を加えると，呈色の感度は，サイズによつて非常に影響され，サイズが大きくなると，感度が落ちた，その比率は，全体量が大きくなることによる稀釈の効果以上であつた。（第5図）

iii) 同一量のニトログリコールを含む，サイズ2cc の試料に，全体の 0～50% (0～1cc) の水を加え，エタノールで2cc に満たして，これに呈色試薬を加え含水量の 呈色に及ぼす影響をみたが，これは有意の結果が得られなかつた。

iv) 0.5cc の水を含む，サイズ2cc の試料につき，呈色試薬を加えて，検量曲線を得たが，曲線全体はよい直線性を示した。呈色した液を常温で放置すると，時間により，曲線は吸光度の大きい方へ平行移動した。そこで呈色した後30分以内に比色することにより，呈色液の時間変化の影響を除いた。尚 0.5cc の水は，20°C，相対湿度70% の空気 50l 中に含まれる水分量に略等しい量である。比色の精度は±10%であつた。

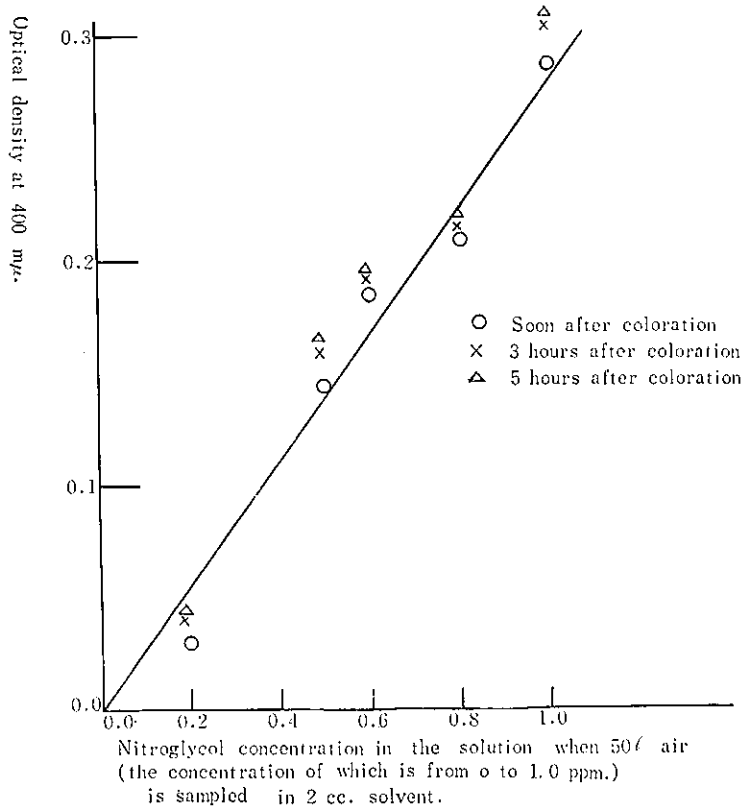


Fig. 4. Calibration curve between nitroglycol concentration and optical density of the solution and effect of elapsed time after coloration on optical density.

v) 濃度の等しい（硝酸イオンの数として）ニトログリコールと硝酸ソーダを夫々含む溶液について比色した結果，両者の吸光度は全く一致した。即ち，ニトログリコール中のニトロ基は，完全に反応しているものと思われた。

以上の結果から，捕集した試料溶液を，常温で2cc に濃縮し，これに呈色試薬を加える方法を採ることに決めた。

C．ま と め

ダイナマイト製造工場に於ける，ニトログリコール，ニトログリセリンの蒸気の環境中濃度を Goldman の方法を若干改変した方法により測定した。もとより測定値は，ニトログ

リコール，ニトログリセリンの混合濃度を示すが，一応これをニトログリコールの量として換算した値で示した。現在作業場ではニトログリコールはニトログリセリンに対して約2：3の割合で用いられているので，ニトログリコールの蒸気圧がニトログリセリンに較べ圧倒的に(100倍位)大きいことを考慮すると，気相ではニトログリコールが殆んどであろうと思われる。この点，他の化合物中にあるニトロ基の影響以外に大きな誤差はないと思われる。

2．測定結果

測定結果は第3表に示した。測定されたニトロ化合物の濃度はニトログリコールの濃度として現わされている。我々の測定値は，測定誤差の範囲で考えられる最小の値であつて，真

