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## 発刊のことば

繊維工業から重工業へ、更に化学工業の発達が加わつて、我が国の産業界は過去半世紀の間に目まぐるしい変遷と発展とを続けて来た。それが敗戦という事実につつかつて一時は奈落の底に突き落されたのであつたが、長年培われた底力は戦後の産業界に新しい息吹きを与え、基礎産業は勿論、機械工業にも、或は化学工業にも逞しい復興を示し、時代の寵児である原子力産業にも新しい一步を踏み出そうとしている。

我が国の労働衛生は、当然のことながら、この産業の変遷に伴つて幾多の推移を示して来たのであつたが、戦後労働基準法の施行を契機として、労働衛生行政の浸透と、これに対する労使の理解によつて新しい進展を示して来たのである。然し乍ら、具体的な問題については今なお未解決の分野が多く、且つ産業の推移発展に伴つて提起される新分野についても亦早急に解決しなければならない問題が極めて多い。

由来、我が国に於てこれら労働衛生上の諸問題を解決するに必要な研究は、大正十年に創設された現在の財団法人労働科学研究所を中心として、大学や民間研究機関で活潑に行われて来たのであつたが、戦後の我が国の労働衛生行政の進展に伴い、行政に直結した国立の研究機関を設置する必要性が痛感され、ここに昭和31年8月1日、労働衛生研究所が設置されることになり、翌32年7月6日、研究所の落成をみることになつたのである。

当研究所は現在組織上は研究部として職業病部と労働環境部とがあり、主として各種職業病の病理、診断、予防等に関する研究、労働環境諸条件の測定、不良労働環境の改善等に関する研究を行つているが、研究の内容から考えて、これに携わる研究者の専門も、医学、化学、物理学、工学、鉱物学等各種の分野に別れている。これらの専門家の研究が綜合されて一つの労働衛生の研究が成り立つものと考えられる。そして、これらの研究は労働衛生行政に直結した立場に於て、科学的な基礎となるべきものでなければならない。当研究所に於ては斯る観点に立つて諸種の研究を進めているのであり、ここに研究所研究報告第1号を刊行することになつ

たのであるが、研究所発足以来日猶浅く、研究も未熟なものが多いが、今後斯界の先輩、同僚の方々の忌憚のない御批判、御叱正を仰ぎつつ、所員一同研鑽を重ねて当研究所に課せられた使命を達成出来るように努力してゆきたい。

昭和 33 年 12 月

労働省労働衛生研究所長

山 口 正 義



## STUDIES ON THE PATHOGENESIS OF SILICOSIS

### FURTHER STUDY ON THE DISSOLUTION OF QUARTZ DUST IN WATER

Hiroyuki SAKABE, Kimiko KOSHI, Kenichi MATSUSHIMA\*  
and Isao SHIMA

In the previous paper(1) we studied on the solution of quartz particles in water. It was concluded that colloidal silicic acid as well as molecularly dispersed silicic acid was released from quartz powder into alkaline solution, and the colloidal silicic acid was not formed by the polymerization of monosilicic acid but was formed by the disintegration or separation of quartz particles. This assumption was led from following consideration. Many workers (2)(3)(4) reported that monosilicic acid was polymerized when its concentration exceeded over 100 mg. per liter, and we found colloidal silicic acid in quartz particle suspension in which the concentration of molecularly dispersed silicic acid did not exceed over 0.01%.

Although many authors (5)(6)(7) assumed that the colloidal silicic acid is toxic and may produce silicotic change, it is not yet clear that the amount of monosilicic acid released from quartz particles reaches to the sufficient level for polymerization in vivo. Therefore in view of pathogenesis of silicosis, it is very interesting that colloidal silicic acid is released from quartz particles without polymerization of monosilicic acid, even if the amount of released colloidal silicic acid is small. In this respect, Clelland and others (8)(9) found that quartz particles were dissolved in the forms of molecularly dispersed and colloidal silica, but Paterson and Wheatley (10) did not find colloidal polymerized silicic acid in the quartz extract.

In this report, release of colloidal silicic acid from quartz particles was reconfirmed by blue colorimetric method which is more sensitive than yellow silicomolybdic method used in the previous paper. And the released colloidal silicic acid was investigated with electron microscope and electron diffraction.

King and others (11)(12)(13) stated that the different forms of free silica such as tridymite, cristobalite, quartz and fused silica caused the difference in the intensity of tissue reactions. If molecularly dispersed silicic acid is responsible for the pathogenicity of quartz, it may be expected that the solubility of these polymorphs of free silica must be proportional to their fibrogenic potency. Concerning this problem, King(11) and Paterson(10) showed that the solubilities of these polymorphs of free silica were nearly the same, Schmidt (13) found the high initial solubility rate of tridymite, and Paterson (10) stated that no colloidal silicic acids were

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\*Mitsubishi Metallurgical and Mining Co.

found in any of the extracts.

In this study, release of molecularly dispersed and colloidal silicic acid from the different forms of free silica i.e. quartz, cristobalite, tridymite and fused silica of high purity and equal size was also studied.

## EXPERIMENTAL METHODS AND MATERIALS

### Determination of Silica:

The molybdenum-blue colorimetric method of Kawachi (14) was employed for the determination of silica in solution. This method was based on the reaction of silica with ammonium molybdate at the suitable pH to form the yellow silicomolybdic acid. Reduced colour of this yellow silicomolybdic acid produced under standard condition was calibrated with various concentrations of silica.

#### Reagent;

10% Ammonium molybdate solution

20% Tartaric acid

0.1% Phenolphthalein ethanol solution

n/10 Hydrochloric acid

1, 2, 4- Aminonaphtol sulfonic acid solution

1, 5 gm. of 1, 2, 4, - aminonaphtol sulfonic acid were added to 7 gm. of sodium sulphite(anhydrous) dissolved in 100 ml. of water (A solution). 90gm. of sodium bisulfite (anhydrous) were dissolved in 800 ml. of water (B solution). A and B solution were mixed and adjusted to 1,000 ml. with distilled water.

#### 1. Determination of molecularly dispersed silicic acid

The silicic acid solution to be determined was pipetted into 100 ml. volumetric flask and diluted to 50 ml. with distilled water. 0.2 ml. of phenolphthalein were added to this solution and followed by the adding of n/10 hydrochloric acid until the pink colour discharged. And then 1.25 ml. of 1:1 hydrochloric acid were added (pH of the solution was made from 1.1 to 1.4). 4ml. of ammonium molybdate solution were added to this solution, and allowed to stand for 15 min. at room temperature until the yellow colour of the silicomolybdate complex developed, and then 4ml. of tartaric acid were added. After 2 min., 1 ml. of 1, 2, 4- aminonaphtol sulfonic acid solution was added, and made up to 100 ml. with distilled water. After 1 hr. the intensity of full developed colour was measured at 815 millimicron with Beckman DU spectrophotometer.

#### 2. Determination of colloidal silicic acid

Colloidal silicic acid was determined by alkali-boiling method. (5) 1 ml. of the supernatant and 0.2 gm. of sodium bicarbonate were put into the platinum dish and then diluted to 50 ml. with distilled water. This solution was boiled for 1 hr. Procedures after boiling were the same as the above mentioned. The amount of silicic

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acid obtained in such way is the sum of molecularly dispersed silicic acid and colloidal silicic acid. Therefore the amount of colloidal silicic acid was obtained by subtraction of the amount of molecularly dispersed silicic acid from this sum value.

### 3. Determination of total silicic acid

Total silicic acid was determined by alkali-fusion method. Procedures after fusion were the same as above mentioned.

### 4. Calibration curve

For the preparation of each standard solution, three kinds of silica i. e. Kalbaum's pro analysis  $\text{SiO}_2$ , pure silica obtained by calcination of hydrolysate of ethylortho silicate at  $1,000^\circ\text{C}$  for two hours, and natural quartz were used. Each weighed silica was fused with sodium carbonate, and after cooling dissolved with distilled water to a certain volume.

The calibration curves obtained from these standard silica solutions are shown in fig. 1.

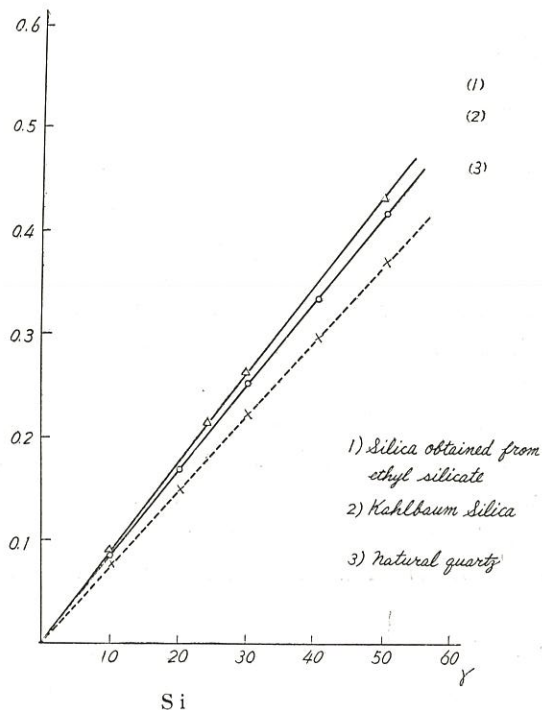


Fig. 1. Calibration curves of various kinds of silica

### 5. Apparatus

In order to eliminate the errors attributable to the dissolution of silica from glass-ware, polyethylene centrifuging tube and bottle were used. Volumetric flask and pipette made of hard glass were used.

## EXPERIMENT 1

The amounts of molecularly dispersed and colloidal silicic acid released from quartz

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particles in a buffer solution of pH 7.3 were measured. Natural quartz (99.8% SiO<sub>2</sub>) was pulverized and the particles which passed through a sieve of 200 mesh were used for the experiment. The pH of solution was simulated to body fluid by using a borate buffer of pH 7.3. 5 gm. of quartz powder were suspended in 100ml. of borate buffer solution. Polyethylene bottles containing this quartz suspension were agitated in water bath of 37°C for 2 hr. daily. After 7, 25 and 40 days, the suspensions were centrifuged at 3,000 r. p. m. for 30 min. and allowed to stand for 24 hr., until fine particles whirled up into supernatant had been precipitated. Concentrations of molecularly dispersed and colloidal silicic acid in the supernatants were measured. Table 1 summarized the data. Colloidal silicic acid as well as molecularly dispersed silicic acid was released into buffer solution from quartz particles, and the amounts of these silicic acids increased with time.

Table 1. Solubility of quartz powder in borate buffer solution of pH 7.3

Time days	7	25	40
Released silicic acid(mg/l)			
Molecularly dispersed silicic acid	9.7	24.0	28.3
Colloidal silicic acid	6.1	7.0	14.0

EXPERIMENT 2

In this experiment, in order to eliminate the possible effect of soaring fine particles after centrifugation of the suspension, relatively large quartz particles about 150 $\mu$ ) collected by water elutriation were used. These particles were suspended in buffer solution of pH 5.18, 6.12, 7.5, 8.18 and 9.10 respectively. All buffer solutions were prepared according to Michaelis' veronal sodium acetate-hydrochloric acid buffer system. 2 gm. of quartz dust were suspended in 50 ml. of each buffer solution and agitated at 37°C for 2 hr. daily for successive 7 days. These suspensions were then centrifuged for 30 min. at 5,000 r. p. m. and were left 24 hr. at room temperature.

Supernatants were divided into three aliquots to measure the amounts of molecularly dispersed, colloidal and total silicic acid by the same method as described previously. In order to eliminate the possible error attributable to fine particles which might be attached to quartz particle, control values were taken in the following procedure; after the suspensions were prepared in the same way as the above mentioned, bottles were agitated vigorously for one minute, and then centrifuged for 30 min. at 5,000 r. p. m. The amounts of three kinds of silicic acid in these supernatants were measured.

The data obtained in this experiment are shown in table 2. As seen in the table, colloidal silicic acid was released only in the alkaline medium, and the amount of



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released colloidal silicic acid into solution increased with alkalinity of the solution. The amount of silicic acid subtracted the amount of molecularly dispersed silicic acid from the total silicic acid may be assumed to be comparable to the colloidal silicic acid. There were not seen marked differences between the amount of colloidal silicic acid obtained by alkali-boiling method and by alkali-fusion method i.e. from total silicic acid.

Table 2 Amounts of silicic acid in the supernatant of quartz powder suspension  
(after 7 days)

pH: initial final	5.18	6.12	7.50	8.18	9.10
Released silicic acid(mg/l)	5.18	6.20	7.80	7.92	—
Molecularly dispersed silicic acid	0	8.5	16.0	27.5	33.0
Colloidal silicic acid	0	0	5.3	5.8	6.8
Total silicic acid	0	8.5	21.8	36.0	42.0
Silicic acid deducted molecularly dispersed from total	0	0	5.8	8.5	9.0

### EXPERIMENT 3

In this experiment, shape, size and crystal pattern of released silicic acid in the supernatant of quartz suspension were observed.

Quartz powder of the size under 200 mesh was suspended in 0.1% ammonium hydroxide solution (pH 10.4), and was kept with occasional shaking at room temperature. After 200 days, the suspensions were centrifuged for 30 min. at 3,000 r. p. m. The supernatant was collected and recentrifuged at 35,000 r. p. m. for 2.5 hr. The precipitated particles were examined by electron microscope and electron diffraction. Electron micrograph shows that the particles of colloidal silicic acid are between 0.3 and 0.01 micron in size (fig. 2), and some of them take a flaky shape. It must be noticed that the fine striations are seen in the particles. Electron diffraction of colloidal silicic acid shows crystalline pattern of quartz (fig. 3)

### EXPERIMENT 4

Solubility rates of quartz, tridymite, cristobalite and fused silica and the amounts of released colloidal silicic acid from these silicas were compared with each other.

Materials:

Quartz: Natural quartz containing 99.8% silica was used.

Tridymite: Quartz powder was mixed with the same amount of sodium tungstate and the mixture was calcined for 2 hr. at 1200°C. After calcination, sodium

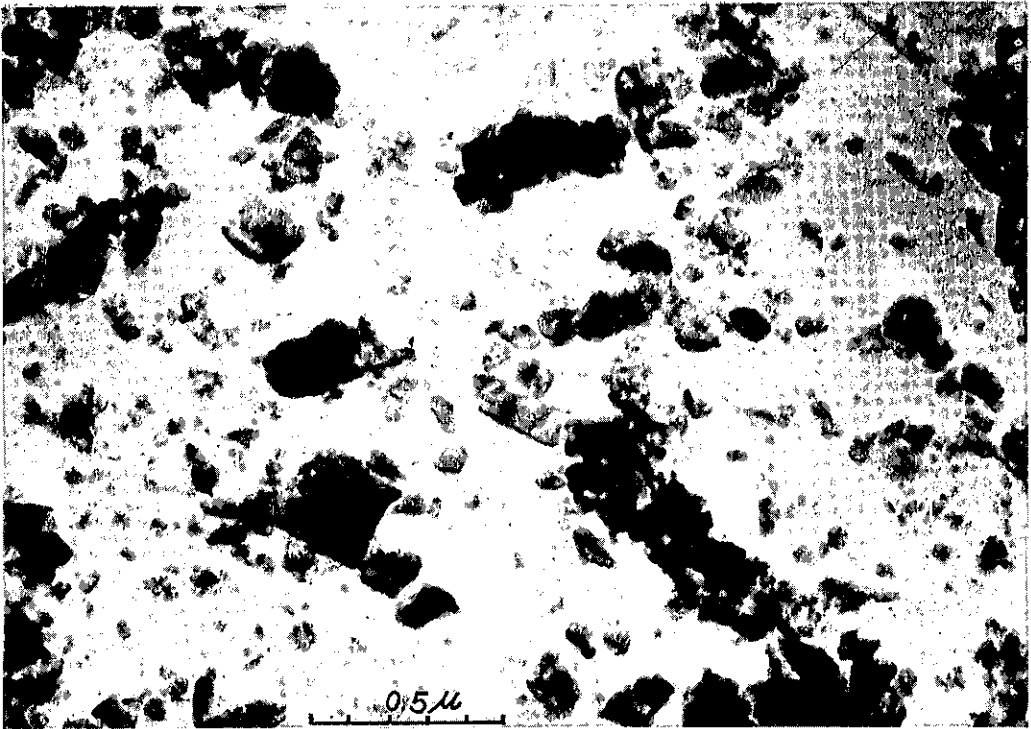


Fig. 2. Electronmicrogram of colloidal silica. Particles seem flaky, and striations are seen in flaky fragment.

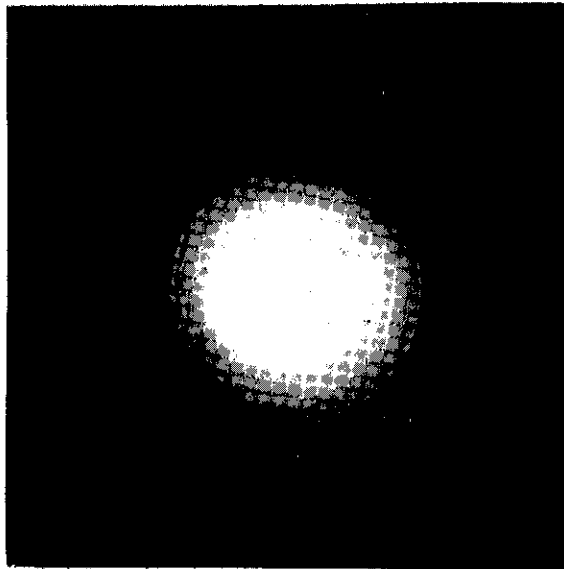


Fig. 3. Electron-diffraction of colloidal silica; Diffraction data shows quartz crystal.

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tungstate was removed by Soxhlet apparatus and then pure crystalline tridymite was obtained.

**Cristobalite:** Cristobalite was prepared by calcination of quartz glass at 1200°C from 4 to 5 hr.

**Fused silica:** Quartz glass was used.

Contamination of the other crystalline material was not observed in each free silica by x-ray diffraction. All silica particles used in this experiment were prepared in the range from 1 to 2 microns by repeated sedimentation in distilled water. To avoid the error which may be caused by the fine particles contaminated in these prepared silica samples, particles less than 0.3 microns were eliminated by centrifugation of the suspension containing these prepared silica samples. The size distribution curves of these silica are shown in fig. 4.

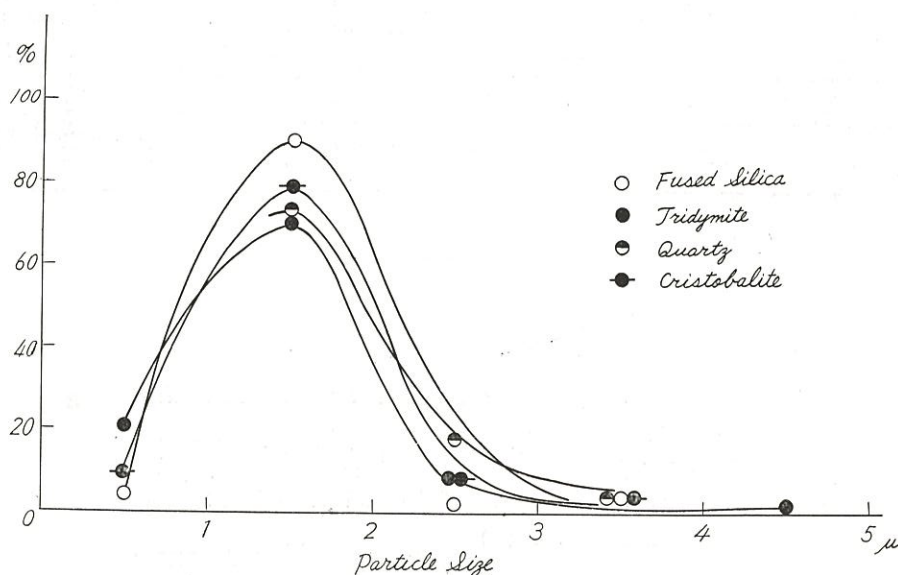


Fig. 4. Size distribution curves of various kinds of free silica

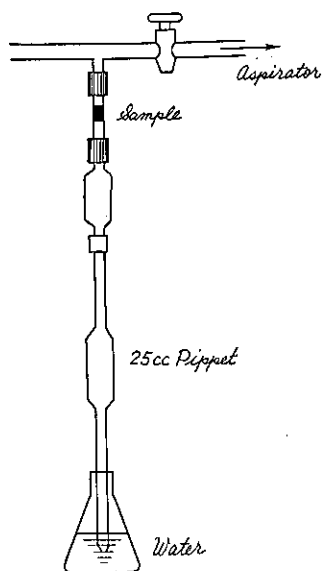
Surface areas of these particles were measured with Pechuchas' apparatus (16) which based on the principle of air permeability. This apparatus is shown in fig. 5, and the measured surface areas of these materials are shown in table 3.

