









**NBSIR 73-400**

# **Preparation of Simulated Environmental Filters Containing Quartz and Clay**

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J. K. Taylor, E. R. Deardorff, C. D. Olson, and R. W. Burke

National Bureau of Standards  
Department of Commerce  
Washington, D. C. 20234

October 1973

Final Report

Prepared for  
**National Institute for Occupational Safety and Health**  
**Division of Laboratories and Criteria Development**  
**Cincinnati, Ohio 45202**



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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director





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## ABSTRACT

This report describes techniques for the preparation of simulated environmentally collected samples consisting of small amounts of mixtures of quartz and clay deposited on membrane filters. The amounts correspond to that which would be collected during an 8-hour period in an atmosphere containing quartz below and above TLV concentrations. An improved spectrophotometric method for the determination of quartz in environmental samples, developed during the course of the work, is also described.

## 1. INTRODUCTION

The purpose of this investigation was to develop techniques to produce filters on which a mixture of quartz and clay are deposited to simulate environmentally collected samples. Such filters would be useful for evaluating the reliability of various analytical methods for determination of industrial exposure to quartz dust in the atmosphere. Except for the collection step, they should simulate all other problems of a typical analytical field sample.

## 2. PRELIMINARY EXPERIMENTS

### 2.1 Preparation of Filters

In conference with the NIOSH Project Officer, it was decided that the samples should consist of a two-component mixture of quartz and clay. The total amount of material on each filter should be approximately 400  $\mu\text{g}$  with three different levels of quartz. The target concentrations selected were:



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<u>Series</u>	<u>Quartz, <math>\mu\text{g}</math></u>	<u>Clay, <math>\mu\text{g}</math></u>	<u>Total, <math>\mu\text{g}</math></u>
100	0	400	400
200	30	370	400
300	80	320	400
400	200	200	400

The first approach which came to mind was to use natural mixtures of clay and quartz, but no suitable substances were discovered. Accordingly, the decision was made to use synthetic blends.

The clay used was NBS Standard Reference Material 97a, Flint Clay, which has the following composition:

<u>Constituent</u>	<u>Percent by Weight</u>
$\text{SiO}_2$ (as silicate)	43.7
$\text{Al}_2\text{O}_3$	38.8
$\text{Fe}_2\text{O}_3$	0.45
$\text{TiO}_2$	1.9
$\text{CaO}$	0.11
$\text{SrO}$	.18
$\text{MgO}$	.15
$\text{Cr}_2\text{O}_3$	.03
$\text{Na}_2\text{O}$	.037
$\text{K}_2\text{O}$	.50
$\text{Li}_2\text{O}$	.11
$\text{ZrO}_2$	.063
$\text{BaO}$	.078
$\text{P}_2\text{O}_5$	.36
Loss on Ignition	13.32

Chemical analysis at NBS indicates that substantially all of the silicon in this sample is silicate. The quartz content

is less than 0.5 percent. Prior to issuing as an SRM the clay was ground to pass a 100 mesh sieve with 80 percent passing a 200 mesh sieve. Particle size measurements made at NIOSH, by Mr. Charles Gorski (Toxicology Branch), indicate the geometric mean diameter (50 percentile) is 0.39  $\mu\text{m}$ .

The quartz used for the samples was a commercial material known as "Min-u-sil 15" with an average particle size of 4.5  $\mu\text{m}$ . This material is more than 99 percent  $\text{SiO}_2$ .

Experience with the preparation of filters containing toxic metals (NBS Report NBSIR 73-256), suggested the use of a similar technique in the present case. Preliminary experiments were encouraging and the following procedure was adopted. The finely divided solid was dispersed in 1 percent aqueous tragacanth solution and 100  $\mu\text{l}$  portions were delivered to the filter by means of a push-button type calibrated pipette.

A simple technique for quality control of the filter preparation would have been weighing before and after deposition, using a direct-reading electrobalance. Experiments were performed to determine the reliability of this procedure by weighing filters that had been alternately wetted and dried. Variabilities of 10 to 100 micrograms were found and therefore a more precise method was sought. While it is believed that this procedure could be improved by careful control of drying and weighing conditions and possibly by the use of less hygroscopic filters, it was abandoned in favor of direct analysis.

The clay and quartz were dried at 110°C for four hours prior to mixing. The mixtures of the two solids were made using a ball mill, a V-blender, and finally a mortar and pestle to assure uniformity and to break apart balls of material formed due to electro-static charges. A total charge of 200 g was used, with appropriate amounts of each component to produce the target concentrations. This procedure was used because it was desired to prepare both bulk samples and deposits on filters. The material proved to be difficult to blend due to sticking on the walls of the mixers. Frequent tapping apparently corrected this, so the process was repeated through many cycles to achieve apparent homogeneity.