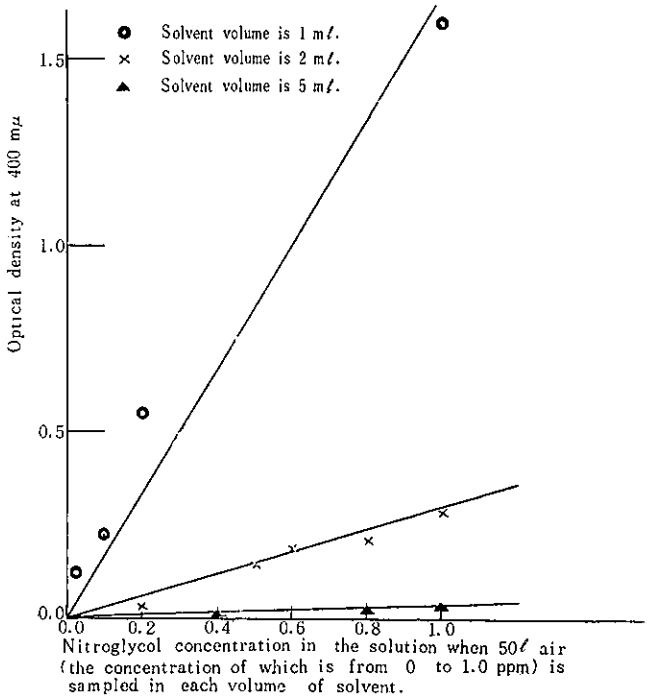


Fig. 5. Effect of solvent volume before coloration on optical density.

Table 3. Atomspheric concentration of nitro-compounds

Working place	Concentration as nitroglycol, ppm
Settling and washing house	0.89
Transfusing house	0.74
Kneading house	0.30
Hand extruding house	0.59
Packing house of gelatinous dynamite	0.60
Cartridging house of powdery dynamite	2.68※

Note : Concentration of nitro-compounds in the air was expressed as nitroglycol concentration.

※ This high value includes perhaps the inorganic nitrates.

値はこの値より10%大きい可能性がある。

Ⅵ 考　　察

1. 発作並びに自覚症状

a) 従来の文献

Symanski[2]はニトログリコールにバクロした労働者に見られる症状として頭痛，食欲不振，酩酊状，頭にベールがかかつたようになる，温熱感，心臓の不快感，アルコールに対する耐性の低下，血圧の異常の低下，遅脈等を上げ，頭痛は新入者又は僅かの期間作業を休んだ後で作業を始めた時に主に感じ，且つこめかみ，後頭部に感ずる。しかし作業を継続しているうちに馴れて，感じなくなるとしている。したがつて独逸では休暇中は作業衣を家に持つて帰つて時々喚いで，休暇明けの頭痛その他の症状を避ける労働者があるという。

Forssman[3]等は従来の文献を綜説しているがこれによると新入工員並びに若干の期間，作業から離れた労働者が再び作業を始める時，しばしば頭痛を，又多くの場合に悪心及びめまいを感ずるとしている。しかしこれらの症状は約4日位続いた後，馴れるようになるという。

これらの症状はニトログリセリンのみにバクロした場合にも見られるが，ニトログリコールに比べると軽症であるという。

時々労働者が1日又は数日，作業から離れた時，普通48～60時間後に，しばしば軽い労作後，典型的な胸痛の出現することがある。この胸痛は強い不安感を伴うことがある。然し軽症の時は，ニトログリコールのない労働環境にかえすと直ちに回復する。しかし疼痛が3～4日間継続することもある。此の発作は一般にニトログリセリン製剤の摂取により，消失する。イタリアでMontecatini工場における経験では休日にTrinitrin-kapselを処方してからは，このような症状は消滅したという。その他ニトロ体による症状中，神経過敏が云われているが，これがニトロ体によるものか他の原因によるものかの区別はむづかしいとしている。又しばしばアルコール耐性が小さくなるということも言われている。

Symanskiはザールランドの火薬工場におけるニトログリコールの中毒に起因すると考えられる3死亡例を報告している。3人共，月曜日，火曜日又は，3日の休暇をとつたあとの火曜日の早朝突然死亡している。二人は会社出勤の途上，一人は起床後それぞれ脱力感を感じた後間もなく死亡している。3人ともそれ迄は健康であつた。三人の死体解剖ではその死因を推定さすような所見は見出されていない。