Table 3. Surface areas of four kinds of free silica

Free silica	Surface area(cm <sup>2</sup> /g)
Tridymite	11.71
Cristobalite	6.46
Quartz	12.05
Fused silica	9.58

0.65 gm. of each silica powder were suspended in 15 ml. of borate buffer solution

of pH 7.3 and agitated in a water bath of 37°C for 2 hr. daily for successive 14 days. After 14 days, the suspensions were centrifuged for 30 min. at 5,000 r.p.m. and allowed to stand for 24 hr. quietly. The supernatants were taken for the measurement of molecularly dispersed, colloidal and total silicic acid. The results are shown in table 4. As seen in the table, the amount of molecularly dispersed silicic acid released from fused silica is slightly greater than that from the other forms of silica. However, the amounts of colloidal silicic acid released from four forms of silica were approximately the same.



$$S_w = K_2 \sqrt{\frac{t}{Q_2}} \times \frac{e^3}{(1-e)^2}$$

$$K_2 = \frac{14}{e} \sqrt{\frac{A \times \Delta P}{\eta L}}$$

$$e = - \frac{W}{\rho A L}$$

- $S_w$  = Surface Area (cm<sup>2</sup>/g)       $L$  = Length of Powder (cm)  
 $\eta$  = Viscosity of Air (Pois)       $A$  = Cross sectional Area of glass Tube  
 $\Delta P$  = Difference from (cm) Atmospheric Pressure       $e$  = Specific gravity of powder  
 $Q_2$  = Air Volume passed into the powder on time,  $t$ .       $W$  = Weight of Powder

Fig. 5. The apparatus used for the measurement of surface area of powder

Table 4. Solubilities of four kinds of free silica in borate buffer solution of pH 7.3. (after 7 days)

Free silica Released silicic acid(mg/l)	Tridymite	Cristobalite	Quartz	Fused quartz
Molecul. disp. silicic acid	54.0	50.0	50.5	68.0
Colloidal silicic acid	19.5	18.0	20.3	21.5
Total silicic acid	78.5	73.5	77.3	89.0

### DISCUSSION

The origin of released colloidal silicic acid in the quartz suspension and the possible role of it on the pathogenesis of silicosis was described in detail in the previous paper.

It was reconfirmed that the colloidal silicic acid as well as molecularly dispersed silicic acid is released from quartz particles into the solution of the pH of body

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fluid or of more alkaline medium.

It may be assumed that the colloidal silicic acid may be formed by the separation of very fine particles attached to the surface of quartz particles. But this hypothesis seems to be improbable, as the quartz used in the experiment 2, 3 and 4 was sedimented by distilled water repeatedly and particles less than 0.3 microns in diameter were eliminated by centrifugation. Therefore, it may be assumed reasonably that the colloidal silicic acid was released into the solution from parent quartz particle itself.

The colloidal silicic acid designated by us is the silicic acid measurable only after alkali-boiling in the supernatant of silica particle suspension.

Electron diffraction showed that the colloidal silicic acid contains very fine quartz particles. But, we could not determine whether the colloidal silicic acid is composed of only crystalline particles or it contains both crystalline and amorphous particles.

It is very interesting that some of colloidal silica released from quartz particles in alkaline solution take flaky shape.

Intratracheal injections of the different forms of free silica into the lungs of rats had shown that tridymite produced the most severe pathogenic reaction, followed in descending order of reactivity by cristobalite, quartz, and fused silica (King (11)(12) and Schmidt (13)). If molecularly dispersed or colloidal silicic acid released from silica particles is responsible for the pathogenicity of free silica, it may be expected that the amounts of these released silicic acid relate to the fibrogenic potencies of these polymorphs of free silica. However there was not seen any significant difference in each released silicic acid among tridymite, cristobalite, quartz and fused silica. Accordingly if we take a solubility theory for the pathogenicity of free silica, further study must be directed to the specific solution mechanism in the mesenchymal tissue cells, or to the difference of biological activity of the modifications of free silica in colloidal size range.

## SUMMARY

Dissolution of quartz particles was studied by molybdenum blue colorimetric method which is more sensitive than the yellow silicomolybdic acid method used in the previous experiment.

It was reconfirmed that colloidal silicic acid as well as molecularly dispersed silicic acid was released from quartz particles into the medium adjusted to the pH of body fluid and of more alkaline. This colloidal silicic acid showed a crystalline pattern of quartz by electron diffraction, and some of them took a flaky shape in electron micrograph.

No significant differences of the amounts of molecularly dispersed and colloidal



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silicic acid released from particles among tridymite, cristobalite, quartz and fused silica were found.

### ACKNOWLEDGEMENT

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### 要 旨

## 珪症病因に関する研究

### 石英粉末の溶出について(続報)

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著者らは、さきに水中における石英粉末の溶出について研究し、アルカリ性の溶液中では分子分散状珪酸の溶出と共にコロイド次元珪酸の溶出すること並びにこのコロイド次元珪酸が、単分子型の珪酸の重合によつて生じたものでなく、石英粉末自身から分離し、分散したものであると推定した。この推定の根拠は、多くの研究者の報告によれば分子分散状珪酸は1/中

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100 mg を超える量において存在する時始めて重合するとしているが、著者等の実験では、分子分散状珪酸量が 1 l 中 100mg 以下であるに拘らず、コロイド次元珪酸が石英懸濁液中に見出されたからである。

本報においては前報の実験を再確認するため前報において、珪酸定量のために使用した、黄色珪モリブデン酸法よりも更に感度のよい青色珪モリブデン酸法を使用して実験した。

石英粉末を pH 7.3 の硝酸緩衝液中で溶出さす時、分子分散状珪酸と共にコロイド次元珪酸が溶出し、且つ、両者共、実験期間の長くなる程溶出量の増加することが見られた。

次に溶液の pH をかえることによりコロイド次元珪酸の溶出は、緩衝液の pH がアルカリになる程増加することが判つた。

コロイド次元珪酸が石英粉末に予め附着しており、之が溶液中で離れる可能性を除外するため、この実験では、比較的大きい石英粒子を使用し、且つ同様な溶出実験を極めて短時間に行つたものを対照とした。

以上の実験から、コロイド次元珪酸の溶出を再確認したが、更にこのコロイド次元珪酸を超遠沈により集め、電子顕微鏡でしらべたが、注目すべきはこの珪酸の微粒子の中に薄片状のもの存在することであり、且つ電子線回折では、石英の結晶構造が見られた。

珪肺の病因について分子分散状珪酸が、原因であるとする所謂溶解説は現在多くの反論があり否定的であるが、著者等のコロイド次元珪酸が珪肺をひきおこす原因とみなされうるかどうかについて考察するため、等重量、等表面積のトリヂマイト、クリストバライト、石英、熔融シリカの 4 つについて同様に溶出実験をこころみて見た。其の結果はコロイド次元珪酸及び分子分散状珪酸の両者共、其の溶出量において、以上 4 つのシリカの間には差は見出されなかつた。若し、報告されているように之等のシリカの線維増殖能に差があるとすれば、シリカ粒子から溶出するコロイド次元珪酸の量から之等のシリカの線維増殖能の差を説明することは出来ない。

## STUDIES ON THE PATHOGENESIS OF SILICOSIS

### EFFECT OF DISSOLVED SILICA ON THE RESPIRATORY SYSTEM OF CELLS

Hiroyuki SAKABE, Kimiko KOSHI, Isao SHIMA\*

and

Kenichi MASTUSHIMA\*

Many workers reported the effect of silica on the activity of a number of enzymes, in order to find out the process of silicotic nodule formation.

In the previous paper (1) the effect of silica on respiratory enzymes was studied in rat liver homogenate and in mitochondria isolated from it. It was found from these observations that succinoxidase activity of liver homogenate and mitochondria was not inhibited by any kind of silicic acid such as quartz powder, amorphous colloidal silicic acid and quartz solution. Staudinger (2) examined the influence of quartz solution on the endogenous respiration of liver homogenate and mitochondria, and he demonstrated the inhibition of endogenous respiration in the homogenate or mitochondria of rat liver incubated with quartz solution for 12 hours at 0°C. This phenomenon was not seen on the succinic dehydrogenase activity of liver mitochondria while oxydation of *B*-oxylactic acid in liver mitochondria and activity of yeast alcohol dehydrogenase were inhibited when DPN (diphosphopyridine nucleotide) as coenzyme had been incubated with quartz water. He assumed that phosphor in the DPN might be replaced by silicic acid.

Schlipkötter (4) and Bargman (3) demonstrated electron-microscopically the morphological change of mitochondria caused by the action of colloidal silicic acid. Recently, Rowsel et al (5) found that the respiration of liver homogenate was inhibited from 30 to 70% when the aged silica sol was added, but the fresh sol showed only slight inhibition, and monosilicic acid had no effect.

In 1956, Watanabe (6) found the rapid development of silicotic nodules in the group of rats inhaled quartz dust and exposed to x-ray irradiation, in comparison with control group of rats exposed only quartz dust. Langerova (7) suggested that the so-called activated quartz (quartz irradiated by x-ray) had more toxic effect than nonactivated quartz on fibroblast in tissue culture. It had been generally assumed that toxicity of colloidal silicic acid was higher than that of monosilicic acid. In our previous paper it was suggested that the possible role of extremely fine crystalline quartz particles released from quartz particles in the pathogenicity of silicosis.

In view of these observations, the present study was undertaken to clarify what

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kind of quartz will produce damage in respiratory enzyme system. In chapter 1 effects of various kinds of quartz on the endogenous respiration of rat liver homogenate and in chapter 2 effects of various dissolved quartz on the DPN were examined.

### CHAPTER 1

*Effect of various kinds of quartz and other dusts on the endogenous respiration of liver homogenates of rats.*

#### EXPERIMENT I

##### *Dissolved quartz:*

1), 20gm. of quartz powder were suspended in 500 ml. of ammonia solution at pH 10.5. The suspension was placed in an incubator at 37°C for 3 months with occasional agitation. After discarding into the platinum dish, the suspension was boiled until neutral solution was obtained. The solution was centrifuged for 30 min. at 3,000 r.p.m. and the supernatant was used as dissolved quartz 1.

2), 5 gm. of quartz powder were suspended in 100 ml. of borate buffer solution at pH 7.3 and placed in an incubator at 37°C for 6 months with occasional agitation. The solution was centrifuged for 30 min. at 3,000 r.p.m. and the supernatant was used as dissolved quartz 2.

3), To 500 ml. of phosphate buffer solution of pH 7.4 prepared according to Soerensen, which was employed by Staudinger, 20 gm. of quartz powder were added. Subsequent procedure was same as above mentioned. This supernatant was used as dissolved quartz 3.

4), Quartz powder was placed in the filter paper tube in Soxhlet apparatus and extracted with water for 48 hours. The extract in acceptor was employed as dissolved quartz 4.

##### *Suspended quartz:*

Quartz particles were ground sufficiently and placed in the mix cylinder containing 500 ml. of water. The suspension was agitated and left at room temperature for 96 hours and then the supernatant was employed as suspended quartz.

##### *Powdered quartz:*

Natural quartz of about 1 micron size was used.

The amounts of molecularly dispersed and colloidal silicic acid contained in the above mentioned dissolved quartz or suspended quartz were determined by molybdenum-blue method according to Kawachi(8) and the obtained values were showed in table 1. In the dissolved quartz 3 the phosphor was removed by the method of King(9) to eliminate the error attributable to phosphor ion.

Table 1. Amounts of silicic acid in dissolved and suspended quartz

	A. M. R. silicic acid ( $\gamma$ /ml.) <sup>*</sup>	Colloidal silicic acid ( $\gamma$ /ml.)
Dissolved quartz 1.	84.0	82.0
" 2.	35.0	9.0
" 3.	30.0	20.0
" 4.	35.0	40.0
Suspended quartz	0.0	200.0

\*A. M. R. silicic acid=ammonium molybdate reactive silicic acid

*Liver homogenate:*

Liver excised from male rat was ground in the medium of M/30 phosphate buffer solution with Potter-Elevehjem glass homogenizer.

1.5 ml. of dissolved quartz, 1.5 ml of suspended quartz and 1 gm. of powdered quartz were added respectively to 1.5 ml. of 10% liver homogenate. After these mixtures were incubated at 0°C for 15 hours, endogenous respiration was assayed by Warburg manometer.

As shown in fig. 1, the endogenous respiration of rat liver was inhibited only by quartz powder, but not by dissolved or suspended quartz.

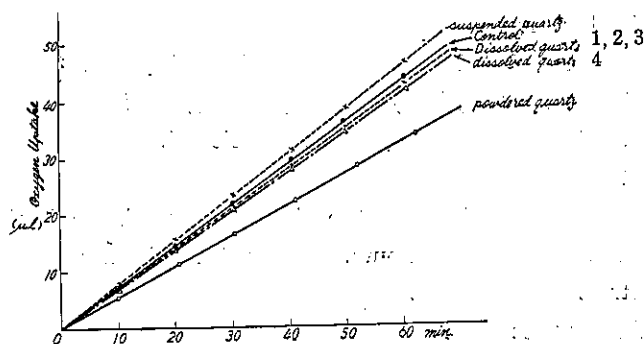


Fig. 1. Effect of various silica on the endogenous respiration of rat liver homogenate

EXPERIMENT 2

In experiment 1, only quartz powder showed an inhibitory effect on endogenous respiration of rat liver. It is assumed that the effect of quartz powder may be attributable to the surface activity of the powder. Therefore, experiment 2 was designed to clarify whether this enzyme inhibitory effect is produced only by quartz particles or by any other particles.

One gram of  $TiO_2$ ,  $ZnO$  and silica gel powder, which were considered far more



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innert than quartz, was added to 1.5 ml. of 10% homogenates respectively. After the incubation of each mixture for 15 hr at 0°C, endogenous respiration was measured. Data were summarized in fig. 2. As seen in the figure, silica gel, TiO<sub>2</sub>, and

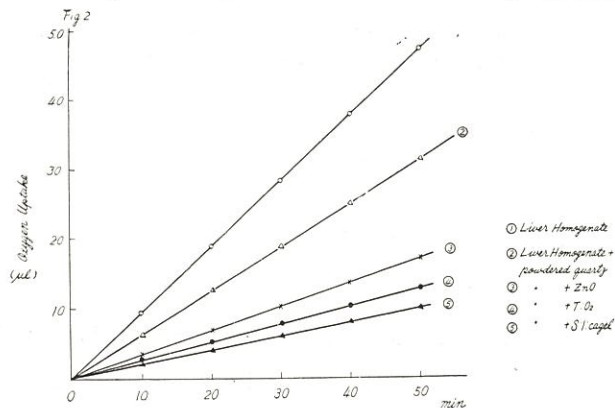


Fig. 2. Effect of various dust on the endogenous respiration of rat liver homogenate

ZnO showed a marked inhibitory effect on the endogenous respiration of rat liver compared with quartz. The inhibitory effect of these powder may be explained by the inactivation of cytochrom c adsorbed on these particles, because we already showed the strong adsorption of cytochrom c on the silica particles. However, the reduction in the rate of oxygen uptake provoked by quartz powder was not recovered by the addition of cytochrom c.

### EXPERIMENT 3

The effect of quartz powder activated by x-ray irradiation on the oxygen uptake of rat liver homogenate was compared with that of nonactivated quartz.

#### *Preparation of the activated quartz:*

Quartz powder was exposed in the beam of x-ray under the condition of 40 KV. 2 mA. and irradiated with 4,000-20,000 r. These irradiated powder showed a clear

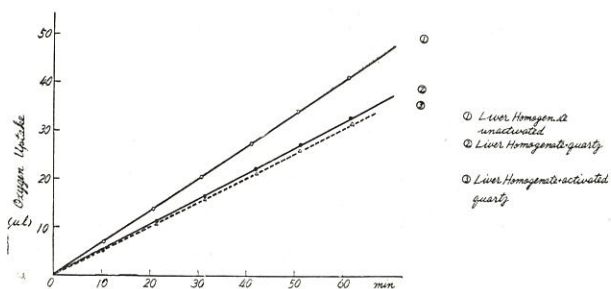


Fig. 3. Comparison of the effect of activated and nonactivated quartz powder on the respiration of rat liver homogenates

afterglow on the x-ray film.

Experimental procedure was the same as that of experiment 2. Data were shown in figure 3. As seen in the figure, no difference was observed between the oxygen uptake of rat liver homogenate with activated quartz and that with nonactivated quartz.

## CHAPTER 2

### *The effects of various silica on DPN*

#### MATERIALS:

- 1) DPN (diphosphopyridine nucleotide):  
DPN prepared by Sigma Co. was dissolved in distilled water. The purity of DPN was about 80%.
- 2) Alcohol dehydrogenase:  
Alcohol dehydrogenase was obtained from dry baker yeast (Oriental Co.), and was purified until the step of acetone precipitation according to the method of Racker.(10) The prepared enzyme was preserved in the form of powder in a refrigerator.
- 3) DPNH (reduced diphosphopyridine nucleotide):  
DPNH was prepared according to LePage's(11) method in which DPNH was obtained by the reduction of DPN with sodium dithionate. DPNH was confirmed by the absorption spectrum.
- 4) Diaphorase (12):  
Lebedow's juice obtained from dry baker yeast was precipitated by 0.33 saturated ammonium sulfate. The precipitate was suspended in 0.167M sodium phosphate dibasic solution and was used as enzyme solution.

#### EXPERIMENT 1

If phosphoric acid in DPN molecule is replaceable by silicic acid under the suitable condition as Staudinger described, the absorption curve of DPN may be changed with dissolved silica. This experiment was designed to examine the possibility of such hypothesis.

To DPN solution was added the dissolved quartz 1 of a half volume of the former solution, and the solution was incubated for 24 hr. at 37°C. The solution without adding quartz solution was used as control. In order to examine the change of DPN after the incubation procedure, absorption curves of the DPN solutions with and without dissolved quartz were examined by Beckman DU spectrophotometer. Results are shown in fig. 4. No significant difference was found between these two solutions. This finding would indicate that the structure of DPN was not altered with

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the solution containing molecularly dispersed and colloidal silicic acid.