Suspensions of the mixtures were made by weighing 400 mg and adding this to 100 ml of water. It was observed that the suspension settled rapidly when not stirred and that stirring by immersion in an ultrasonic bath was not completely effective. A magnetic stirrer, used continuously, left small amounts of material unsuspended.

Experiments to determine the uniformity of suspension were made in which 100  $\mu$ l of slurry were pipetted into micro-beakers, dried and weighed. This showed a relative standard deviation of 15 percent which was considered to be unacceptable. Inspection of the suspension showed that, although constantly stirred, visible amounts of solid material were settling and/or distributed in patterns in the liquid. Accordingly, a means to prevent this was sought.



It was found that the addition of gum tragacanth to the suspension prevented settling or at least retarded it for periods of days. The gum also was considered to be beneficial in serving as a binder for the deposit, after drying, to prevent loss by abrasion. A 1-percent solution appeared to be most satisfactory. The suspension was prepared by heating the 1-percent tragacanth solution to about 90°C, then adding the SiO<sub>2</sub>/clay sample mix, and letting the solution cool. This operation was done using a hot plate-stirrer and a magnetic stirring bar. Although no visible settling occurred, the suspensions were stirred continuously, during filter preparation.

### 3. PREPARATION OF FILTERS

The deposits were placed on membrane-type filters, type HAWP, 47 mm in diameter. A single filter was placed in the bottom portion of a plastic petri dish-type container and 0.1 ml of the suspension was transferred by a push-button pipette. The cover was loosely placed on the dish, and the filter was air dried before closure. The filter containers were given a serial number, indicating the order of preparation, to assist in identifying any systematic error of preparation.

The filters were arranged in rows of 10, which were prepared in sequence. Then a second set of 10 was prepared. It was possible to make the final transfers to 50 filters in about one hour.

The numbering system used was as follows:

Blank - 100 Series - 000101 to 000199

Level 1 - 200 Series - 000201 to 000299

Level 2 - 300 Series - 000301 to 000399

Level 3 - 400 Series - 000401 to 000499

#### 4. ANALYTICAL METHOD

The filters were analyzed by a spectrophotometric method to determine the amount of quartz present. The NIOSH method was used initially but difficulties were experienced. For example, apparent assay values of 20 to 50  $\mu\text{g}$  were found on series 100 filters which were not believable. Also, unacceptable values were obtained at all assay levels with very large standard deviations. Accordingly, research was conducted to determine the cause of this and to develop an analytical procedure to eliminate the problems. Some of the details of this and the method finally developed and used are given below.

##### 4.1 Sample Treatment

Place the membrane filter containing the sample in a 125 ml pyrex Erlenmeyer flask and gently heat over a Meeker burner until it chars flames. Then heat the Erlenmeyer strongly until all visible carbon is burned off. Add 25 ml of 85 percent phosphoric acid to the beaker. With a thermometer inserted in the beaker, heat the solution on a hotplate to 200°C and continue heating for 12 minutes while the temperature rises to 225° to 245°C. Swirl the solution occasionally to rinse the sides of the beaker. Allow the solution to cool to 100°C, and



add 100 ml of hot water. Swirl to mix and filter with suction through a 25 mm HAWP membrane filter, pore size 0.45  $\mu$ . Wash alternately with hot HCl (1+10) and hot water at least five times and finish washing thoroughly with hot water. Transfer the 25 mm filter to a wet 47 mm HAWP membrane filter, pore size 0.45  $\mu$ , on the suction flask. Wash the edges of the 25 mm filter with water to rinse out the  $H_3PO_4$  from the portion of the small filter which was not adequately washed during the first filtration.

Place the two filters flat in the bottom of a 250 ml Teflon beaker. Add 1 ml of HF (1+1). Place a thin polyethylene disc, cut to fit the bottom of the beaker, on top of the filter papers and cover the beaker with a Teflon cover. Allow it to stand for 30 minutes. Add 40 ml of 5 percent boric acid solution. Remove the polyethylene disk and the two membrane filters, washing them with small amounts of water. At this point samples containing more than 80  $\mu g$  of  $SiO_2$  can be diluted to a convenient volume with boric acid and an aliquot taken for analysis. The aliquot is pipetted into a 250 ml Teflon beaker and diluted to 40 ml with boric acid: Following this, 10 ml of a 10 percent  $H_2SO_4$ -10 percent  $HNO_3$  solution (ultra pure acids) is added to the solution. The molybdenum blue color is developed and read on the spectrophotometer as described in Section 4.4, Color Development. A blank should be run through all steps of the sample treatment. It was observed that the reagents and the membrane filters contributed some background

color to the samples. This background absorbance must be subtracted from the observed sample absorbance.