Symanskiはザールランド以外の状況を報告しているが，原文献が入手出来ないので彼の発表に従うと米国では1927～1936年の間に37人死亡し，その殆どは，1～2日の休日の後で，主として月曜又は火曜日に死亡しており，自転車に乗るとか，かがんで靴ひもを結ぶとかいう軽い労作の時に発作がおこつている。しかもその75%は27～40歳の若い強健な労働者であつた。その他の国では，スコツトランドに6～8例，西独1例が1952年に報告されているので死亡報告は約50例になるとしている。死亡の原因については種々の論議があるが決定していない。

然し，Symanskiの報告によれば，米国では捏和，填薬等の工程では，作業場内ガス濃度を低下さす為，新鮮な空気（冬は温めた）を労働者に送るようにしてから死亡例はなく

なつたとしている。日本では他の某火薬製造会社で昭和33年1月～35年9月の間に4例の心臓疾患による急死例が報告されているが，3名が月曜日，1名が日曜日に発生している。

b)　当工場での経験

以上の報告と当工場での3発作例とを比べると見事な一致が見られる。即ち1～2日の休日後に発生し，強い胸部緊迫感を訴えて，意識を喪失している。第一，第二例では先づ脱力感を感じ（彼等はだるやみと表現）ている。これらの症例をひきおこした原因について，まづこれが，ダイナマイト製造作業に由来することは明らかである。次にダイナマイト製造工程においてニトログリコールの使用量の増加と共に世界的にこうした症例の増加をみたこと，ニトログリセリンに比してニトログリコールの方が圧倒的に蒸発し易いこと，作業場内におけるこれら物質の濃度を低下させることにより死亡例のなくなつた事実，又休日にニトログリセリン製剤を摂取することにより，休日後の障害を除き得た事実等よりして，その作業が爆発に対して不断の注意を必要とするため，絶えず精神的負担がかかるということはあるが，ニトログリコール又はニトログリセリンの長期にわたる吸入，殊にニトログリコールに起因するものと考えてよいと思う。従つて我々はニトログリコールに相当の期間バクロして，頭痛等にも馴れ健康に作業に従事している労働者が，その作業から離れて一定期間（Forssmanによれば48～60時間）後に，脱力感，胸部緊迫感を主とする狭心症様発作をおこし，重症の時は速やかに死亡することがあると考えるのである。又自覚症状並びに発作例のところで述べたように，この発作には軽度のものも存在するのである。作業から離れて48～60時間後の発作の出現が一般には1～2日の休日あけということで発作は月曜日にもつとも多く見られているが，然し，本質はニトログリコールからの離脱後と考えれば，週日にもおこる可能性が考えられるわけである。

次に作業中止後の期間については，本工場の第3例では作業を離れてから5日目にも小発作を経験している点は注目すべきであろう。

上記3例の大発作並びに外国の死亡例では多く早朝発生しているが，その原因は不明である。

作業中止後に出現する発作症状と自覚調査に現われた作業中の胸部圧迫感，心悸亢進，嘔気等を訴える症状とが，同一のものであるかどうかは容易に決定出来ない。次に自覚症状のうちまず頭痛は明らかにニトログリコール摂取に起因すると考えられる。然し頭痛のうち，ニトログリコールによるものとそうでないものとを確然と区例することは困難である。然し作業につき始め，又は休日あけの作業日の頭痛は薬害によるものと考えてよいであろう。手のしびれ感については作業の性質が手先を使用する性質のものであることも考慮に入れる必要があるが，中毒性のものでないと言い切ることは出来ないように思う。その他の自覚症状については，尚多くの研究をまつて決定すべきであろうと思う。

Forssman 等の調査では頭痛と倦怠感が主要な自覚症状として現われているが，本工場でも倦怠感が頭痛に次いで訴えが多く「だるやみ」というように表現されている。

2.　血　　圧

最高血圧の低下はニトロ体の血管拡張，血圧降下の作用を考えると，一応ニトロ体によりひきおこされたものと考えたいが，地域性のものでないということを保証しかねるのでこの点は目下検討中である。