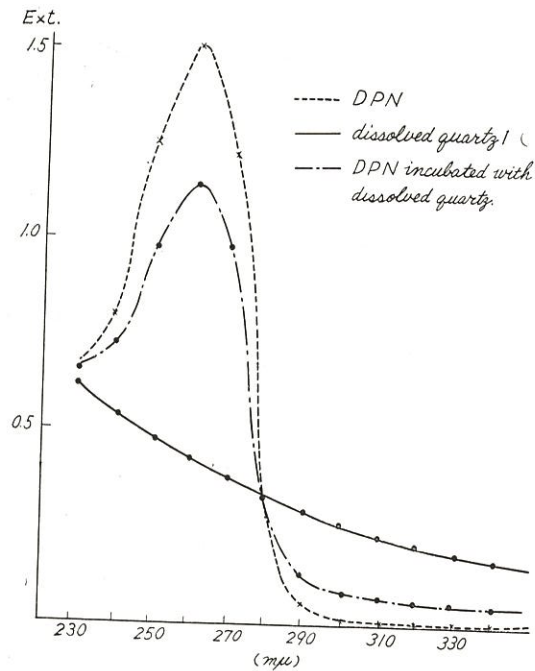


Fig. 4. Absorption Curves of DPN and the mixture of DPN and dissolved quartz 1.

### EXPERIMENT 2

This experiment was designed to study the activity of dehydrogenase system

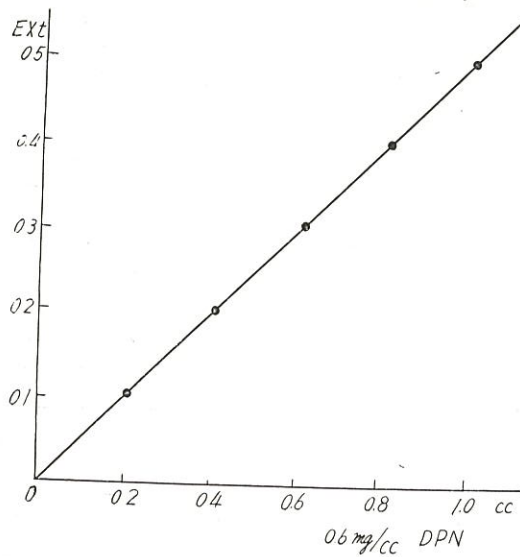


Fig. 5. The Amount of DPNH produced from DPN in yeast alcohol dehydrogenase system

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when DPN, which was incubated with dissolved quartz in advance, was added into the system as coenzyme.

1 mg. of powdered alcohol dehydrogenase was dissolved in 1 ml. of 0.03 M phosphate buffersolution(pH7.5) containing glycine. This enzyme solution was clear. 5% ethylalcohol was used as substrate and 0.5mg/ml. of DPN was used as coenzyme. In order to keep the pH of the solution above 9.0, 1 ml. of 0.03 M sodium pyrophosphate solution was added. The mixture was kept at room temperature and then the value of DPNH produced from DPN by alcohol dehydrogenase was determined at 340 m $\mu$  using spectrophotometer.

The amount of DPNH produced from DPN in this system was proportional to the added DPN. The relation is shown in fig.5.

To each 0.5 ml. of DPN solution were added the dissolved quartz 1,2 and 3 respectively.

These DPN solutions treated with dissolved quartz and untreated control DPN solution were incubated at 37°C for 70 hr. After the incubation, these solutions were added to the alcohol dehydrogenase system. The amount of DPNH was determined. As shown in table 2, the slight increase in the amount of DPNH was observed in the solution containing dissolved quartz 1 compared with the control.

Table 2. Effect of various dissolved quartz on the formation of DPNH from DPN by alcohol dehydrogenase.

Dissolved quartz	Volume of dissolved quartz (cc)	A. M. R. silicic acid ( $\gamma$ )	Colloidal silibic acid ( $\gamma$ )	Amounts of DPNH formed ( $\gamma$ )
Dissolved quartz No. 1	5.00	495	130	139.2
	3.75	371	97	134.4
	2.50	247	65	120.0
	1.25	124	32	120.0
Control	0	0	0	105.6
Dissolved quartz No. 2	0.5	18	5	177.0
Borate buffer only	0.5	0	0	177.6
Control	0	0	0	345.6
Dissolved quartz No. 3	0.5	15	10	307.2
Phosphate buffer only	0.5	0	0	307.2
Control	0	0	0	374.4

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And the production of DPNH was inhibited in the solutions containing dissolved quartz 2 and 3 in which phosphate or borate buffer solution was used as medium. It was assumed that this inhibition was not produced by the action of dissolved quartz, but by the buffer solution, as the inhibition occurred also in the solution buffered by borate or phosphate without dissolved quartz.

Then the possibility of the production of DPNH-X which was suggested by Chaykin (13) was examined on the absorption curves of these mixtures and it was proved that a negligible amount of DPNH-X had been formed.

#### EXPERIMENT 3

In this experiment, the activity of dehydrogenase was measured by the reduction of methylene blue in order to examine the possibility of transfer of hydrogen from DPNH to methylene blue.

1 ml. of the enzyme solution and 0.4 ml. of DPN incubated with dissolved quartz 1 in advance in the same way as experiment 2, was placed in Thunberg tube and 0.5 ml. of 0.01% methylene blue 1 ml. of 5M ethylalcohol and 0.03 M sodium pyrophosphate were put into the side arm cap of Thunberg tube. After evacuation had been completed the tubes were preincubated in the water bath at 37°C. Then the substrate and enzyme were mixed and the reduction time of methylene blue was measured. Data were summarized in table 3. The time for the reduction of the dye was prolonged proportionally to the amount of dissolved quartz added.

Table 3. Decolouring time of methylene blue

Dissolved quartz No. 1			Decolouring time of methylene blue
Volume (ml)	A.M.R. silici acid ( $\gamma$ )	Colloidal silicic acid( $\gamma$ )	
0	0	0	6' 55"
4	396	104	31' 55"
3	297	78	27' 40"
2.4	234	62	18' 50"
0.5	49.5	13	7' 6"
0.2	19.8	5	7' 5"

#### EXPERIMENT 4

As the possibility of injury to the diaphorase system by the dissolved quartz might be assumed, the 4th experiment was undertaken to examine the effect of dissolved quartz on diaphorase.

To 0.2 ml. of diaphorase was added 1.8 ml. of dissolved quartz 1, and the mixture was incubated for 48 hr. at 0°C. As the control, to the same volume of diaphorase was added 1.8 ml. of distilled water. 2 ml. of sample was put into the side



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arm cap. To 1 ml. of 0.5 mg/ml. DPNH in the tube was added 1 ml. of 0.01% methylene blue.

After substrate and enzyme were preincubated for 15 min. at 37°C., the sample in the stopper was tipped into the tube and the reduction time of methylene blue was measured.

No significant difference was observed in the activity of diaphorase between the group containing dissolved silica and the control group.

EXPERIMENT 5

From the data obtained in the former experiment, it could not be explained that the enzyme or coenzyme taking part in the reduction of methylene blue was inhibited by the dissolved quartz. Therefore, the possibility of adsorption of methylene blue on the surface of fine particles in the solution of dissolved silica was investigated in this experiment. To 1 ml. of 0.02% of methylene blue was added 20 ml. of dissolved quartz 1 and the mixture was incubated for 24 hr. at 37°C. As the control, 20 ml. of distilled water was added to 1 ml. of 0.02% methylene blue and incubated under the same condition.

The activity of alcohol dehydrogenase was measured by the time taken to decolorize methylene blue in Thunberg tube and it was found that the reduction of the dye in the group of sample with dissolved quartz took twice time of the control group with distilled water.

DISCUSSION

1) As shown in experiment 1 in chapter 1, endogenous respiration of rat liver homogenate was not inhibited by the solution containing molecularly dispersed and colloidal silicic acid released from quartz particles. But quartz powder inhibited the respiration after the incubation for 15hr. at 0°C. It is interesting that the quartz powder did not inhibit the respiration immediately after the addition to homogenate, as reported in the previous paper, but it did after the incubation for 15 hr. at 0°C. However, as the lowering of respiration was observed when  $\text{TiO}_2$ , ZnO and silica gel powder which were proved to be rather inert were added to the homogenate, the inhibitory effect of quartz powder on the respiration may be considered as nonspecific reaction.

Whether this phenomenon was caused by the adsorption of enzyme or coenzyme on the surface of these powder or by the denaturation of protein on the surface of particles is still obscure.

2) The authors had expected some change in the property of quartz when it was irradiated by x-ray. However, no difference was found in the effect of quartz on the respiration of liver homogenate between the x-ray irradiated and the control.

## EFFECT OF DISSOLVED SILICA

3) From the results of experiment in chapter 2, it was demonstrated that the structure of DPN was not changed by the solution containing molecularly dispersed and colloidal silicic acid.

The formation of DPNH from DPN with yeast alcohol dehydrogenase was not inhibited by the aqueous solution containing silica, but it was done when the phosphate or borate buffer solution was used instead of water. It was assumed reasonably that the inhibition in these buffer solutions was produced by the action of inorganic ions involved, because only phosphate or borate buffer solution without silica showed the same inhibition.

4) When the activity of alcohol dehydrogenase was estimated indirectly by the measurement of reduction time of methylene blue, the prolongation of reduction time was observed in accordance with increase of the amount of silicic acid in the solution. What is the cause of this phenomenon? Dissolved quartz did not injure the transfer of hydrogen from DPN to DPNH, and also not disturb the diaphorase system. From these considerations and experiment 5, the prolongation of reduction time of the dye was assumed to be ascribed to the adsorption of methylene blue on the surface of fine silica particles in the solution.

## SUMMARY

1) The endogenous respiration of liver homogenate of rat was not inhibited by the solution containing molecularly dispersed and colloidal silicic acid of various proportion released from quartz particles.

2) The endogenous respiration of rat liver homogenate was reduced when the homogenate had been incubated with quartz powder. But, silica gel,  $\text{TiO}_2$  and  $\text{ZnO}$  powder showed the same inhibition on the homogenate. Therefore, the reduction of endogenous respiration by quartz was not a specific reaction distinguishing from other sort of particles.

No difference was found in the endogenous respiration of liver homogenate of rat between the sample with x-ray irradiated quartz particles and the sample with un-irradiated.

3) The function and structure of DPN was not changed by the aqueous solution containing molecularly dispersed and colloidal silicic acid.

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## 要 旨

## 珪症病因に関する研究

## 細胞呼吸系に対する溶出石英の影響

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( " ) 松 島 健 一

何故石英粉末が珪肺症をひきおこすかという疑問を解決するために著者等は既にいろいろの方面から研究したが、前報において呼吸酵素系に対するシリカの影響に関して検討し、肝ホモジネート及び遊離ミトコンドリアに、石英粉末、無定型コロイド次元珪酸、溶出石英を添加した直後において、それらの琥珀酸化酵素活性が阻害されない事を報告した。最近 Staudinger らは肝ホモジネート及びミトコンドリアを 9mg/dl の単分子珪酸を含む石英水と 0°C. 12時間 incubate した場合、肝及びミトコンドリアの endogenous respiration を阻害する事を述べ、この現象の原因を DPN (Diphosphopyridine nucleotide) の障害に求めている。又 Rowsel は呼吸酵素系に対して、珪酸の aged sol は fresh sol より阻害作用の強い事を述べている。一般的にいつても、分子分散状珪酸よりもコロイド次元珪酸がより毒性が高いと考えられている。又、前報で著者らは、石英から溶出したコロイド次元珪酸が珪症の原因となりうる可能性のある事を示唆した。又、Staudinger らの用いた 9mg/dl の単分子珪酸を含む石英水は、著者らの経験から恐らくコロイド次元珪酸を含有するのではないかと考えた。

そこで本報において、分子分散状珪酸とコロイド次元珪酸を種々の割合に含む溶出石英を作製し、これら溶出石英及び粉末石英をラット肝ホモジネートとも 0°C. 15時間作用させ、これら肝の endogenous respiration を未処置肝のそれと比較した。結果は、粉末石英を加えた群にのみ呼吸の低下がみられた。しかし、この呼吸の低下は粉末シリカゲル、酸化チタン、酸化亜鉛を加えてもむしろ石英より強くおこるので、石英の特有の作用とは言い難いと考えられる。最近 Langerova は、X線照射を行つた後の石英粉末は、照射しないものに比べ有害作用が強いという結果を出しているので、この点についても前記と同様な実験方法で検討してみた。其の結果は、X線照射により残光をX線フィルム上に示す所謂 "activated quartz" を加えた群と、

## EFFECT OF DISSOLVED SILICA

非照射石英を加えた群との間に酸素吸収の差を見出すことが出来なかつた。

次にこれら溶出石英のDPNに対する影響を検討した。まず、溶出石英と incubate した DPN は、吸収曲線から検討した場合、構造上に変化がおこつたと考えられなかつた。又、これら溶出石英と作用させたDPNは、パン酵母アルコール脱水素酵素系において DPN からDPNHへの水素転移において機能的変化をおこさないと考えられる。又、ヂアフオラーゼ系に対する阻害作用も見出せなかつた。著者らの用いた溶出石英は、単分子珪酸もコロイド次元珪酸も充分量含まれていると考えられるが、結果は Staudinger らのものと一致しない。又、溶出石英の作製方法によつて、作用が異なる事も期待したが、この実験の範囲では、これらの影響を見出せなかつた。

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## DESIGN OF A PORTABLE PHOTOELECTRONIC DUSTINESS METER

Shigezi KOSHI

It has been employed many methods for the measurement of air-borne dust concentration in workshops.

Those methods are classified into the following three categories,

- 1) the measurement of particle numbers per unit air volume,
- 2) the measurement of mass concentration per unit volume,
- 3) the intensity of scattered light by dust particles or the amount of light absorbed by dust particles etc..

For the measurement of particle numbers per unit air volume, jet dust counter (Owens(1), Roken(2), Funken(3), Konimeter (4)(Zeiss), thermal precipitator (5)(6), Settlement counter(7), photoelectronic aerosol counter(8)(9)(10), cascade impactor(11) and impinger(12) can be used.

As the volume of the air collected by these instruments, excluding cascade impactor and impinger, is usually very small, the fluctuation in the counting is unavoidable(13).

Electric precipitator(14)(15), impinger and filter-method (16)(17)(18) are used for the measurement of mass concentration. In many instances, a large volume of sampling air must be collected for the determination of weights of particles caught by these instruments, moreover electric or other power should be prepared for sampling. These powers will, however, not be obtained in some cases such as small stone cutting shop, mine, etc., and occasionally the use of instruments meets with a difficulty.

Leitz Tyndallometer is a well known convenient instrument for the estimation of dust concentration, because of its ease in handling and of needlessness of counting or weighing procedures involved, and results obtained show less fluctuation than that of other methods. Therefore, indirect method are useful in certain cases for the evaluation of dust concentration in an industrial environment especially when it is not required to estimate an absolute dust concentration.

Leitz Tyndallometer was designed originally for the measurement of air-borne dust in mine, where usually very high concentration of dust exists, so that the instrument is inadequate to estimate dust concentration in general industrial environment where relatively small quantity of dust exists.

On the contrary, the portable apparatus invented by author is designed to measure the intensity of scattered light from dust particles with high sensitivity and



## DUSTINESS METER

has an advantage of lightness in weight.

### APPARATUS

The section of apparatus is shown in Fig. 1-A and 1-B, the diagram of electric circuits shown in Fig. 2.

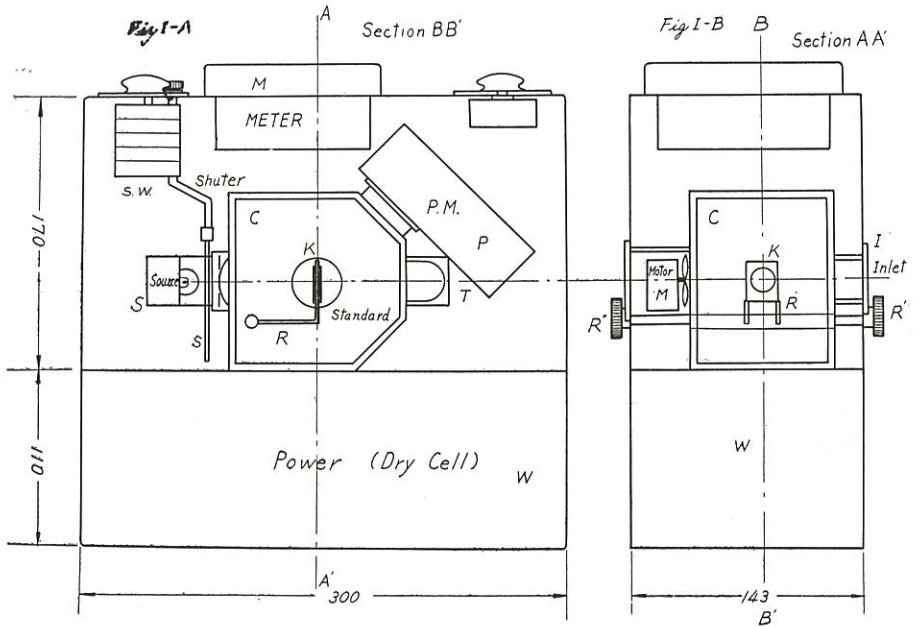


Fig. 1. Section of Apparatus

Fig. 1-A shows the section parallel to the incident beam and Fig. 1-B shows the section at right angle to the light beam.

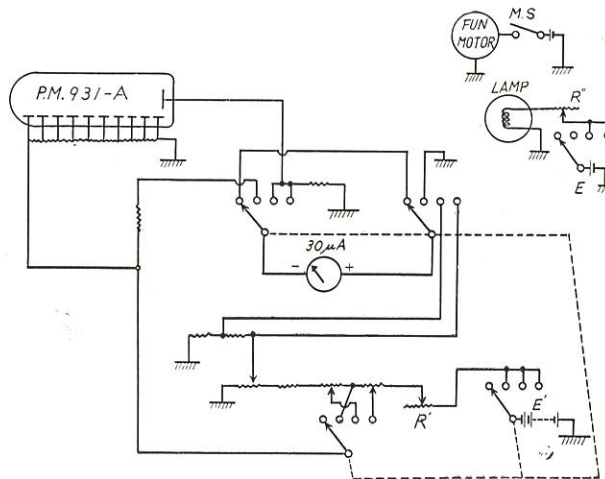


Fig. 2. Electrical circuit of apparatus



## S. KOSHI

The dust laden air is introduced to the chamber C passing through the inlet 1 by the midjet fan with motor M.

In the chamber C, the beam of light from the source S are scattered by dust particles. The scattered light is caught by the photomultiplier P(931-A) mounted at an angle of  $135^\circ$  to the incident beam.

T is light trap for elimination of stray light. The light intensity is adjusted with rheostat R'' in Fig.2, to the fixed value on the microammeter M, under the condition where the standard plate K is set at the right angle to the beam direction. The standard plate is the brass plate with hole to which carefully chafed two thin glass are affixed and fixed on the shaft R which is handled with Knob R''. Only the scattered light, which is scattered from dust particles is caught by the photomultiplier under the condition that the standard plate was removed from the light beam.

Close shutters connecting with knob R are set inside of the inlet and outlet of chamber to avoid the fluctuation of the scattering light intensity caused by the light from the outside of chamber.

As shown in Fig. 2, microswitch M.S connects with the fan motor circuit and starts to rotate simultaneously with opening the shutters.

When the close shutter is opened, the fan motor is driven, and air is drawn into the chamber.

Shutter S is used for the check of zero point of electric circuits.

Dry cells, E and E' are used as electric source for circuit and set in the cell box W, and voltage of E and E' are 1.5 V and 900 V respectively.

Selector switch S.W. is involved five circuits and each circuit has four contact point 1-4: 1-circuit off or shant, 2-adjustment of high voltage for 931-A, 3-adjustment of light strength and 4-measurement of scattered light by dust particles(see Fig.2).

Procedures for the measuring of dust concentration by this apparatus are as follows : after selector switch S.W. is moved to the position 2, the voltage of photomultiplier are adjusted with rheostat R'.

Then, selector switch is slid to the position 3, and the standard plate is set in the light beam. The beam intensity is adjusted with rheostat R'' to a fixed value. After that, the standard plate is removed from the light beam.

After the close shutter is opened with knob R and air is introduced to the chamber, the intensity of light scattered from dust particles are measured ; at this time the selector switch has 4th position and the closed shutter is closed. The relative dust concentration is indicated by microammeter. Approximately 20 sec. is required for all procedures.

### SENSITIVITY AND FLUCTUATION

The sensitivity and fluctuation of the author's apparatus were compared with Leitz Tyndallometer using quartz powder as test aerosol. The size of quartz

## DUSTINESS METER

particle used in this experiment was less than 3 micron in diameter.

Dust concentrations were determined by both apparatus at the same time in the dust chamber after one hour from cloud-up of quartz powder into the chamber.

The measurement was repeated several times at the same dust concentration to estimate the fluctuation involved each methods. The mean values of Tyndallometer reading was inverted to the dust concentration in mg. per cubic meter. Curve 1 shows the relation between dust concentration and reading angle of Tyndallometer, and meter reading of the author's apparatus is shown by curve 2 in Fig. 3.

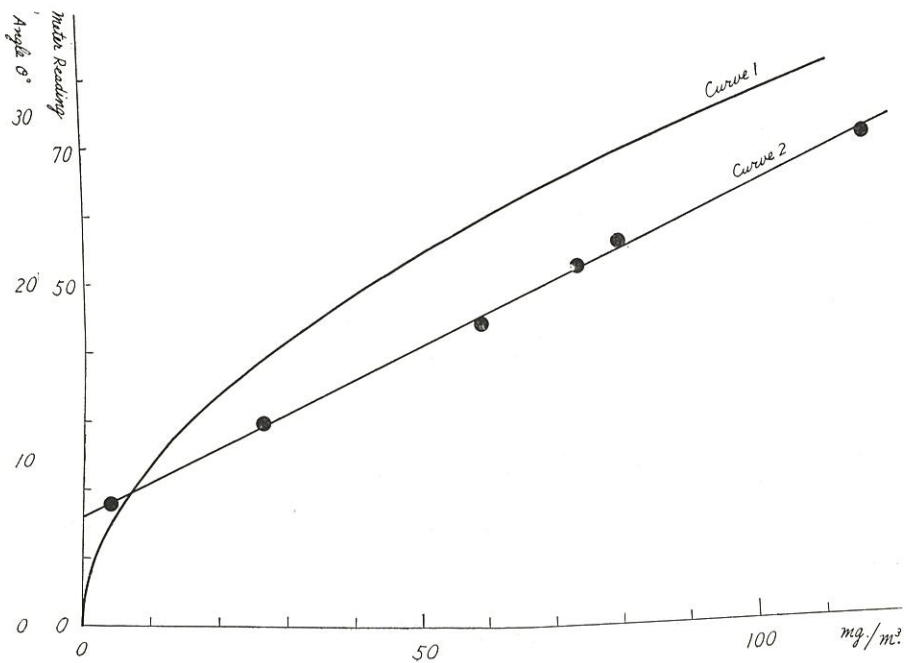


Fig. 3. Calibration curves of Leitz Tyndallometer and new apparatus

On the author's apparatus, the minimum 1 division of meter reading are corresponds to 1.4 mg. per cubic meter of quartz particles.

According to ReyLeigh's equation(19) for particles smaller than wave length of light and Tolman's equation(20) for particles larger than wave length with uniform size particles, it is easy to understand that the intensity of scattered light from dust particles are linerly proportional to the dust concentration represented by weight. In the case of Tyndallometer dust concentration is developed as the function of  $\sin^2\theta$ ; however, in the author's apparatus the meter reading is proportional to the dust concentration.

The fluctuation estimated from several measurements under the constant dust concentration was less than  $\pm 1$  division of microammeter on the author's apparatus and about  $\pm 1^\circ\theta$  on the Tyndallometer with the vernier (1/10). Relatively large

fluctuation obtained in the estimated values using Tyndallometer may be considered due to the inadequacy of dark adaptation of operator's eyes.

On the measurement of dustiness in industrial environment, the complete dark adaptation of operator may not be expected in all times so that the fluctuation of Tyndallometer reading may be assumed to be same order as above mentioned.

The changes of relative errors of dust concentrations are shown in Fig. 4. In Fig. 4, the abscissa is dust concentrations, and the ordinate is per cent errors of apparatus.

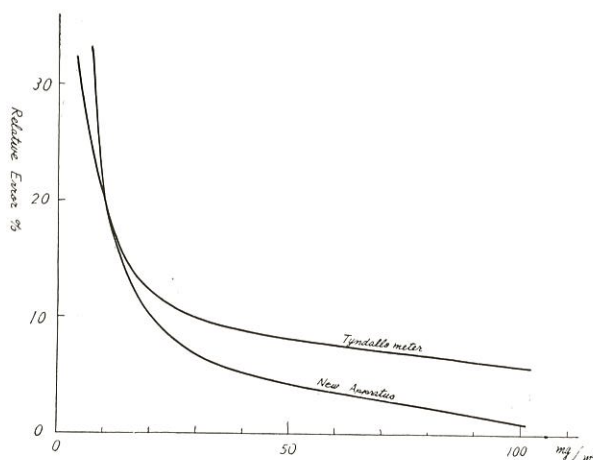


Fig. 4. Relative error of Leitz Tyndallometer and new apparatus

In dust concentration over 10 mg. per cubic meter, the author's apparatus shows less fluctuation than Leitz Tyndallometer.

## DISCUSSION

The theory of the light scattering by spherical particles was described by G. Mie(21) in 1908. He stated that the intensity of scattered light from spherical particle was complicated function depending on particle radius, index of refraction, wave length and direction of incident light. Hence, the absolute dust concentration is not obtained directly by the author's apparatus. However, it has the advantage of simplicity in handling for the measurement of dustiness of industrial environments.

The intensity of light scattered by each particle is influenced by others in high dust concentration; therefore, the meter reading are not linearly proportional to the dust concentration. Sinclair(22) mentioned that particles of uniform size scattered the light independently each other, if the distance of each particle is larger than 10 to 1000 times of the particle radius.

The dust concentration calculated from above mentioned condition is approximately million particles per cubic centimeter for the particle with radius less than 10



## DUSTINESS METER

micron.

Such higher dust concentration is uncommon in ordinary industrial environment.

The effect of interference of each particle may be considered negligible in ordinary dust concentration.

The sensitivity of the author's apparatus can be improved easily by increasing the intensity of the light beam. The maximum sensitivity is expected to be reached without the improvement of electric circuit, to the order of dust concentration of 1 mg. per cubic meter.

## ACKNOWLEDGEMENT

I wish to thank Mr. Kurata, S., Tokyo Electric Corp. for technical advice on the electric circuit.

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S. KOSHI

## 要 旨

### 携帯用光電式粉塵器の試作

興 重 治

労働環境中における粉塵濃度の測定方法は非常に多く、測定して得られる濃度も重量濃度、粒子数濃度或いは粉塵濃度と関係のある物理量で表わしたりする方法等があつて測定の目的に応じて適当なものが選ばれている。

多くの方法は測定時に粉塵濃度を直接知ることができず資料を研究室で測定して初めて濃度を知ることができるようなものが殆んどである。環境測定では測定時に粉塵濃度を直接知ることができる方が好ましく、この点ではチンダロメーターがすぐれている。しかしチンダロメーターは感度が低いことと、測定が目による比色を必要とするところに難点がある。著者は計数や秤量などの手段を用いなくて粉塵濃度を簡易に測定する方法を考案した。

装置に用いられた原理は粉塵粒子による光の散乱光の強度を光電子増倍管によつて測定するものである。

坑内や野外での測定を考慮し、光源、電気回路、小型ファンモーターの電源には全て乾電池を用いてある。

散乱光の強度を読みとるメーターの指針は、粉塵の重量濃度に比例するから、濃度を直読するようにすることができる。

測定器の感度は、石英粉塵に対して、メーターの最小目盛が粉塵量 $1.4\text{mg}/\text{m}^3$ に相当する。但し感度は光源の改良によつて更に上昇させることができる。一回の測定に必要な時間は約20秒前後である。

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## MICRODETERMINATION OF CHROMIUM BY BENZIDINE AND ITS DERIVATIVES

Noboru HARA

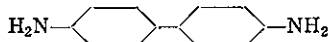
While many methods have been employed for the determination of chromium in air, it is generally accepted that the method using diphenylcarbazid proved to be most satisfactory. (1)(2). However, the author maintained that in this method several disadvantages are involved, such as high cost of reagent, impossibility of restoring as stock solution and so on. The determination of chromium by benzidine and its derivatives has been employed only in qualitative and detective tests because of their unstableness of color(3).

A new method has been devised by the author for microdetermination of chromium by benzidine derivatives as reagents in suitable pH using acetic acid and sodium acetate buffer solution. The procedure of the method is to be described in the present paper.

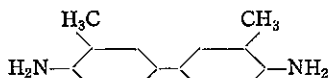
### EXPERIMENTAL METHODS

In the present experiment, following reagents were employed.

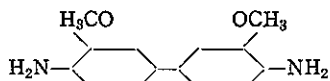
1) benzidine



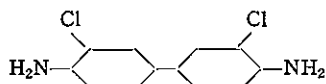
2) o-tolidine



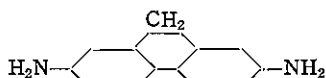
3) o-dianisidine



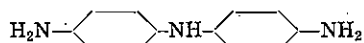
4) 3-3 dichlorobenzidine



5) 2-7 diaminofluorene



6) 4-4 diaminodiphenylamine



Colored solutions are so unstable that they begin to fade shortly. Rate of coloring and fading are surely influenced with the kind and pH of solution, variety of reagent and other factors. Therefore, it may be required a suitable buffer solution.

Procedure for the measurement.

After the refined potassium bichromate is dissolved in buffer solution, two or three drops of methyl alcohol solution of these reagents are added, and then the intensity of color developed is measured by Beckmann's Spectrophotometer.



## RESULT

## 1) The effect of acidity of solutions.

The more acidity of solution increases, the more rate of coloring and fading become faster. This relation is shown in Fig. 1. In this case, 0.2cc of methyl alcohol

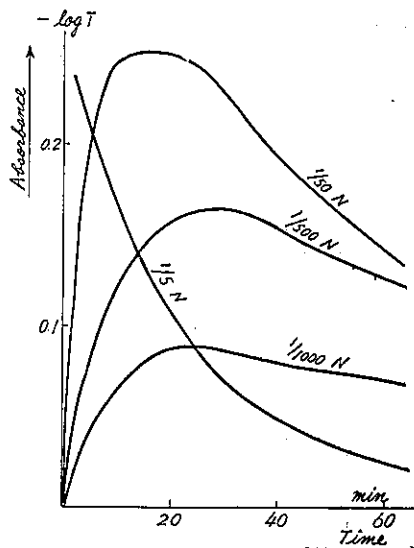


Fig.1. Effect of acidity of solution.

solution of 2-7 diaminofluorene was added to 0.4 $\gamma$ /cc of Cr per 10 cc of acetic acid.

In the range of too strong acidity, rate of coloring and fading was so rapid that it was impossible to measure precisely about maximum value of absorption of light. When the acidity was too weak, the reaction could not proceed, and preparation of a suitable buffer solution was accordingly required.

## 2) The effect of buffer solution.

In order to obtain a color with consistent extinction coefficient at one of the peaks, the pH of solution must be controlled in adequate range. The effect of pH was studied with three kinds of buffer solutions (1) citric acid and sodium ortho phosphate (2) hydrochloric acid and potassium chloride (3) acetic acid and sodium acetate, in measuring the absorption intensity at various time intervals. It was proved the buffer solution of acetic acid and sodium acetate was most suitable for this purpose.

Fig. 2. shows an example of employing inadequate buffer solution.

The buffer solution was adjusted to various pH with citric acid and sodium ortho

## DETERMINATION OF CHROMIUM

phosphate. To 10 cc of this solution containing 0.4 $\gamma$ /cc of Cr was added 0.2cc of

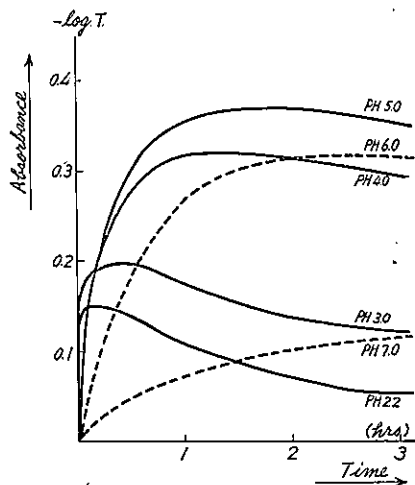


Fig.2. Development with 4-4' diaminodiphenylamine  
in buffer solution of  
citric acid and sodium orthophosphate.

methyl alcohol in which 4-4' diaminodiphenylamine has been dissolved. As is clearly noticed in the figure, a slight fluctuation of pH caused a great variation of absorption of light, therefore it may be required to adjust pH within a definite limit.

### 3) Buffer solution of acetic acid and sodium acetate.

Proportion of buffer solutions prepared according to Walpole are as follows. 0.2 N  $\text{CH}_3\text{COOH}$  and 0.2 M  $\text{CH}_3\text{COONa}$  are mixed.

	PH										
	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6
$\text{CH}_3\text{COOH}(\text{cc})$	18.5	17.6	16.4	14.7	12.6	10.2	8.0	5.9	4.2	2.9	1.9
$\text{CH}_3\text{COONa}(\text{cc})$	1.5	2.4	3.6	5.3	7.4	9.8	12.0	14.1	15.8	17.1	18.1

When six reagents are used in above solutions, maximum absorption of light are as follows.

benzidine	500 $\text{m}\mu$	3-3' dichlorbenzidine	620 $\text{m}\mu$
o-tolidine	620 $\text{m}\mu$	2-7 diaminofluorene	607 $\text{m}\mu$
o-dianisidine	480 $\text{m}\mu$	4-4' diaminodiphenylamine	675 $\text{m}\mu$

Of these reagents, the use of benzidine, o-tolidine, o-dianisidine and 3-3' dichlor benzidine may be avoided, because of their long reaction times and of insufficiencies of color development. In Fig. 3. shows the changes of color developed using these inadequate reagents.

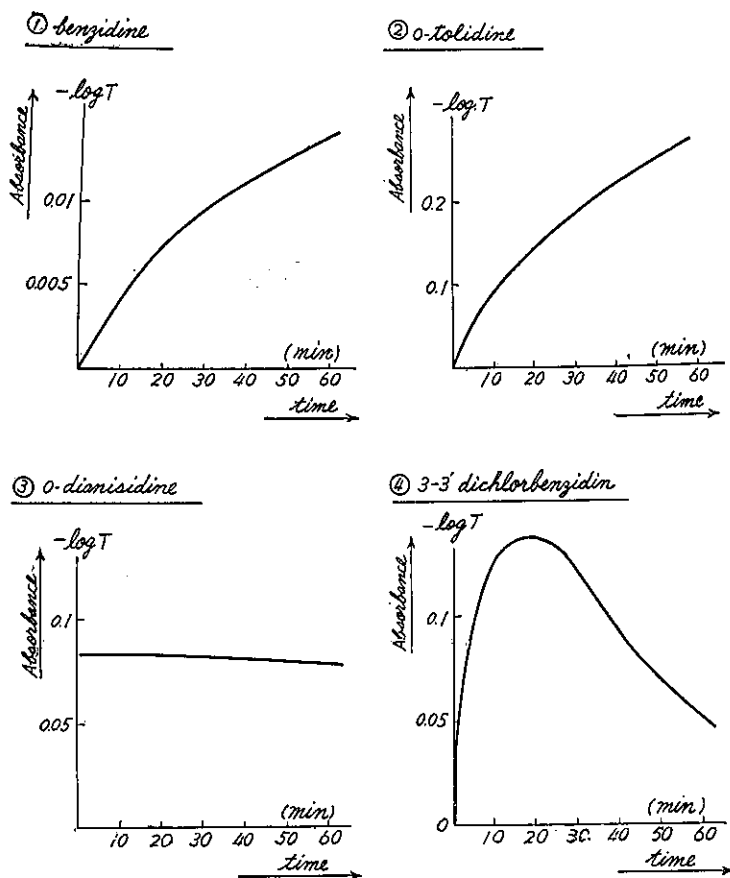


Fig. 3. Development with benzidine, O-tolidine, O-dianisidine and 3-3' dichlorobenzidine.

a) Development of color with 2-7 diaminofluorene.

In Fig. 4. shows the fluctuation of absorption of light with time in pH 3.6, 5.0 and 5.2, using 2-7 diaminofluorene in methyl alcohol as reagent. Below the pH 5.0, color fades so rapidly that the measurement of maximum value of light absorption can not be obtained with ease. However, measurement at pH 5.2 are little significance because the solution is unstable, and over pH 5.4, too long time is required to reach maximum value of absorption of light.

b) Development of color with 4-4' diaminodiphenylamine.

4-4' diaminodiphenylamine is dyestuff named "Fast black Base". Sulphate of this dyestuff was employed in this experiment. Only about 0.2% of this reagent can be dissolved in methyl alcohol, however, such insolubility of reagent does not affect on the development of color. In Fig. 5. shows the data in various pH. Procedures for the measurement is same as that of 2-7 diaminofluorene. From pH 3.6 to

## DETERMINATION OF CHROMIUM

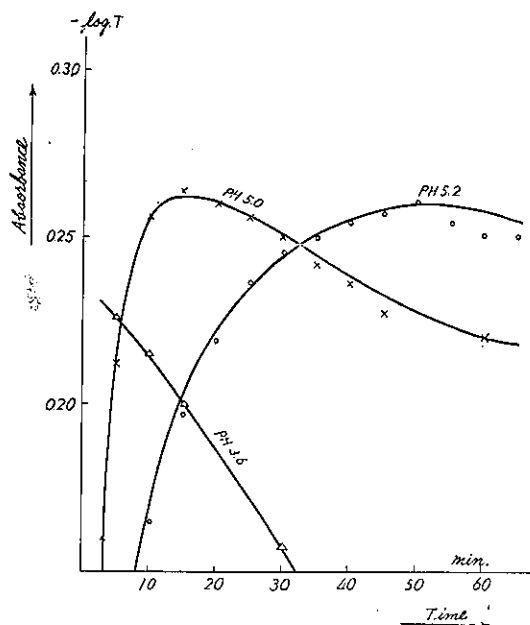


Fig. 4. Development with 2-7 diaminofluorene.

5.6, absorption coefficients are nearly equal. Therefore, the reagent is satisfactory for the measurement within the limit of pH 3.6 to 5.6 and about thirty minutes are necessary to gain maximum absorption and stable for three hours.

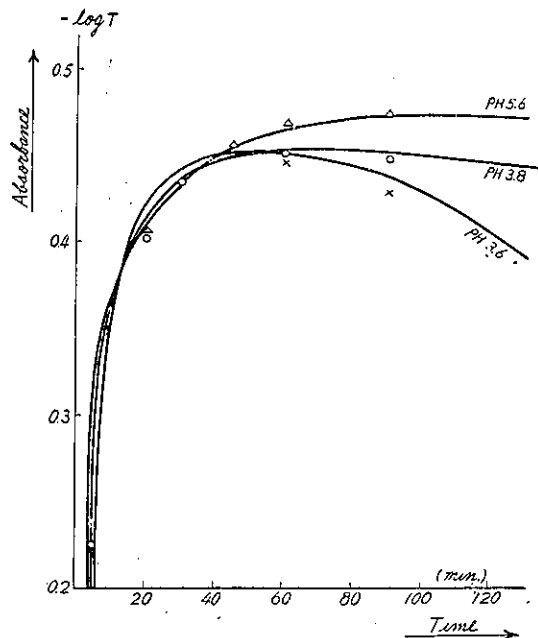


Fig. 5. Development, with 4-4' diaminodiphenylamine.

c) Calibration curve of three reagents for determination of Cr.