Forssmanはニトログリコールは拡張期圧上昇の慢性効果をもつという，然しこの拡張

期圧上昇は拡張期圧を低下さす急性のニトロ効果のため蔽われて見えないという。我々は一応休日あけの作業前後の血圧変化をしらべたわけであるが，最低血圧は作業後むしろ増加の傾向を示し，最高，脈圧は低下している。しかし，火薬製造以外の一般作業でも血圧の変化はおおむね類似の経過をとると推測されるので我々はこの調査から何等かの結論を得ることは困難であるが，機会があれば労働者を確実にニトロ体から遮断し（家庭でも吸入，接触の可能性は否定出来ない）年令別に変化をくわしく検討する必要があると思う。

Forssman の調査結果でも，同様な調査で若干の異常者を見出した他には休日あけの作業日の作業前後についての血圧調査から認むべきものを見出していない。

3. 環気中ニトログリコール濃度

ニトログリコールとニトログリセリンとを夫々別個に測定する研究の必要はあるが，我々は取敢えずの調査という意味で，5日間の準備期間しかなかつたので，硝酸イオンの一般的な定量法を用いた。従つて測定値にはニトログリコールの他，ニトログリセリン及びその他の硝酸塩又は硝酸エステルも含まれるが，ニトログリコールの蒸気圧がニトログリセリンのそれに比べて約100倍も大きいこと並に両者の使用量の比が約2:3である点を考慮すると，気相中に存在するガス状のニトロ体のほとんどはニトログリコールと考えて大きな間違いはないと思う。我々の調査の結果を検討すると粉状ダイナマイト填薬工室で2.68ppmが最高であるが，この価には無機硝酸塩による影響があると思うので実際の価は，低くなるであろう。次に洗滌沈澱室が0.89ppmであるが，この室には常時作業者はいない。作業者は沈澱槽にたまつたニトロ体を取り出しに入るのみであるが，取り出す作業時に頭痛を覚えている。

この点は低濃度で頭痛に馴れても高濃度にバクロすると再び頭痛を感ずるのではないかとも考えられる。次に移替 0.74　圧伸(手動) 0.59　捏和 0.30である。

当工場に発生したる3名の大発作例はすべて圧伸に発生し，且つ圧伸に作業員の訴えの多い点は注目を要する。ニトロ体は吸入により体内に入るだけでなく，皮膚からも侵入する。圧伸では皮膚からの侵入の機会が極めて多いと考えられる。(従来は手袋を使用していなかつた)。更に圧伸の作業員の年令構成が中年者も含んでいる点に考慮を払う必要があるが，フアンで作業者に送風しているに拘らず，0.59ppmという高い価を示している点には注目を要するかと思う。Yee等[4]の調査では各作業室の平均濃度はニトログリコールとして大体 0.3ppm 以下であつたとしている。Forssman 等の資料では圧伸の濃度が高く 6.3 mg/m³，然し一般には 5mg/m³ 以下になつている。米国の例で見ると技術的には0.3以下に下げることは一応可能のように考えられる。

(協力を頂いた工場の堀田医師に感謝します)

労 衛 研 報 第4号, 72~76 (1960)

市街地、大交通量地点における大気汚染調査

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AIR POLLUTION STUDY AT HEAVY TRAFFIC ROAD

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Katsunori HONMA　Kosuke NOZAKI

東京都から大気汚染調査の依頼を受けた大気汚染調査委員会の一員として，都の大気汚染状況の共同測定に参加した。

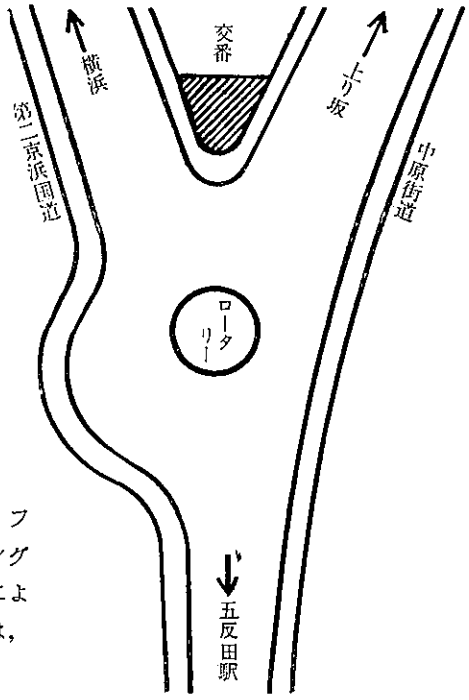
概　　容

我々の班は，昭和35年3月3日，4日の両日に亘り，第二京浜国道と中原街道の分岐する五反田ロータリーに於て，午前8.00から午後7.00まで，ほぼ一時間置きに，気象条件と数種のガスの濃度を，委員会が指定した方法で測定した。