N. HARA

Comparison of the sensitivity of 2-7 diaminofluore and 4-4' diaminodiphenylamine were undertaken with Cr ions, and the results are represented in Fig. 6. Potassium bichromate was dissolved in the buffer solution of acetic acid and sodium acetate in order to obtain the concentration of Cr ion listed in table 1. To 10 cc of this solution was added 0.2 cc of methyl alcohol solution of these reagents and after one hour reading were taken. The data using diphenylcarbaid are presented for comparison in Fig. 6. It was proved to obey Beer's law up to a concentration of 0.1 microgram of chromium per millilitre of final solution using 2-7 diaminofluorene and to 0.025 micrograms per millilitre using 4-4' diaminodiphenylamine as reagents.

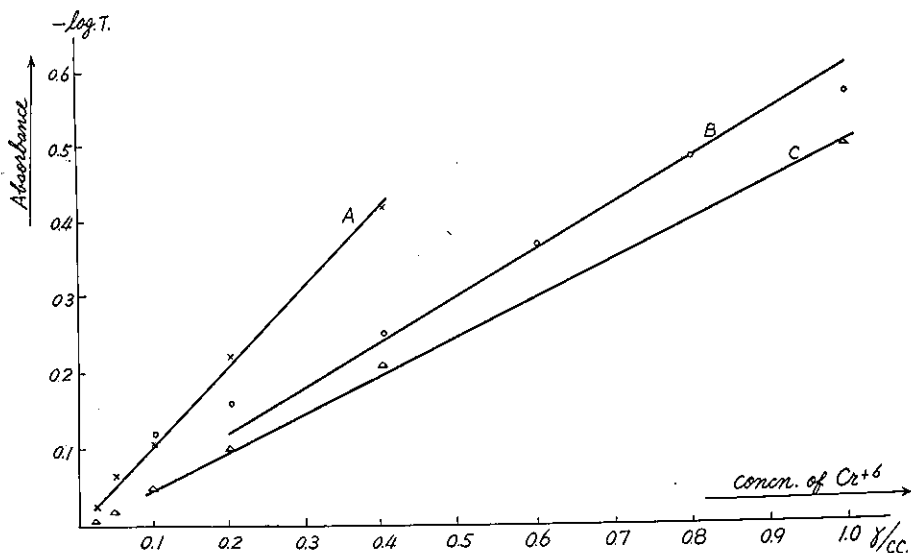


Fig. 6. Development of chromium compound. A: 4-4' diaminodiphenylamine B; 2-7' diaminofluorene C: diphenylcarbaid.

Table. 1. The Comparison of Color Development with three reagents.

2-7diaminofluorene		4-4'diaminodiphenylamine		diphenylcarbaid	
pH 5.2		pH 3.8		0.2N-H <sub>2</sub> SO <sub>4</sub>	
Cr(γ/cc)	-logT	Cr(γ/cc)	-logT	Cr(γ/cc)	-logT
1.0	0.560	1.0	0.472	1.0	0.494
0.8	0.478	0.4	0.417	0.4	0.210
0.6	0.367	0.2	0.223	0.2	0.103
0.4	0.251	0.1	0.108	0.1	0.048
0.2	0.160	0.05	0.066	0.05	0.023
0.1	0.121	0.025	0.028	0.025	0.009

## DETERMINATION OF CHROMIUM

### DISCUSSION

When these two reagents were compared, it was proved that 4-4' diaminodiphenylamine is superior than 2-7 diaminofluorene in the following points:

(1) Minimum determinable concentration by the former reagent is 0.025 micrograms of chromium per millilitre, and this is far more sensitive than by the latter.

(2) The intensity of the color developed with the former reagent varies little in spite of the fluctuation of pH of the buffer solution from pH 3.8 to 4.8.

(3) And this intensity remains unchanged for three hours after the development.

4-4' diaminodiphenylamine should be used at pH 3.8 of the buffer solution. This may be ascribed to the following two reasons:

(I) About one hour is required to reach the maximum absorption of light above pH 5.0.

(II) After two hours, at pH 3.6, it begins to fade.

However, in the range from pH 3.8 to 4.6, the maximum absorption of light is influenced very little with the fluctuation of pH, and the developed color is stable for three hours.

### CONCLUSION

For the determination of small amounts of chromium in air, it was proved that 4-4' diaminodiphenylamine is satisfactory as the color reagent. Chromium is dissolved in a buffer solution (pH 3.8) of acetic acid and sodium acetate.

Methylalcohol solution of 4-4' diaminodiphenylamine is added to the solution, and measure the intensity of color at  $675m\mu$ . Minimum determinable concentration is 0.025 micrograms of chromium per millilitre.

Using this reagent, higher color intensity can be developed than the method used diphenylcarbaid.

This method is simple, however, involves many points requiring some further consideration, namely:

(1) As the development of color is dependent on the oxidation of power of  $Cr^{+6}$  ions, it is impossible to measure directly other chromium ions and metallic chromium.

(2) Color reaction by benzidine and its derivatives is not specific for  $Cr^{+6}$ . Many other interfering metallic ions should be eliminated or suppressed.

(3) Further precise experiments are required on many other buffer solutions.

Despite these incompleteness, the method has several advantages compared with diphenylcarbaid. Therefore it is desirable that this method may be applied to practical uses in future.

### ACKNOWLEDGEMENT

The author wish to thank all members of this institute for their kind encouragement and



criticism of this work.

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## 要 旨

## ベンチデン及び其の誘導体による 微量クロムの定量

## 原 登

クロムの比色定量には、従来主としてデフェニルカルバジドが用いられ、ベンチデン及び其の誘導体は、クロムの検出と定性試験に使われるに過ぎなかつた。

此等の試薬は何れも重クロム酸塩又はクロム酸塩の酸化力により発色する事を利用している。一般にベンチデン及び其の誘導体を使用する時、反応液の酸性が大であると発色及び褪色が極めて早く、比色定量は困難であり、反対に酸性が小であると発色褪色共に甚だ遅くなり、且十分の発色を示さない。この様に反応液の酸性度が、発色に至大な影響を与える事が、定量に使用されない一因である。然し、その発色反応は極めて鋭敏であり、その条件を適当に調整すれば、クロム定量には甚だ恰好の試薬となる。

著者は、此所に着眼し、ベンチデン誘導体の中より、最も適当な試薬と思われる 4-4'ジアミノデフェニルアミンを取り、そのメタノール溶液を、色々の条件の下でクロムと反応せしめその発色状況を詳細に検当した。即ち、ワルポール氏の醋酸と醋酸ソーダより成る緩衝液を用い反応液のpHを3.8に維持すると、最大発色量に達する迄に約30分かかかる欠点はあるが、発色物は安定で発色量は以後約3時間変化しない。この試薬による発色量は、この近傍で pHの変動に対して殆んど影響を受ける事なく、pH3.8~4.6に於ては殆んど同一の発色量を示し、且同様に約3時間安定であるから比色定量は甚だ容易である。定量にはベックマン型光電比色計を用い、最大吸収を示す波長675m $\mu$ に於て吸光度を測定した。この試薬の利点は、同一量のクロムに対し、その発色量がデフェニルカルバジドのそれより遙かに大きいので、デフェニルカルバジドを用いるより遙かに微量のクロムを定量出来る事である。即ち、この試薬を用いるとCr<sup>6+</sup>の濃度(0.5~0.025) $\gamma$ /ccの範囲に於てベールの法則が適合し、その下限までのCr<sup>6+</sup>の定量は容易である。

ベンチデン誘導体の中で、此の外の試薬で2-7ジアミノフルオレンが比較的勝れている。即ち、そのメタノール溶液を用いると、上記の緩衝液の下でpH5.0の近傍では、同一量のクロムに対し、その発色量は4-4'ジアミノデフェニルアミンには及ばないが、デフェニルカルバジ

## DETERMINATION OF CHROMIUM

ドより大きく、 $\text{Cr}^{+6}$ の濃度(1.0~0.2) $\gamma/1\text{cc}$ の間では略ぼベールの法則に従う。この場合の最大吸収波長は607 $\text{m}\mu$ である。けれども、pHの僅かの変化によつても、その発色及び褪色の速度は極めて大きな影響を受けるので、実用面では4-4'ジアミノヂフェニルアミンに大に劣ると考える。

両試薬共、六価のクロムの酸化力を利用しているのであるから、クロムが其の他の形を取つた場合には、そのままでは使用出来ない。

此等の所見より、4-4'ジアミノヂフェニルアミンを微量クロムの定量に応用して、実用面に使用出来るようにするため、種々の要因を吟味したものである。

## 某自動車修理工場における騒音 並びに職業性難聴の調査

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### NOISE MEASUREMENT IN MOTORCAR REPAIR PLANT AND AUDIOMETRIC EXAMINATION OF WORKERS

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は し が き

騒音を発生する職場に於ける騒音強度とその騒音によつて引き起される難聴との関係に関する調査は既に数多く行われている。

しかしながら夫々の研究者によつて騒音強度の測定方法や聴力損失の評価の方法が異なるために多くの既に行われた調査資料から職業性難聴の発生強度と被曝露騒音強度、騒音の種類及び曝露年限等との客観的な関係を求めることは容易ではない。

上述の関係をより正確に求めるために以下に述べるような方法により騒音と職業性難聴との調査を始めた。

この報告は一連の計画のうちの一部であつて、某自動車修理工場に於ける調査を要約したものである。

#### 作 業 の 概 要

対象工場は自動車の修理工場で戦争中航空機の格納庫に用いられていた建物を改造したもので、この中でニューマチックハンマー、ハンマーによる成形作業、リベット等の騒音発生作業が行われている。常時、騒音に曝露されている労働者数は約 550 人である。なおこの工場が開設されたのは昭和23年であつて、本調査は昭和33年9月である。

保護具としては労研式 2 号耳栓が使用されていた。

#### 労働環境中における騒音測定

##### 1) 測 定 方 法

騒音の性質の測定のためには少くとも音の大きさとその時間的分布及び周波数特性が必要となつて来る。そのためには工場に於ける騒音を直接測定するよりも、これを一度録音して解析した方が取扱いに便利であり、且測定繰返えしが可能である点で優れているので、当研究所では騒音測定には簡易騒音計による現場での測定と同時に騒音の性質に応じて一定時間工場騒

## 騒音並びに職業性難聴調査

音を録音し、これを解析することになっている。録音機の周波数特性はマイクロフォンの特性を含まないで100~8000 c/sで±2db以内で録音レベルを決定するために予め、音響レベルと更生された1000c/sの電氣的発振機を内蔵している。録音前に予めこの標準レベルを録音するようにした。

此の録音テープに就いて下の分析を行つた。

定常的騒音及び刻々変化する騒音（パルスの騒音）の大きさの時間的分布を求めするためにリレーの時常数が0.4秒であるレベルセレクターを用いた。本器は特に後者の分析に便利である。之により時間的に騒音がどのような強度分布をもつかを測定した。

難聴をひきおこす要因として騒音の大きさと共にその音源の周波数が問題になると考えられる。周波数分析の方法にはいろいろあるがここでは直視型騒音周波数分析器と、band pass filterの出力を Brüel 記録計を用いて記録する方法を用いた。前者は100c/s~8000c/sの間を $\frac{1}{2}$ オクターブに分割した20チャンネルのフィルターの出力をデカトロンを用いた電子管式切換スイッチにより自動的に切換えてブラウン管上に画くものである（日本電子測器製）。本機はパルスの音の周波数分析が可能であると考えられる。

後者は75~9600c/sの間をオクターブに分割した7チャンネルのフィルターの出力をBrüelの記録計で記録した。この場合各周波数バンドについてテープレコーダーを1分間スイープさせその平均をとるようにした。比較的定常的な騒音に対して前者より実験的に便利な方法である。

## 2) 測定結果

### 騒音の強度分布

レベルセレクターによつて測定した騒音の強度分布は第1図より第8図までに示した通りである。録音時間は5~10分間のものである。測定番号に対応する作業の内容は第1表を参照せられたい。図中騒音計として記入してあるのは録音時に騒音計によつて測定された騒音レベルの最大と最小の平均である。第1~8図の縦軸には一定時間中の頻度を全体を1として表わしてあり横軸には音の大きさのレベルをホンで示してある。実線は累積分布である。（レベルセレクターが直接指示した値で通常の累積分布の逆である）すなわち、第2図では110ホン以上の音が全測定時間の100%を占め、即ち少なくとも105ホン以下の音には常にさらされていることになる。110ホン以上の音が84%、125ホン以上の騒音29%を占めていることを示している。又点線はこれを頻度分布で書いたもので105~110ホンの音が全体の16%、110~115ホンの間の音が5%、120~125が46%を占めていることを示している。

第1~3図からわかることは先ず第1図第2図の比較からこの“はつり”作業を行う作業場では周囲の仕事が行われていて“はつり”作業が行われていないときの騒音は100~110の間に殆んど含まれるのに対し、“はつり”を始めると第2図のように120ホン程度の騒音に常時さらされるようになることがわかる。次に第6図 air hammer の作業では115~120の間に最も頻度の高い山がみられ、又第7図よりリベットイングはリベットが行われているときは100ホンを超えるけれども、リベットを打つ時間の全時間に対する割合が小さいため100ホンを超える時間は50%以下であることがわかる。

直視型周波数分析機による各作業場の騒音周波数分布を図9~20に示す。又 Brüel 記録計による分析値を第21図に示す。図18~20を除いて $f=1.5$ ,  $\frac{1}{60}$  sec シャッターにて撮影したものである。図18~20は図15~17に夫々対応したパルス音を含む約3秒間露出である（パルプを

用いた)この図では基底の最左端が100c/s最右端が8000c/s になつていてその間が $\frac{1}{2}$ オクターブづつに切つてある。従つて第10番目(図では真中)が800c/sになつている。作業の形態による相違及び主作業をしているときとしていないときの周波数分布の相異がはつきりわかる。そしてこの工場に於ける騒音は一般に 1000c/s 以上の周波数に主勢力をもつ場合が多い。又図15~17は“いもの”をたたく音であるが、たたき方やたたく場所によつて周波数分布に移動が認められる。

騒音の種類によつて適当な写真フィルムの露出時間の存在すること及び騒音周波数成分のレベルを如何に読むか(平均値か最大値か等)が考えられるが、この問題は今後の問題としてここにはふれない。

第21図 Brüelの記録計による分析値によると、②のニューマティックハンマーの場合主騒音エネルギーは300~4800c/sの間にあり音源より40cmの距離では100dbを超えている。(図10でも同様であることがわかる。)特に600~1200c/sの騒音は最も強い。大きいハンマーで自動車のボデーをたたく作業は比較的低い方にエネルギー成分を有し150~300c/sに約100db程度の最大値を示している。又中小ハンマー使用の作業は300~2400c/sに主成分を有し、リベッティングは1200~4800c/sに主成分をもっている。以上の測定よりみて物体をたたく場合その物体の固有振動が最も問題となるが、ハンマーの衝突の際の接触時間、及び物体の保持の方法によつても周波数成分が変化する事がわかる。

## 2) 聴 力 検 査

### 1) 測 定 方 法

難聴者として工場側で指定した19名(音又による検査で選出された)について検査した。測定は本研究所の無響室に於いて、岩崎通信機株式会社の Audiometer(Type SA-3)を用い気導検査を行った。なお被検者は月曜日(休日の翌日)作業を開始する以前に聴力測定を行い、前日の騒音曝露による影響を極力排除する事に努めた。

### 測 定 結 果

各被検者の検査成績は第2表に示した。職種を鍛造、リベット、熔接、鍍金と各種に亘り、曝露年数も1→20年と変動が大きいので、一律に取扱うことには無理もあろうが、工場騒音分析の結果から各職種共に有害な職業性難聴発現場であり、聴力型(Audiogram)からみても高音域から聴力障害が現われており、職業性難聴の特長を有している(第22図)。

各被検者の聴力型では、No. 6, 9, 11は異常な型を示めさず、No. 9の如く曝露年数20年でありながら正常な聴力型を示す者も観察された。その他の者は多少とも高音域に聴力障害を示した。但し No. 4は曝露年数7年で全周波音域に聴力障害を認めたが、この被検者は高年令による老人性難聴その他の耳疾患も合併せるものと考えられる。又No. 13は曝露年数2年で全周波音域に聴力障害を示している。これは更に他の耳疾患との鑑別を必要とする。なお鍛造工3例の聴力型を第23~25図に示しておいた。左右両耳の聴力型の差異は第22図にみる如く低音域では右耳が左耳に比し聴力損失が大きい傾向を示し、高音域では左右両耳に差異を認めず、曝露年数別に観察してもこの傾向はみとめられた。

曝露年数による聴力型の差異については第26図に示した。0~4年では強い変化を認めず、5年以上で高音域に強い聴力損失を示し、更に15年以上になると聴力障害が漸次中音域に及ぶこ

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とが認められた。

言語聴力損失度 ( $db = \frac{a+2b+c}{4}$ , a: 500 cps, b: 1000cps, c: 2000cps の最少可聴閾値(db))は第2表に示した如く、30db以下が84%で、大多数の者は普通会話に障害を認めない。30~45dbを示せる者が3例、46~60dbが2例、60~70dbが1例認められた。

言語聴力損失度の曝露年数による影響については第27図に示した。即ち曝露年数が長い者程、この損失度も大きくなる。なお両耳を比較した場合、この損失度は右耳に強く、左耳の約2倍を示している。

第 1 表

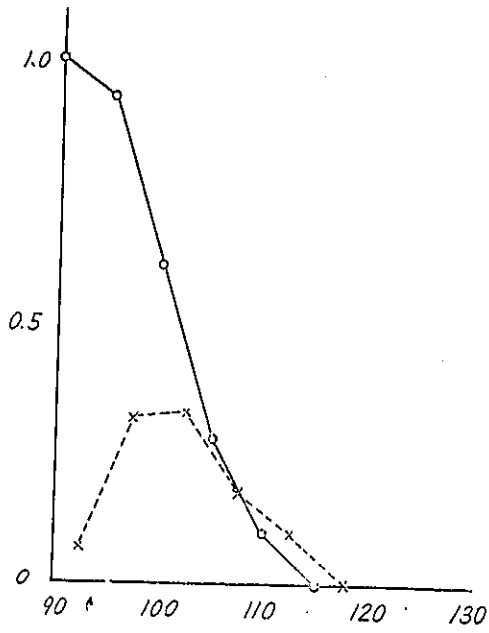
測定番号	作業内容	騒音計測定値 ホン	最多騒音レベル	50% 騒音レベル	ピークレベルの ある周波数範囲
1	ハツリ作業場でハツリ作業のない場合	99	105~110	104	150~300
2	ハツリ作業中	115	120~125	123	600~1.2K
3	小ハンマー及びヤスリ作業(Tale Gate)	110	110~115	113	600~1.2K
4	大ハンマーで車体をたたく作業	105	110~115	112	150~300
5	小ハンマー及びヤスリ作業(cab Shop)	93	100~105	102	1.2K~2.4K
6	エアハンマー作業	109	115~120	116	2.4K~4.8K
7	リベッティング	100	95~100	100	2.4K~4.8K
8	熱鍍物をたたく作業	90	100~110	105	1.2K~4K



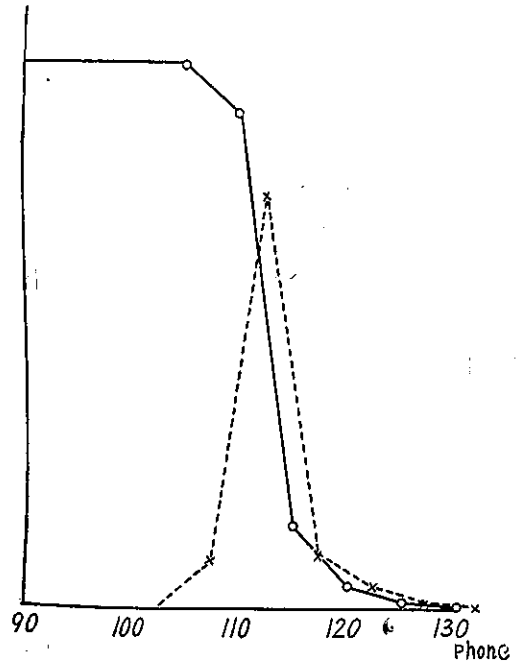
第2表 検査成績

No	年令	職種	曝露年数(年)	耳疾患 その他の 既往症	オーディオグラム (db)																言語聴 力損失度 (db)					
					250cps 右	250cps 左	500cps 右	500cps 左	800cps 右	800cps 左	1000cps 右	1000cps 左	1500cps 右	1500cps 左	2000cps 右	2000cps 左	3000cps 右	3000cps 左	4000cps 右	4000cps 左		6000cps 右	6000cps 左	8000cps 右	8000cps 左	
1	34	造 造	15	なし	-10	-10	-10	-10	-5	-10	0	-5	30	20	35	20	45	60	60	60	60	55	55	10.0	0	
2	41	鍛 造	1	なし	0	0	-5	-5	-5	-5	0	-5	0	-10	0	-10	5	5	15	20	10	15	40	60	-1.3	-6.3
3	41	リベ ット	16	なし	5	5	5	10	0	10	5	20	25	60	60	60	65	75	75	70	80	75	70	21.3	18.8	
4	52	鍛 造	7	なし	60	25	70	30	60	45	70	55	70	55	65	45	80	65	95	90	90	95	85	90	68.7	46.3
5	27	鍛 造	11	なし	10	0	10	0	10	-5	5	-5	5	0	40	20	50	50	50	45	45	40	25	35	15.0	2.5
6	27	鍛 造	2	なし	10	-5	10	-10	10	-10	5	0	10	10	15	10	15	5	25	15	25	15	30	25	8.8	0
7	31	鍛 接	15	外耳炎	-10	-5	0	5	5	0	0	0	0	0	20	25	45	50	40	50	40	50	35	60	5.0	7.5
8	27	鍛 造	7	なし	-5	-10	0	-5	5	0	5	0	5	10	20	25	50	55	40	50	55	50	70	65	7.5	5.0
9	40	鍛 造	20	なし	15	5	20	5	10	0	15	0	5	35	10	35	15	30	20	15	25	25	25	30	15.0	10.0
10	34	鍛 金	9	中耳炎	0	0	0	-5	0	0	5	5	5	5	10	45	50	55	50	55	55	50	70	70	2.5	5.0
11	25	鍛 金	3	なし	0	10	0	15	-5	-5	-5	-10	-5	-5	0	-10	0	-5	0	15	5	5	25	10	-2.5	-3.8
12	43	鍛 金	14	なし	0	5	5	0	-5	-10	0	-10	20	5	20	5	30	10	50	30	45	25	20	30	6.3	2.5
13	26	鍛 金	2	なし	60	25	60	25	55	25	55	30	60	35	65	40	70	50	70	55	70	60	70	55	58.3	31.3
14	32	接 接	11	なし	15	10	10	15	20	20	25	20	25	20	30	25	40	35	55	55	60	75	60	60	25.0	17.5
15	25	接 金	8	なし	30	20	35	20	40	20	35	20	40	20	35	25	45	45	50	50	55	65	55	70	35.0	21.3
16	33	鍛 造	8	なし	-5	-10	0	-10	0	-10	-5	-10	0	-10	0	0	45	55	50	55	75	70	55	55	5.0	-7.5
17	38	鍛 造	18	なし	30	15	25	10	30	20	35	20	40	40	50	50	65	65	65	65	75	80	70	75	36.3	25.0
18	43	鍛 造	19	中耳炎	10	0	10	-5	10	0	10	10	25	15	45	25	55	45	65	50	60	55	55	70	18.8	8.8
19	43	鍛 造	10	なし	10	5	5	5	5	0	5	0	-5	0	-5	0	-5	25	25	25	40	30	50	40	-1.3	3.8
平均	10.8				11.8	4.5	13.1	5.0	12.9	4.2	13.7	6.6	18.7	13.9	26.8	21.0	40.0	38.4	48.1	51.3	50.3	48.9	50.5	53.9	16.0	9.6

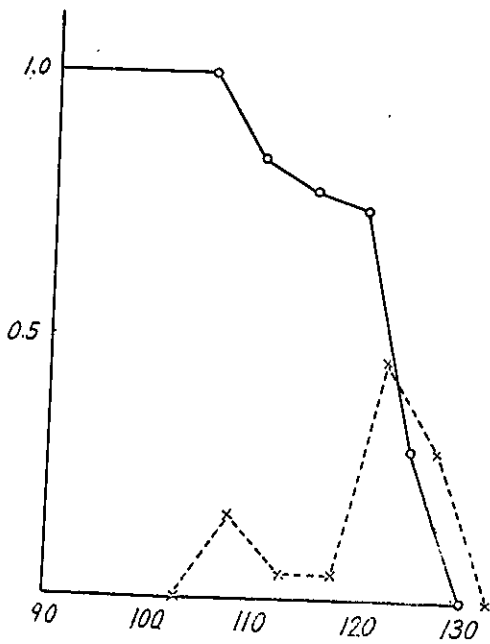
三 把 (調) 盤 川



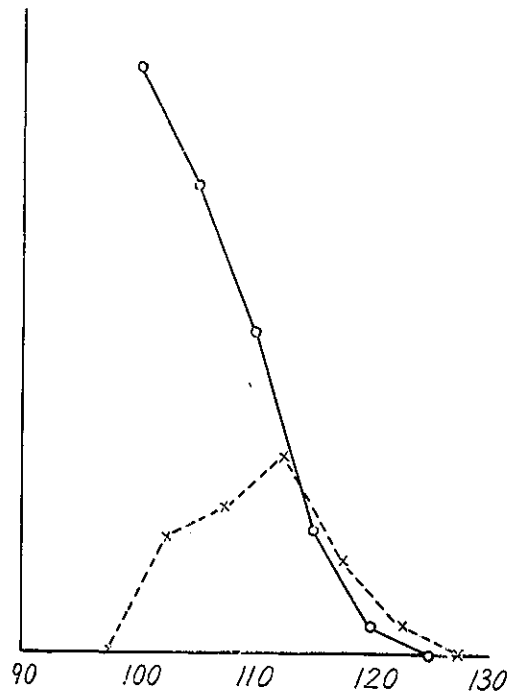
第 1 図  
(測定番号1)ハツリ作業場でハツリ作業のない場合



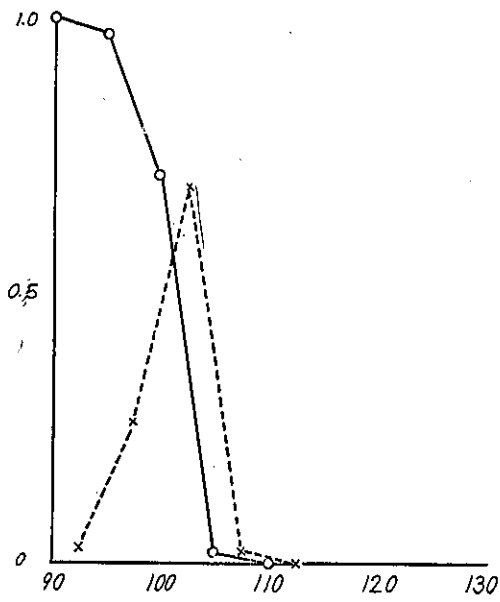
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(測定番号 3)



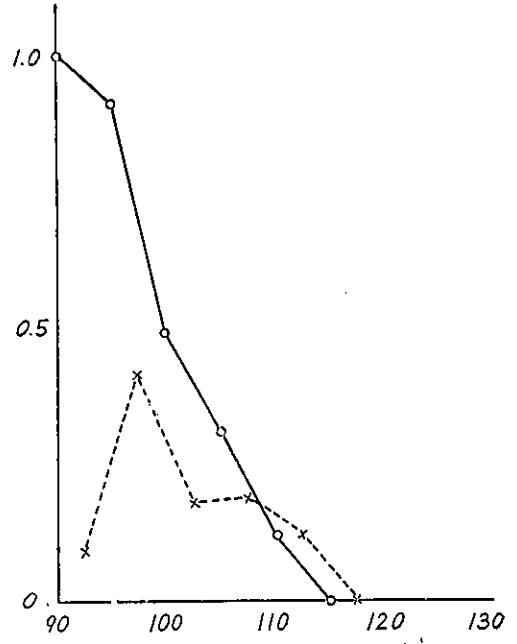
第 2 図  
(測定番号 2) ハツリ作業



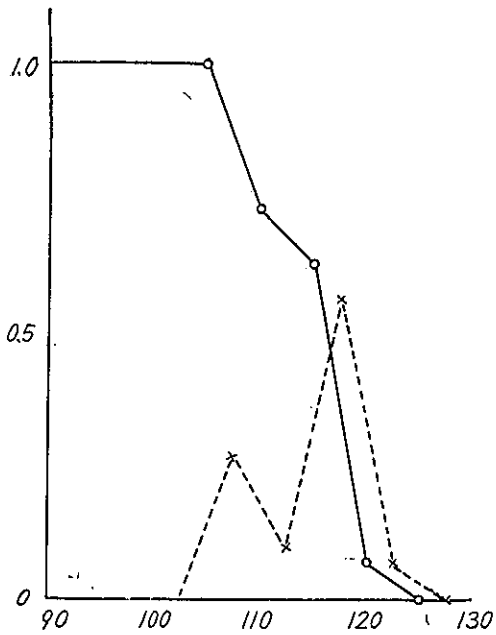
第 4 図  
(測定番号 4)



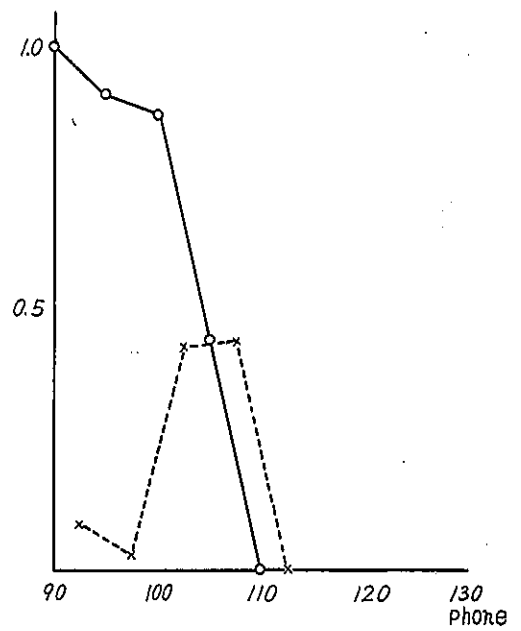
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(測定番号5)



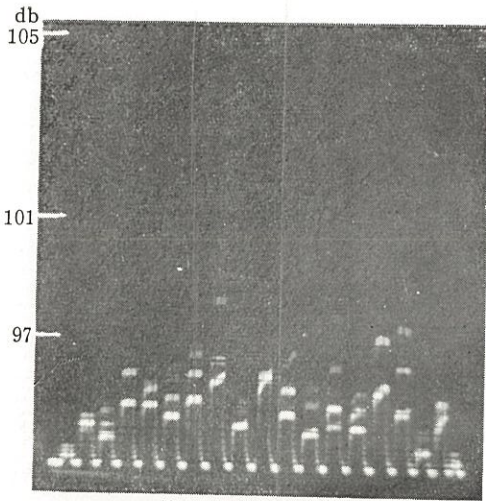
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(測定番号7)



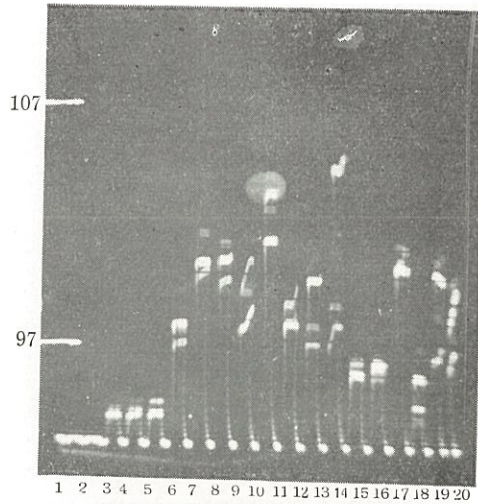
第 6 図  
(測定番号6)



第 8 図  
(測定番号8)

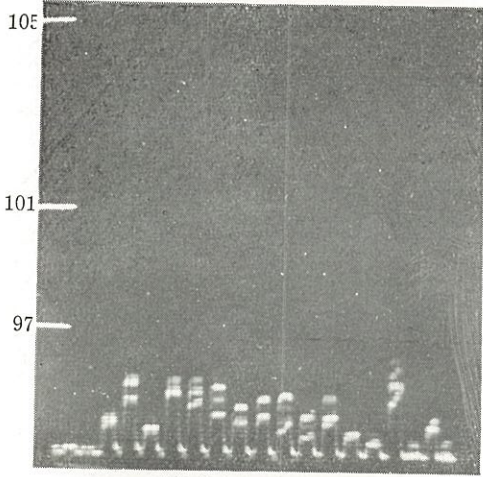


第9図 測定番号1  
ハツリ作業場でハツリ作業のない場合

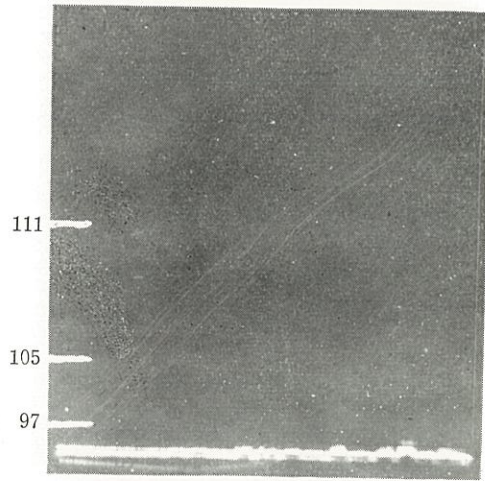


第10図 測定番号2 ハツリ作業

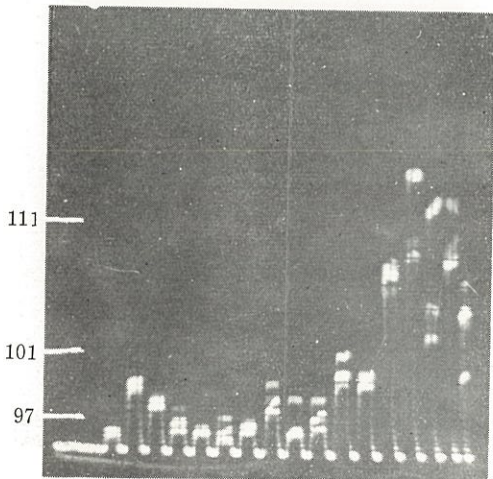
- 中心周波数
- 1 100
  - 2 125
  - 3 160
  - 4 200
  - 5 250
  - 6 320
  - 7 400
  - 8 500
  - 9 640
  - 10 800
  - 11 1000
  - 12 1250
  - 13 1600
  - 14 2000
  - 15 2500
  - 16 3200
  - 17 4000
  - 18 5000
  - 19 6400
  - 20 8000