測定項目は次の通りである。

気象条件：気温，湿度，風速，主風向
汚染物質：一酸化炭素
　　亜硫酸ガス
　　窒素の酸化物
　　フォルムアルデヒド

これらの項目のうち，亜硫酸ガス，窒素の酸化物，フォルムアルデヒドの測定は，現場に於いてサンプリングした試料を，当研究所まで即時運搬し，化学的操作による濃度決定は，研究所で行つた。他の項目については，直接現場で結果を得た。



第1図

測　　定

(Ⅰ) 気　　温

自記記録式温度計で，地上約50cmの高さで，風をさけ，測定した。

(Ⅱ) 湿　　度

アッスマン 湿度計及び自記記録式湿度計を併用した。アッスマン湿度計は，地上 150cmの高

さで，風をさけて約3分間羽を回転させた時の値を測定し，自記記録計は地上約50cmの高さで，風をさけて測定した。

(Ⅲ) 風　　速

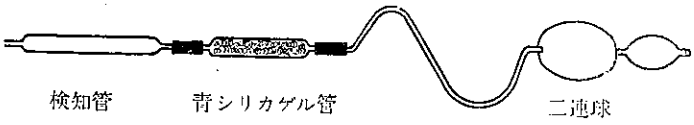
風向に合わせ，ビーラム風速計により，地上約 150cm の高さで測定した。

(Ⅵ) 主 風 向

軽い和紙の吹き流しで大体の方向を知り，ビーラム風速計で，風速の最も大きく感じる方向として，風速と同時に測定した。

(Ⅴ) 一酸化炭素

北川式一酸化炭素検知管C型を用いた。



第 2 図

サンプリングは第2図の様に，二連球，青シリカゲル管，検知管を連結し，二連球で空気を送入した。送入開始時の時間と気温を記録し，二連球を絶えずふくらんでいる様に注意しながら送入を続けた。この間，空気は一定に 10m*l*/min で流入するものとした。

検知管の呈色が，カラー・スケールの0.01%と同じかそれ以上になつた時，検知管をはずし，この時の時間を読み，両端をゴムキャップで封じ，5分後の示度をカラー・スケールで読み，ノモグラフで通気時間と温度の補正を加えて，濃度を決定した。カラー・スケール 0.02%附近で測定する方が，読みが精確になるが，低濃度の時は，時間がかかり過ぎるため，0.01%の所で測定した。又，暗くなつて後の測定は，昼光色螢光ランプの光で行つた。

(Ⅵ) 亜硫酸ガス

トーマス法によつて分析した。吸収溶剤や試料を入れる容器は，微量のアルカリ性物質の溶出による妨害を防ぐため，（ガラス製でなく），ポリエチレン製のものを用いた。

サンプリング

自動サンプリング装置を用いた。これは30分を一周期として――捕集瓶に10cc の吸収溶液を流入し，被検空気を 3*l*/min で 30 分間捕集した後，吸引ポンプが止り，それと同時に電磁弁が開いて，捕集瓶中の溶液を下の小瓶の中に流出する――ことを繰り返す装置である。空気の取り入れ口には東洋濾紙 No. 1 の粉塵フィルターを附けた。

吸収溶剤は，市販の分析用過酸化水素（30%）を稀釈して，H_2O_2 0.003%（wt）含有の溶液を調製し，安定剤として，又CO_2 の吸収による影響を防ぐ為に硫酸を滴下して pH 4.5～5.0 に調製したものを用いた。

濃 度 測 定

SO_2の溶解した溶液の入つた小瓶の中に，BCG–MR混合指示薬（0.1% Bromcresol green の alcohol solution 3 容と，0.2% Methyl red の alcohol solution 1 容とを混合したもの）0.1cc を精確に加え，1/250 Nの Borax 液で滴定した。変色点で指示薬は赤から緑に鋭敏に変色する。各サンプルの Borax 消費量から，ブランクの Borax 消費量を差し引いた量を $x$cc. とすると，吸引空気中の SO_2 濃度は次の式で示される。