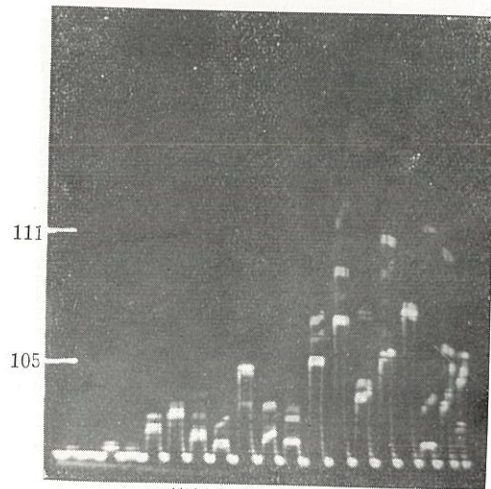
第11図 測定番号5



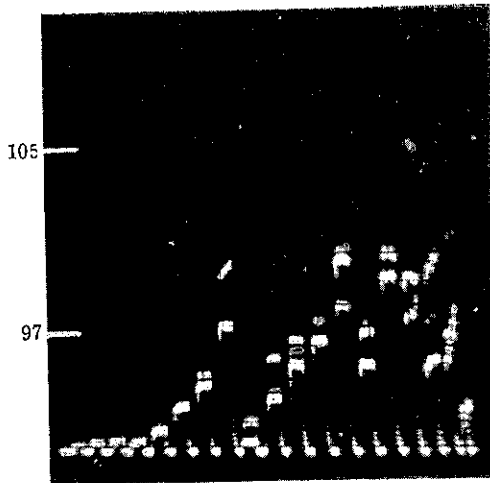
第12図 測定番号6, airhammer中止



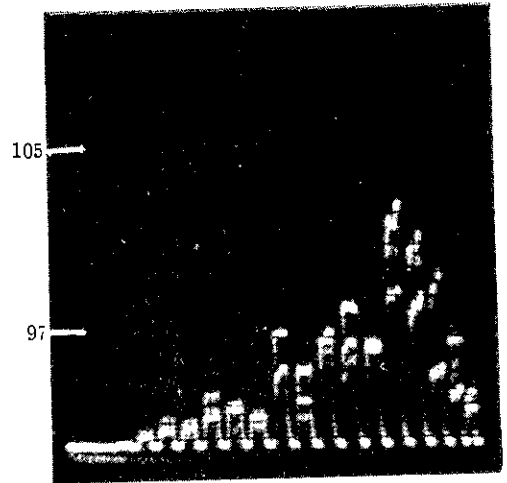
第13図 測定番号6 air hammer 作業中



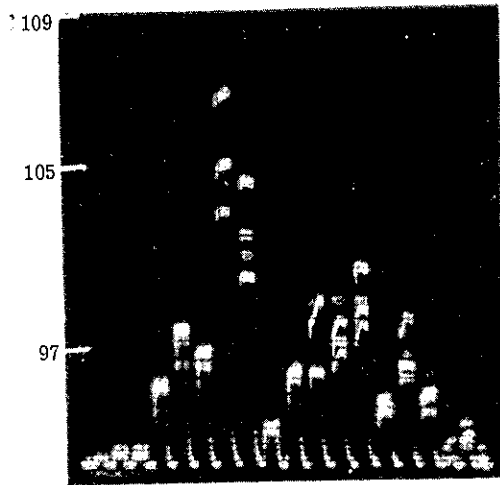
第14図 測定番号7



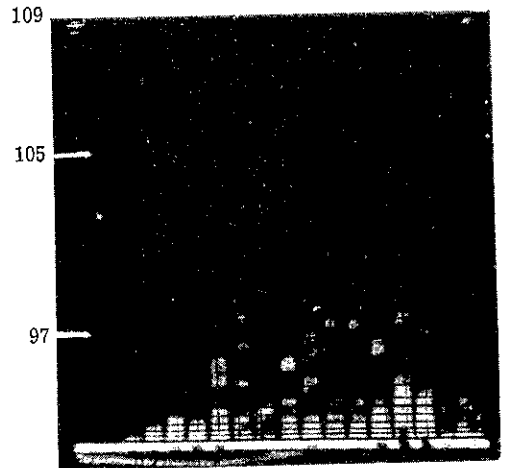
第15図 測定番号8,  $\frac{1}{60}$  sec



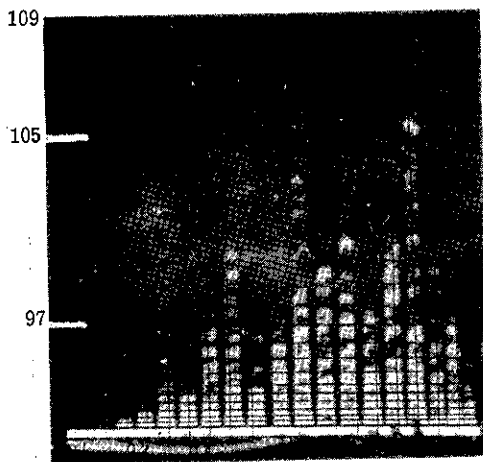
第16図 測定番号8,  $\frac{1}{60}$  sec



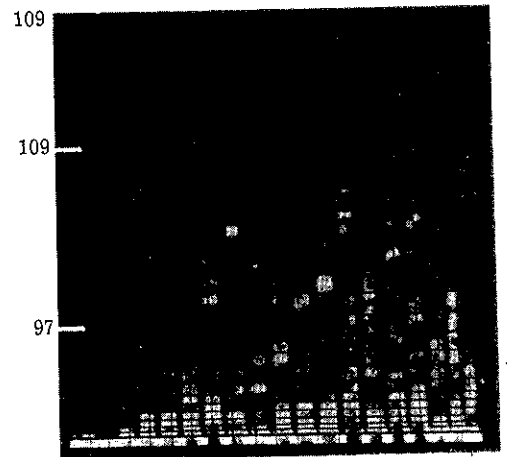
第17図 測定番号8,  $\frac{1}{60}$  sec



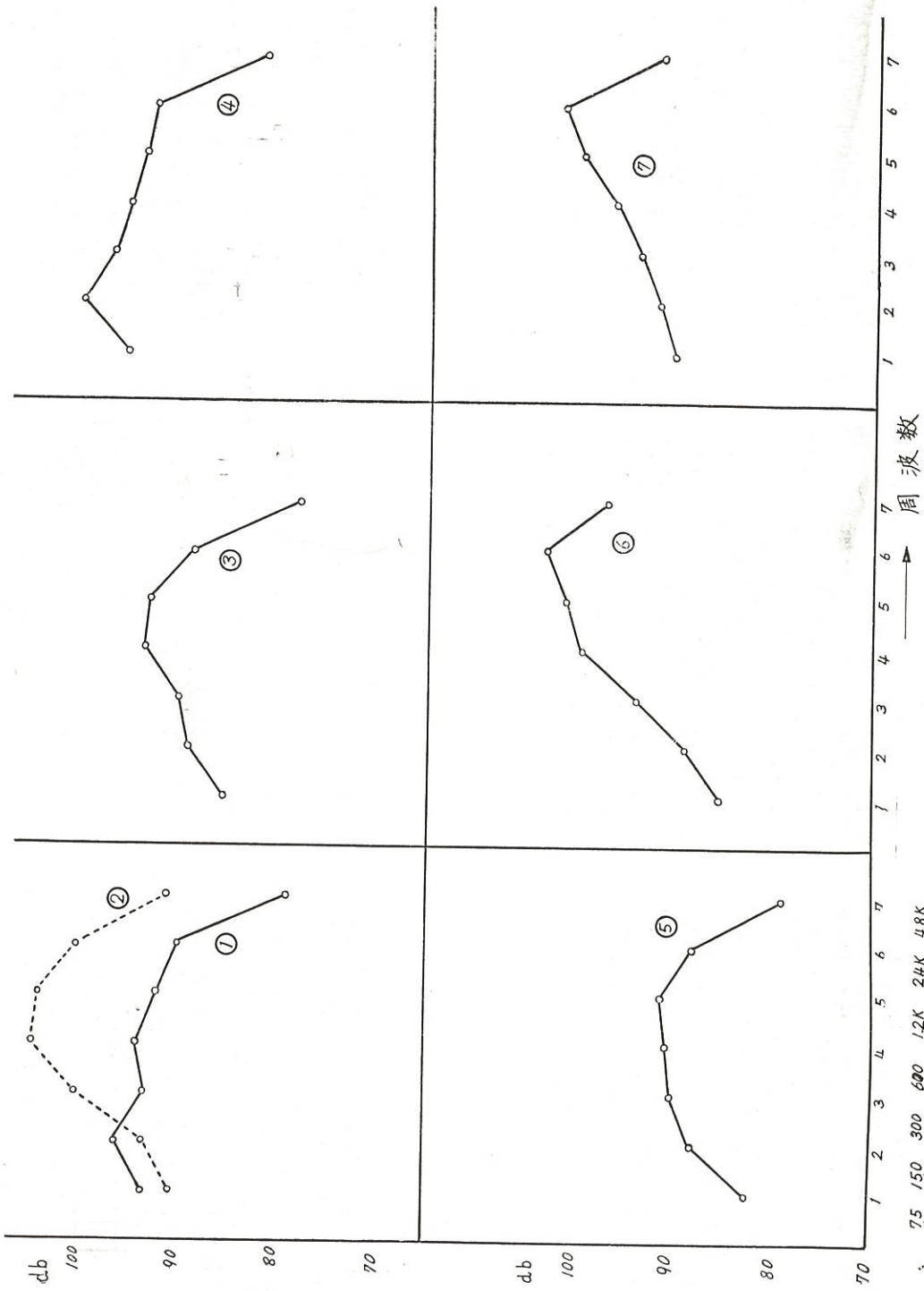
第18図 測定番号8, 3sec



第19図 測定番号8, 3sec

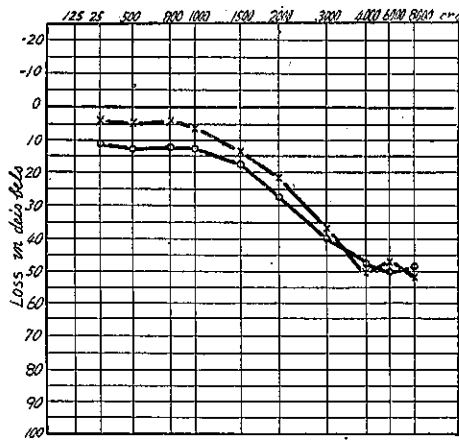


第20図 測定番号8, 3sec

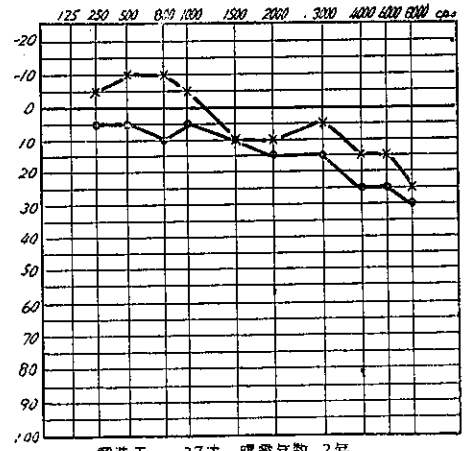


第21図 (数字は第一表中の測定番号)

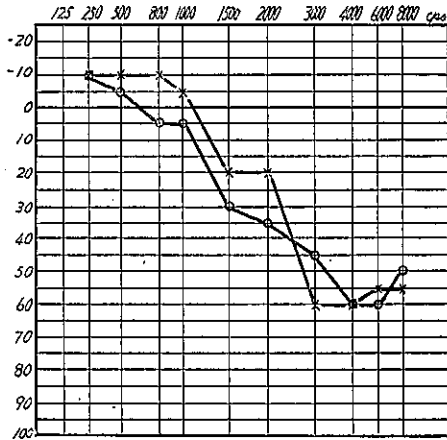
75 150 300 600 1.2K 2.4K 4.8K  
 150 300 600 1.2K 2.4K 4.8K 8.6K



第22図 聴力型 (19例の平均)

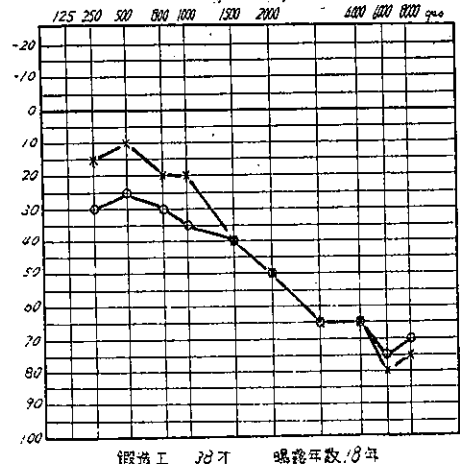


第23図



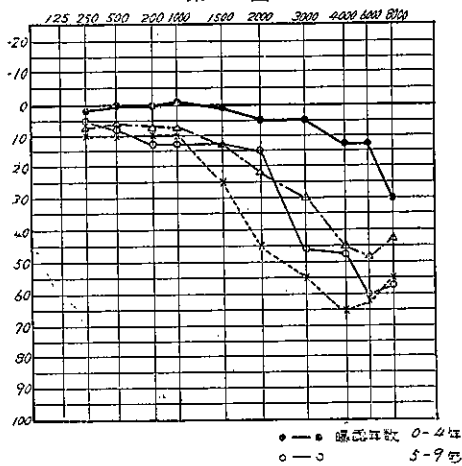
鍛造工 34才 曝露年数 15年

第24図

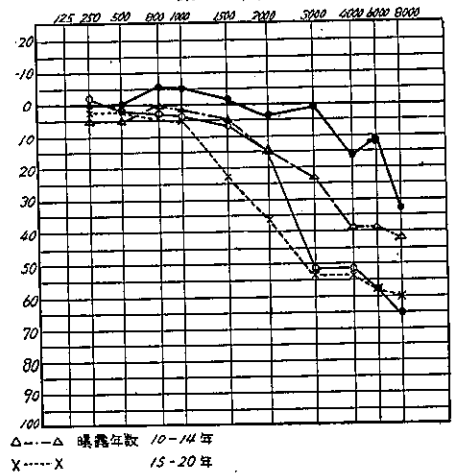


鍛造工 18才 曝露年数 18年

第25図



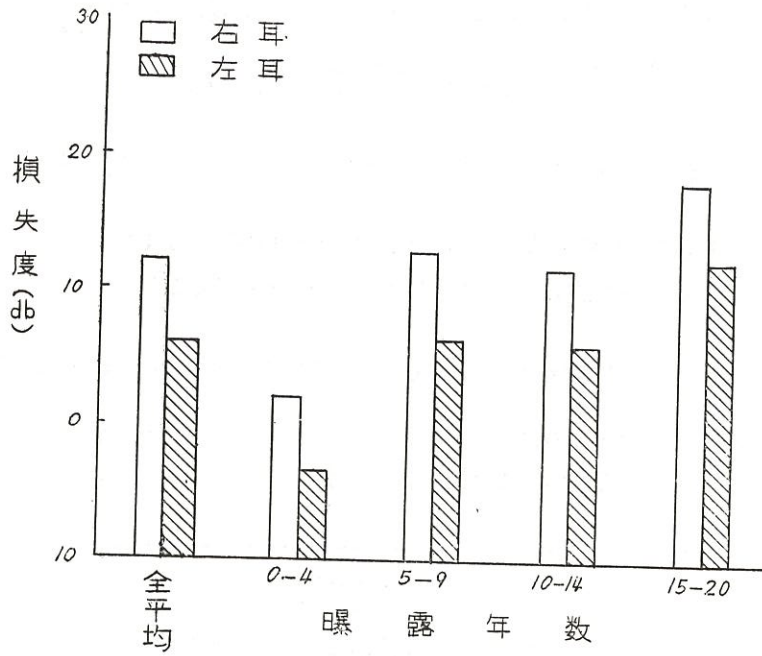
(A) 右耳



(B) 左耳

第26図 曝露年数別の聴力型





第 27 図 曝露年数別の言語聴力損失度

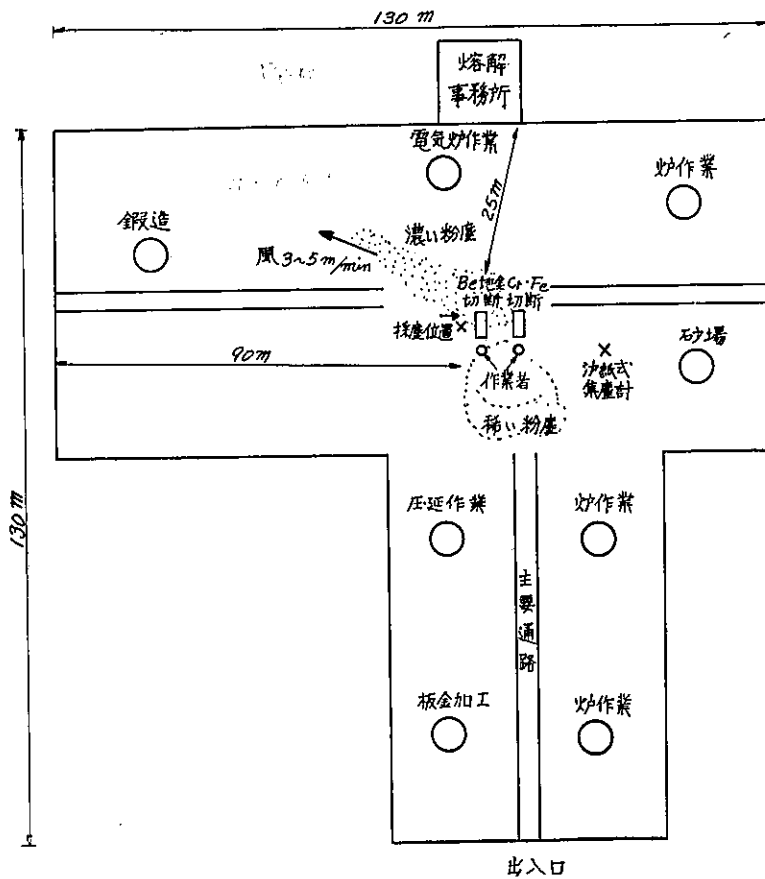
# ベリリウム取扱工場に於ける気中 粉塵測定調査報告

原 登 浜 田 晃 野 崎 恒 右 坂 部 弘 之

## BERYLLIUM CONCENTRATION IN THE AIR OF BERYLLIUM ALLOY HANDLING FACTORY

Noboru HARA, Akira HAMADA, Kosuke NOZAKI and Hiroyuki SAKABE

ベリリウムは所謂ベリリウム肺を起す有害物質であることはよく知られて居るが、その合金の熱処理の際に発生するベリリウムの定量測定は殆んど行われていない。この合金熱処理行程



第 1 図

に生ずるベリリウム量を推定するために昭和33年9月17日及び18日, 某工場に於ける熱間圧延作業場のベリリウム粉塵を下記のように測定した。採塵は交流型大型電気収塵器並びに濾紙式集塵器を使用した。

§. 切金切断作業 (9月17日午後, 暴風雨)

ベリリウム合金の地金を, すを除く目的で真空熔融するため, 特殊鋼製のホイールで乾式に切断して, 大きさを揃える作業である。

(1). 採塵位置略図其の他は, 第1図に示す。

(2). 採塵過程

集塵管 I ……米国より輸入した地金 (ベリリウム 4%含有) を 2本切断した。地金の 1本の断面積は約 $25\text{cm}^2$ で切断10回, 他の1本は断面積が約 $38\text{cm}^2$ で切断5回行つた。

本作業と並んで, 傍でクロムと鉄の合金の切断作業が終始つづけられた。

採塵時間は 100分, その中でベリリウムの地金の切断作業の行われたのは21分である。

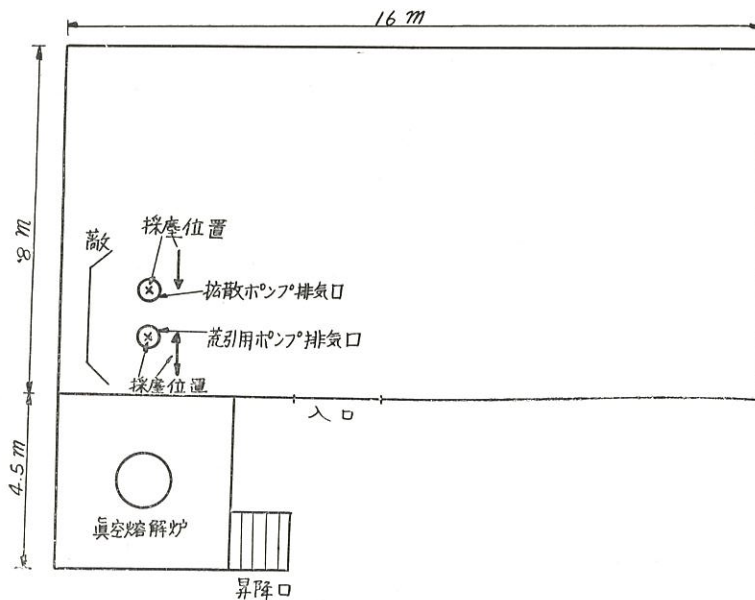
集塵管 II ……再生の地金 (ベリリウム 2%含有) を 1本, 20回切断した。この地金の断面積は約 $65\text{cm}^2$ である。

本作業と並んで, 傍でクロムと鉄の合金の切断作業が終始つづけられた。

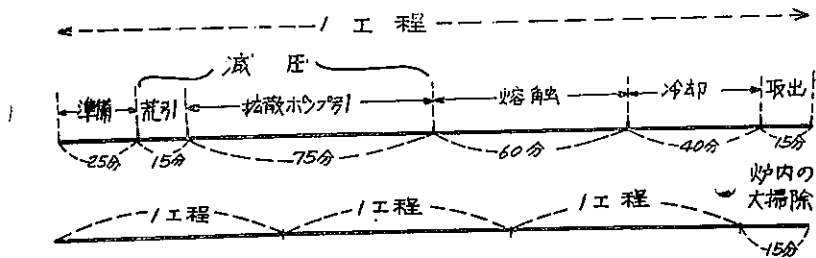
採塵時間は 128分, その中でベリリウムの地金の切断作業の行われたのは90分である。

§. 真空熔融作業 (9月18日, 午前中風雨, 午後晴)

すを除いて製品の強度を向上させるため, 含ベリリウム地金を真空熔融して再鋳する作業である。平常作業に於ける工程を図示すると, 次の頁の工程表のようになる。



第 2 図



註・平常では、夜勤者が4工程を行い、翌朝、日勤者が炉内の大掃除をするのであるが、測定の都合のため、昼間3工程作業の後、大掃除をした。

(1). 採塵位置略図其の他は、第2図に示す。

(2). 採塵過程

集塵管Ⅲ……拡散吸引15分と熔融工程60分を併せて採塵し、作業終了後も更に5分採塵する。

熔融が終ると直ちに、アルゴンガスが炉内に注入される。

尚、拡散ポンプよりの排気ガスは、そのまま作業場内に拡がる。

集塵管Ⅳ……荒引行程15分間と、その前後の各5分間も併せて採塵した。

この時、始めロータリーポンプより油煙と思われる濃厚な発塵があつたが次第に衰へ、8分後には肉眼で発塵が認められなくなった。この排気ガスは、そのまま作業場内に拡がる。