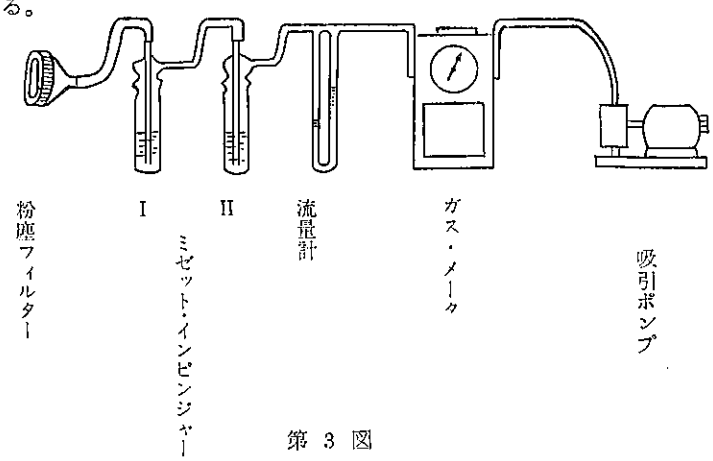
$$44.8\times\frac{x}{\text{吸引空気量}(l)}=SO_2 ppm$$

但し，捕集瓶の効率については，明らかでないので，その補正は委員会に委任した。我々のデータは補正される前の値である。

(Ⅶ) フォルムアルデヒド

5%の亜硫酸水素ナトリウム液に吸収し，クロモトロプ酸ナトリウムによる呈色で比色定量した。

サンプリング



第 3 図

装置は第3図の様に，粉塵フィルター，ミゼットインピンジャー二本，流量計，ガスメーターを連結し，吸引ポンプで引いた。粉塵フィルターには東洋濾紙 No. 1 を用いた。ミゼット・インピンジャーを二本用いたのは，捕集効率を，各試料毎に求める為である。各ミゼット・インピンジャーに，夫々5%亜硫酸水素ナトリウム溶液 4 cc.，及び水 2 cc. の計 6 cc. を入れ，3l/minで30分間吸引した。その後捕集溶液を摺合共栓付試験管に移した。

濃度測定

試料溶液の 1 cc. を大型（30cc.）試験管に移し，氷水で冷却しながら呈色試薬（硫酸20cc. 中に 0.1g/cc.aq のクロモトロプ酸ナトリウム液 0.4 cc. を，水冷しながら加えたもの）を 3 cc. 加え，充分混和して，薬包紙で軽く覆い，沸騰水浴中で10分間加熱後，15分放置冷却して，波長570mμの光で，吸光度を測定した。濃度は各試料につき比色の補正曲線から求めた値に，捕集効率の補正を加えて得た。即ち同時に得られた二本のミゼット・インピンジャーの溶液濃度を C_1，C_2 とし，両者の捕集効率が等しいとすると，真の（捕集効率100%の時の）濃度は

$$C=\frac{C_1^{\,2}}{C_1-C_2}$$

の式に従つて得られる。加熱する時薬包紙で覆つたのは，溶解しているフォルムアルデヒドが，反応する以前に蒸発し，同時に処理している他の試料に再溶解することを防ぐ為である。

(Ⅷ) 窒素の酸化物

大草，多田の方法によつた。（【環境の有害物測定法】 290 頁参照）

サンプリング

装置はフォルムアルデヒドの場合と同様である。吸収溶剤としてN/10苛性ソーダ溶液 10cc. を用いた。3*l*/min で10分間採気し，採気後，試料溶液を摺合共栓付試験管に移し，3時間以内に測定した。

濃度測定

試料溶液の4cc.を試験管にとり，2cc.の呈色試薬を加えて20分後に波長 545mμの光で吸光度を測定して，比色の補正曲線から濃度を決定した。捕集効率による補正もフォルムアルデヒドの場合と同様にした。呈色試薬は (a) N-(1-naphthyl)- ethylenediamine dihydrochloride 1g, (b) P-aminobenzene sulfonamide 4g (c) tartaric acid (結晶) 95g を夫々デシケーター中で乾燥し，混合して乳鉢で粉砕したものを，日光を避けてデシケーター中に貯え，必要に応じて，これを 15g/dlの水溶液にしたものを用いた。