この時の風速20~25m/minであつた。

集塵管Ⅴ……荒引行程20分間と、その前の5分間を併せて採塵した。

前回同様の濃厚な発塵があつたが、13分後には肉眼で発塵が認められなくなった。

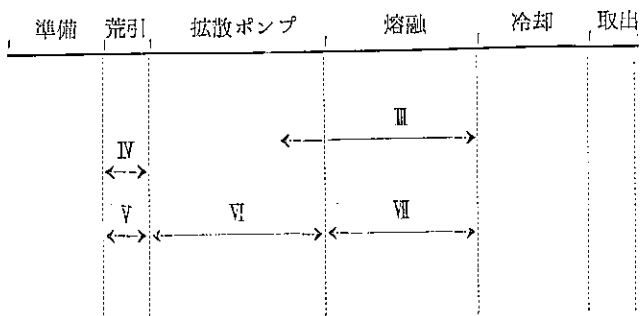
この排気ガスも作業場内に拡がる。この時2~3m/minの渦状の風があつた。

集塵管Ⅵ……拡散吸引工程22分の採塵を行った。拡散ポンプより出る排気ガスは作業場内に

拡がるが、ポンプよりの発塵は肉眼では認められなかつた。

集塵管Ⅶ……熔融作業60分と、その後の5分間は採塵した。この時0~1m/minの風があつた。この作業中には全く発塵が認められなかつた。

真空熔融作業時の採塵を要約すると、下図のようになる。

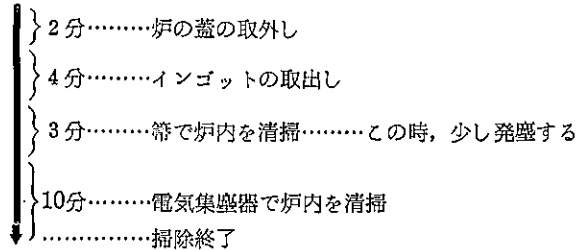


番号は集塵管の順序である。

集塵管Ⅷ……第2図に示した直径約1.5mの熔融炉の内壁を、腰を屈し、必要によつては炉内に顔を入れて掃除する。更に、場合によつては、ベンゾールで洗い落す事もある。ベンゾールを使う理由は、後に早く乾燥するからである。

## ベリリウム粉塵測定

炉内の大掃除に約20分かかり、その前後各5分間を併せて採塵した。  
掃除中、各個の操作に要する時間を図示すると、下のようになる。



### §. 濾紙式自動粉塵捕集器

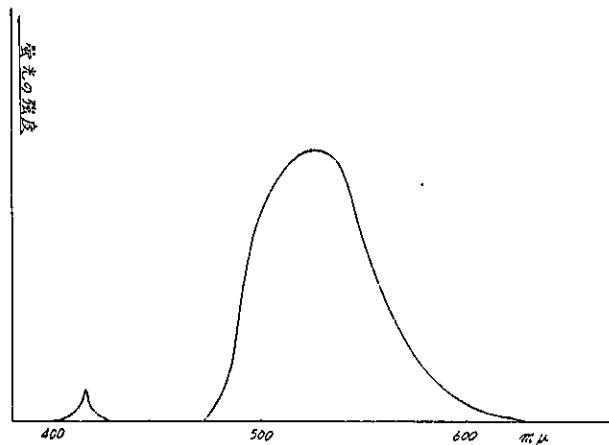
この集塵器を設置した位置は第1図に示した通りである。此の器械により9月17日午後1時より翌18日午後8時までの31時間連続に、1時間毎の空中粉塵を捕集した。

### §. 分析法

粉塵の付着している集塵管を、先ず約10ccの加温メチルアルコールで2回洗う、これは大量の油脂分が付着した粉塵に含まれているためである。次に大量(約500cc)の蒸留水で内壁を完全に洗滌する。両洗滌液を合せて濾過し、濾液は捨てる。残渣は濾紙と共に白色磁性るつばに入れて、約3時間強熱して有機物を破壊すると白色の灰分を得る。

濾紙式集塵器で捕集した粉塵の分析には、それが付着した濾紙を、そのまま白色磁性るつばに入れて3時間強熱して有機物を破壊すると、集塵管の場合と同様の白色の灰分を得る。以後の分析は、両者同一である。

るつば中の灰分に、熱濃硫酸1ccを加えて存在するBeOをとかし、冷えてから蒸留水を4cc追加し、稍加温してBeOの溶解を徹底する。此の液をガラス濾過器をとおして、10ccメスフラスコに取る。るつばは更に蒸留水で反復洗滌し、その洗滌液は同じく濾過して、10ccメスフラスコ中に注加し、最後に蒸留水で線まで満す。



第 3 図

分析試薬

1. 2N-NaOH. 水溶液
2. 飽和ピロリン酸ソーダ水溶液…高温で飽和水溶液を作り, 冷却してから濾過して使用する。
3. 5%青化カリ水溶液
4. 0.2%モリンのアセトン溶液

分析

25ccメスフラスコに10ccメスフラスコ中の溶液1ccを取り, 此に2N-NaOH液10ccを加え, 更に飽和ピロリン酸ソーダ水溶液5ccと, 5%KCN水溶液2ccを加え, 水を加えて線まで満し, これにモリン溶液0.2ccを加える。

此の溶液をセルに取り, これに紫外光を当てると, 含有されるベリリウムの量に比例して黄色の蛍光を発生する。この蛍光は第3図に示すような波長による強度を有する。測定は特定の波長の光を用いず, 蛍光の全量の強度を測定して, ベリリウムの量を求めた。

妨害イオンの影響

切断作業に於けるベリリウム地金の切粉をスペクトル分析にかけると, 次の元素が存在する事が分る。

比較的大量……………Si, Cu, Al.

少量……………Ti, Mn, Mg, Zn, Ca, Be, Fe.

微量……………Ni, Co.

分析に於いて, ピロリン酸ソーダを加えたのは, Caの蛍光発生を抑えるためであり, 青化カリを加えたのは, Cuの妨害作用を除き, 合せてZnによる蛍光の発生を抑えるためである。其の他の元素は, 分析途中の濾過で除かれるか, それが微量であるため, その妨害作用は無視してよいと考える。

§. 結果

(1) 電気集塵器による粉塵

	(集塵管)	(操作及び原料)	(Beの量 $\gamma/m^3$ )
切断作業	I	輸入地金	1.41
〃	II	再生地金	0.58
真空熔融	III	拡散, 熔融	0.11
〃	IV	荒引	1.44
〃	V	荒引	1.65
〃	VI	拡散	0.52
〃	VII	熔融	0.16
〃	VIII	掃除	1.83

ベリリウム粉塵測定

(3) 濾紙集塵器による粉塵

時刻	濃度	ベリリウムに関する作業
(17日午後)	(Be $\gamma/m^3$ )	
1～2時	0.25	輸入地金切斷6回
2～3	0.20	再生地金切斷9回
3～4	0.97	再生地金切斷5回
4～5	0.20	再生地金切斷6回
5～6	微量	
6～7	微量	
7～8	微量	
8～9	微量	
9～10	微量	
10～11	微量	
11～12	微量	
(18日午前)		
0～1	微量	
1～2	微量	
2～3	微量	
3～4	微量	
4～5	0.15	
5～6	微量	
6～7	0.15	
7～8	0.20	
8～9	0.50	
9～10	0.55	拡散ポンプ運転
10～11	0.20	10時36分より、炉の冷却開始
11～12	0.38	11時37分荒引拡散両ポンプ運転開始
(18日午後)		
0～1	0.20	昼休、作業中止
1～2	0.40	両ポンプ同時運転、1時12分以後熔融作業
2～3	微量	2時10分熔融終了、冷却作業となる
3～4	0.20	作業中止
4～5	0.20	荒引ポンプ15分運転、後拡散ポンプ運転
5～6	微量	熔融作業
6～7	0.23	6時2分作業中止、6時54分炉の掃除開始
7～8	0.30	7時13分全作業終了

「微量」と記したのは、濃度0.01  $\gamma/m^3$  以下とす



## ウラニウム取扱工場に於ける 気中ウラニウム粉塵濃度調査

原 登 興 重 治 野 崎 恒 右 坂 部 弘 之

### URANIUM CONCENTRATION IN THE AIR OF AN URANIUM PROCESSING PLANT

Noboru HARA, Shigezi KOSHI, Kosuke NOZAKI and Hiroyuki SAKABE

原子力産業の急速な発展に伴い核燃料としてのウラニウムの採掘並びに精錬が新しい産業として登場して来たが、ウラニウムによる職業性疾患の防止対策のための基礎資料に得る目的で某工場に於けるウラニウム鉱石及粉塵を取扱っている現場に於いて、作業場の空気中のウラニウムの量を測定した。

#### 1. 作業の概要

工場内における粉碎室、ダクト（乾式工程後及び湿式工程後）の中、実験室については33年12月19日に測定し、基礎実験室、撰鉱室、測定室、ウラニウム溶解及び切削作業場は34年1月12日に測定した。両日とも天候は晴天であつた。

##### (1). 粉碎室

80m<sup>3</sup>程の大きさの部屋で、ウラニウムの発生源は3カ所、何れもガラス密閉容器中の作業である。ウラニウムは、ガラス容器に付着しているゴム手袋で扱われる。容器には夫々排気装置があり、此等が運転している状態に於いて採塵した。

ここで発生するウラニウムは殆んど UO<sub>2</sub> で、作業員は概ね5名である。

肉眼では室内に浮遊粉塵を認めない。

測定時の室温は 20°C, 湿度は60~56%であつた。

##### (2). ダクト（乾式工程後）の中

##### (3). ダクト（湿式工程後）の中

##### (4). 実験室

約360m<sup>3</sup>の大きさの部屋で、中央にある水素焼結炉でウラニウムを強熱し、之より出るガスはフッドの直下に出る。

フッドの前方約1m, 高さ1.2mの処で採塵する。

室内の浮遊粉塵は肉眼では殆んど認められなかつた。

##### (5). 基礎実験室

ウラニウム鉱石を粉碎する部屋で、約100m<sup>3</sup>の大きさがある。採塵した時、全機械は運転しておらず、機械にウラニウム粉塵は全く付着していなかつた。

## ウラニウム粉塵調査

### (6). 撰鉱室

一般の化学実験室と酷似している。100m<sup>3</sup>程の大きさがあり、作業員は6~7人である。

### (7). 測定室

計量機器の並ぶ部屋で、約 20m<sup>3</sup>の大きさがある。部屋の一隅で、ガラス密閉容器中でウラニウム鉱石を研磨しており、多くの机の上にウラニウム粉末が散在している。

この部屋のファン及びフードは全然動いて居らず、排気が全く行われていない状態で採塵した。

室温は23°Cであった。

### (8). ウラニウム熔融作業場

ウラニウム合金を高周波で密閉容器中で、減圧状態で溶解している。作業中、拡散ポンプより出る排気ガスはそのまま室内に拡がる。この部屋は250m<sup>3</sup>程の大きさがあり、戸口は殆んど閉じ、排気操作は全く行っていない。

ポンプより約1m距てた所で採塵する。

### (9). ウラニウム切削作業場

旋盤により、ウラニウム地金を削る。

作業者はゴム手袋を付けている。作業者の顔面と切削点との距離は平均30cmである。

採塵位置は切削点より1m距てた同一の高さの点である。採塵時間は20分であるが、その中、旋盤の操業時間は8分である。

約 200m<sup>3</sup>の大きさの部屋で、フードは3つあるが、何れも動いていない。

室内の作業者は1~2名である。

## 2. 粉塵捕集方法

粉塵は交流型大容量電気集塵器を用い、流量50l/minで20~30分採塵した。

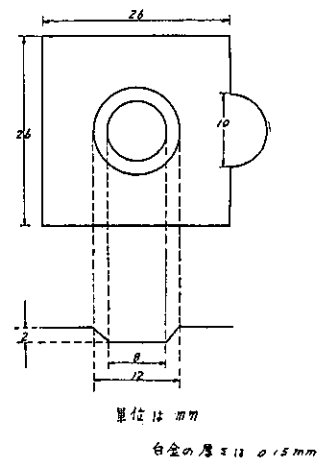
## 3. 分析法

粉塵を捕集した各集塵管は夫々、con. HNO<sub>3</sub> 約5ccで十分に洗い、次にその洗液に蒸留水約15ccを加えて再び十分に洗い、後に蒸留水で各管を更に完全に洗い、使用した硝酸の洗滌液及び洗滌した蒸留水を合せて、ガラス濾過器No.3(直径約10mm)で濾し、25ccメスフラスコ中に取り、蒸留水で線まで満す。

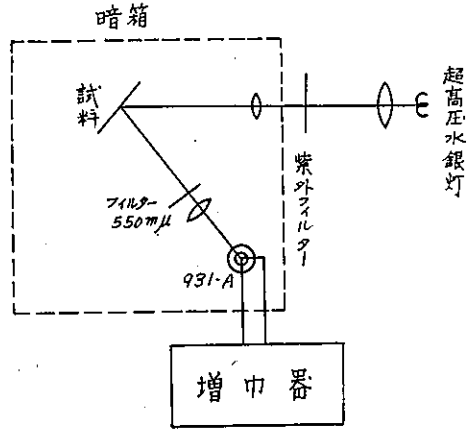
この液1ccを第1図の白金皿上で蒸発乾涸し、その残渣に NaF 粉末 200mgを加えて強熱して白色熔融体とする。熔融時間は約3分である。

白色熔融体に紫外光を当てると、含有されているウラニウムの量に比例して蛍光を発生するので、次に示す方法で蛍光の強度を測つて、ウラニウムの量を求めた。

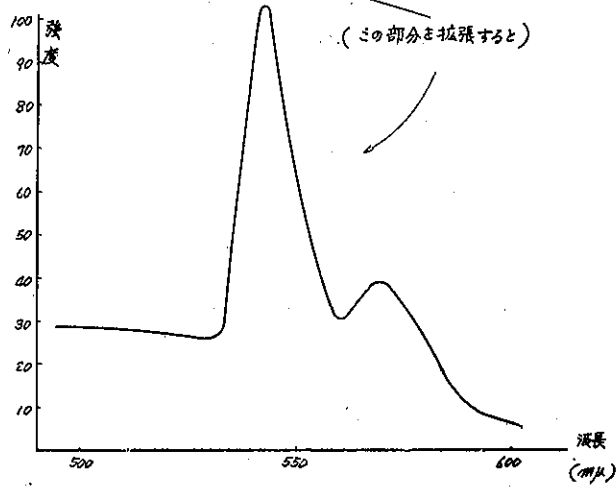
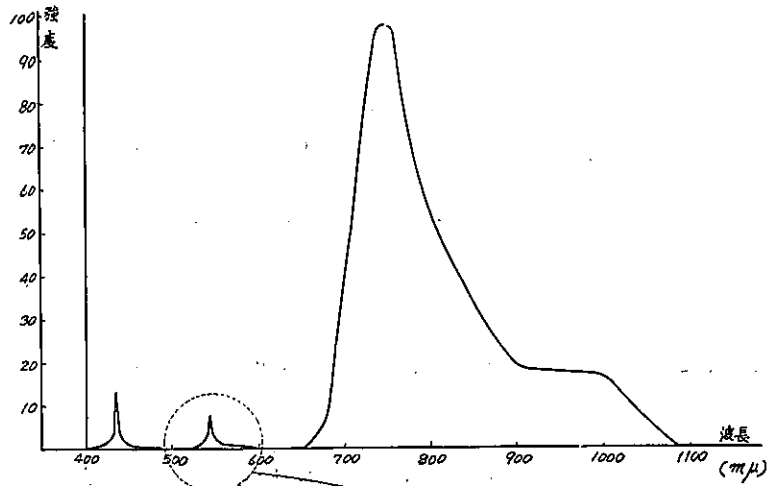
蛍光測定は一般に光電分光々度計が多く用いられているようであるが、空気中のウラニウム濃度あるいは尿中排泄量などのように微量となると充分な感度を期待し得ない。事実光電分光々度計では試量中に存在するウラニウムが



第1図



第 2 図



第 3 図 発生する蛍光の強度と波長の関係

0.01 $\gamma$  以上でないと測定できなかつた。

そこで蛍光分析のために第2図のような装置を組立てた。原理的には光電光度計と全く同じ原理を用い、光源の強度を増加させ、受光部と測定部の感度を増加させたものである。光源には200w超高压水銀電灯を用い、集光後310m $\mu$ 以上の可視線を通さないようなフィルターを通した後暗箱に入れ試料面で試料の大きさと同じ焦点の大きさにしぼつた。

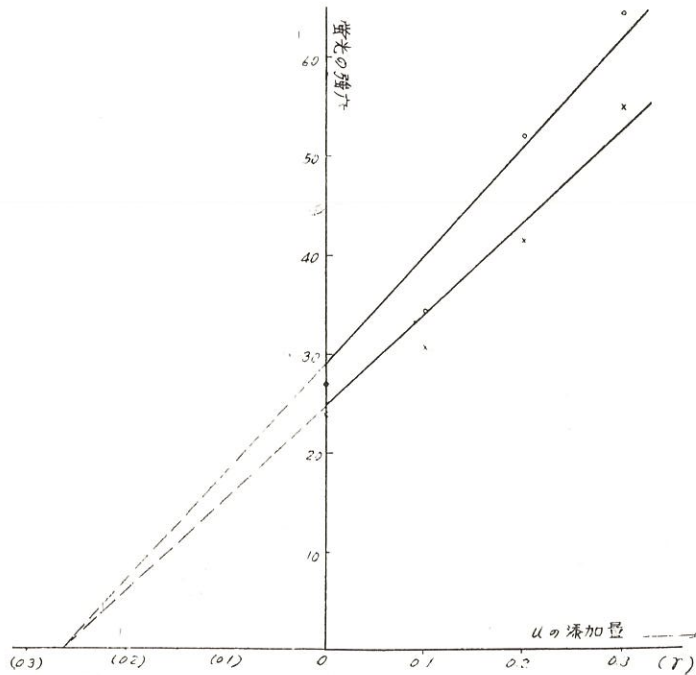
試料皿上で試料ののつていない他の部分からの散乱光を防ぐため試料保持部は金属板をいぶしたものの中央に径1cmの穴をあけ、熔融体全体がこの穴を通して光に露出されているようにした。

熔融体からの蛍光は入射光と45°の角度で受け550m $\mu$ の干渉フィルターを通し、光電子増倍管931~Aに集光した。蛍光のスペクトルは第3図の通りであり、750m $\mu$ に最大の山をもっているが、931~Aの感度特性は700m $\mu$ で殆んど0になつてしまうので、この波長での測定は出来ない。そこで543m $\mu$ 付近にある蛍光の山を利用し550m $\mu$ の干渉フィルターを用いたわけである。感度は増幅器の感度切替を5レンジとしたが最大感度は一目盛5/10000 $\gamma$ であつた。

#### 4. 妨害元素の影響

粉碎室のフードの上の堆積粉塵を、スペクトル分析で調べてみると、下記の元素が含まれている事が分つた。

- 比較的大量……………Si
- // 中量……………Fe, Al, Mg, Ca, Ti, Cu, Mn.
- // 少量……………Zn, Co, Pb, Ni, Sn, Sr.
- // 微量……………K.



第4図

此等の元素の中には、螢光の発生を抑制する性質を持つものがある。然し、皆、その量が生成されたNaFの白色熔融体に比べると極めて微量であるため、その抑制作用は無視出来る。これを立証するため、第4図の実験を行った。

一資料中のUを測定する時、これに夫々Uを0.1r, 0.2r, 0.3r加へたものと、加へないものについて、夫々の発生する螢光の強度の測定を行ったが、実験は2回共、資料中のUは2.64rと一致する(第4図)。

尚、白金皿上で検液1ccを蒸発乾固した時、最大量の残渣を示す粉碎室の液でも0.013mgであり、他の液では此より遙かに少量であるから、妨害元素の影響全く無視出来る。

## 5. 結果

	Uの量 (γ/m <sup>3</sup> )
粉 碎 室	3.22
ダ ク ト (乾式工程後) の中	0.60
ダ ク ト (湿式工程後) の中	0.15
実 験 室	0.70
基礎実験室	0.066
撰 鋏 室	0.15
測 定 室	0.62
ウラニウム 熔融作業場	0.20
ウラニウム 切削作業場	0.56



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