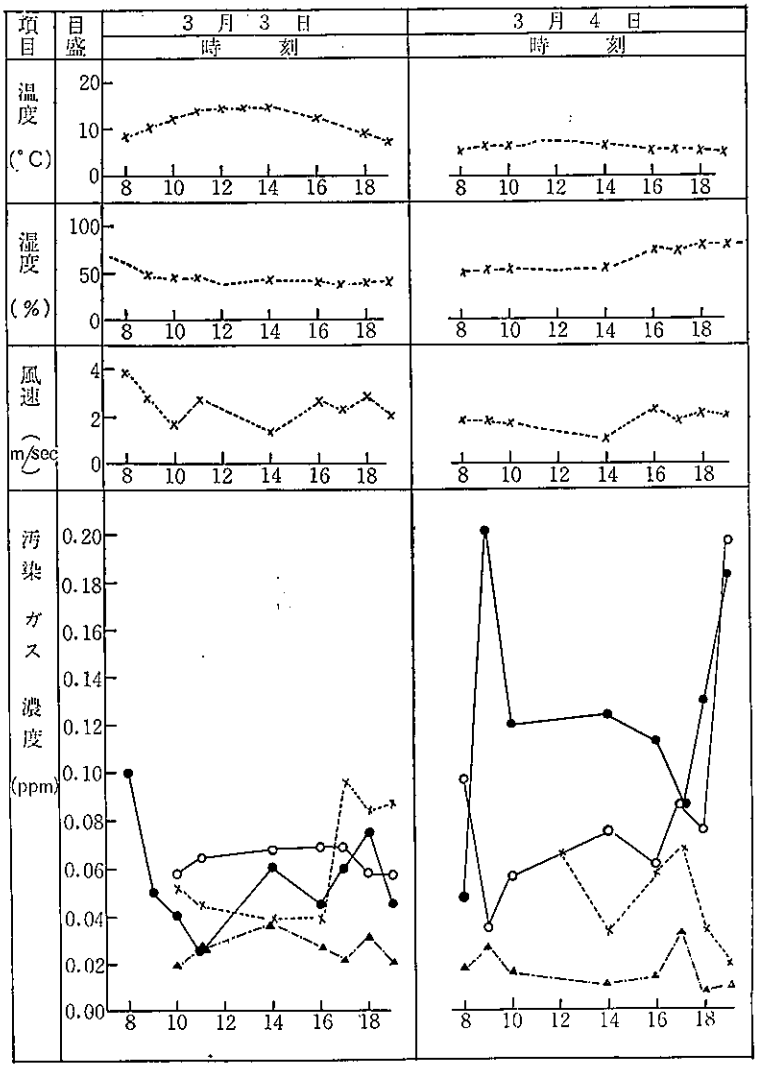
結　　果

第　一　表

月日	時	気温 (°C)	湿度 (%)	風速 (m/sec.)	主風向	CO (ppm.)	SO_2 (ppm.)	HCHO (ppm.)	NO & NO_2 (ppm.)
3月3日	8	8.8		3.9	*NNW*	10.0	①	①	①
	9	10.0	49	2.8	*N*	5.0			
	10	12.0	46	1.6	*N*	4.0	0.052	0.057	0.019
	11	13.7	45	2.7	*NNW*	2.5	0.045	0.064	0.027
	14	14.1	43	1.3	*NNW*	6.0	0.039	0.068	0.036
	16	12.2	41	2.6	*SW*	4.5	0.039	0.069	0.027
	17	9.9	38	2.2	*N*	6.0	0.097	0.069	0.022
	18	9.1	39	2.8	*NNW*	7.5	0.084	0.058	0.032
	19	7.9	41	2.0	*N*	4.5	0.087	0.057	0.020
3月4日	8	5.6	49	1.8	*NNE*	4.8	②	0.097	0.018
	9	6.4	53	1.8	*NNE*	20.2		0.035	0.027
	10	6.7	53	1.7	*NNE*	12.0		0.056	0.016
	12						0.066		
	14	6.4	53	1.0	*NNE*	12.4	0.033	0.075	0.011
	16	5.7	73	2.3	*N*	11.3	0.057	0.061	0.015
	17	5.4	72	1.8	*N*	8.3	0.068	0.086	0.033
	18	5.1	78	2.1	*NNE*	13.0	0.034	0.075	0.008
	19	5.0	78	2.0	*NNE*	18.3	0.020	0.197	0.011

附　① 停電の為，吸引ポンプが駆動出来ずサンプリング不能となつた。
　　② 自動サンプリング装置の故障の為，サンプリング不能となつた。

第 4 図



附 ガス濃度のグラフに於て，●はCO濃度×10^{-2}，×はSO_2濃度，
○はHCHO濃度，▲はNO 及び NO_2濃度を表わす。

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