#### 4.2 Determination of Free Silica

This recommended spectrophotometric method for the determination of silicon was developed in 1963 at NBS for use on SRM zirconium and zircaloy. At that time, experiments were performed to determine the concentration of reagents required, the optimum pH and temperature for maximum complex formation and color development, the conditions for extraction of molybdosilicic acid into butanol, and the use of a backwash step to remove interfering elements. The molybdenum (V) complex was reduced with stannous chloride to form the heteropoly molybdenum blue complex whose absorbance was then measured on a spectrophotometer at 635 nm.

The first problem encountered in adapting this spectrophotometric method to the determination of quartz on the membrane filters was separating it from the soluble silicates. This difficulty was subsequently circumvented by dissolving the soluble silicates with hot phosphoric acid and collecting the insoluble  $\text{SiO}_2$  on another membrane filter. However, this procedure presented a second problem of how to remove all of the phosphoric acid from the filter. This is necessary since phosphate interferes with the molybdenum blue determination of  $\text{SiO}_2$ . A clean separation was not possible because the 25 mm membrane filter could not be washed well enough on the edges of the filter that were covered by the glass funnel fittings.

The last traces of phosphoric acid could be washed away by transferring the 25 mm filter to the center of a 47 mm filter placed on the 47 mm glass filter frit, and carefully washing the clean edges of the 25 mm filter with water.

#### 4.3 Calibration Curve

A standard silicon solution of 200  $\mu\text{g}$  Si/ml was prepared by fusing 213.9 mg of pure  $\text{SiO}_2$  with 2 grams of sodium carbonate, dissolving the melt, making up to 500 ml with water and storing in a plastic bottle. A dilute standard working solution was prepared by diluting 25 ml of the standard solution (200  $\mu\text{g}$  Si/ml) to one liter and storing in a plastic bottle. This dilute solution contains 5  $\mu\text{g}$  Si/ml, equivalent to 10.7  $\mu\text{g}$   $\text{SiO}_2$ /ml. Aliquots of this dilute solution were used to prepare a calibration curve.

#### 4.4 Color Development

The following procedure is used for color development. Transfer 0, 1 ml, 2 ml, 4 ml, 6 ml and 8 ml of the dilute standard silicon solution to six 250 ml Teflon beakers. Add 10 ml of 10 percent  $\text{H}_2\text{SO}_4$  - 10 percent  $\text{HNO}_3$  (use highest purity acids) and 0.5 ml HF, 48 percent. Add 40 ml of boric acid solution (50 g per liter). Add potassium permanganate solution (0.6 g per liter) dropwise to produce a permanent pink tint. Add 4 ml of molybdic acid solution (25 g of ammonium molybdate tetrahydrate in 200 ml of  $\text{H}_2\text{SO}_4$  (1+9) diluted to 250 ml with water and filtered through close-textured

paper). Adjust the pH of the solution to 1.7 - 1.8 with ammonium hydroxide solution (prepared by bubbling ammonia gas, using plastic tubing, into ice cooled distilled water in a polyethylene bottle until solution is saturated ). Cover the beaker with a Teflon cover and heat for 10 minutes on a steam bath. Cool in water at approximately 20°C for 10 minutes. Add 4 ml tartaric acid solution (200 g per liter). Mix thoroughly, and transfer the solution to a 250 ml glass separatory funnel with Teflon stopper and stopcock. Wash the beaker twice with water and add the water to the funnel. Dilute the solution to a volume of approximately 90 ml, and add 14 ml of H<sub>2</sub>SO<sub>4</sub> (1+1) and mix. Cool the separatory funnel in cold running water. Add 50 ml of normal butyl alcohol, and shake vigorously for one minute. Allow the layers to separate; drain, and discard the lower acid layer. Wash the butyl alcohol layer by adding 20 ml of H<sub>2</sub>SO<sub>4</sub> (1+99) to the separatory funnel and shake for 30 seconds. After the layers separate, drain, and discard the lower acid layer. Repeat this washing two more times. Transfer the butyl alcohol layer to a dry 50 ml volumetric flask. Wash the funnel twice with 1 to 2 ml of butyl alcohol, and add washings to the flask. Add 0.5 ml of stannous chloride reducing solution (Dissolve 2 g of SnCl<sub>2</sub> · 2H<sub>2</sub>O and 1 mg CuCl<sub>2</sub> · 2H<sub>2</sub>O in 100 ml of HCl and store in glass stoppered bottle. Prepare fresh solution every week.) to the flask, dilute to the mark with butyl alcohol, and mix.

Fill a 1 cm reference cell with normal butyl alcohol and adjust the photometer to 635 nm. Take the photometric readings of the calibration solutions in a 1 cm cell vs. the reference solution. Plot the photometric readings of the calibration solutions with respect to the micrograms of silicon per 50 ml of solution ( $\mu\text{g Si}$  multiplied by 2.139 equals  $\mu\text{g SiO}_2$ ).

## 5. SUMMARY OF RESULTS

Table 1 summarizes the analytical results obtained with the method as finally developed. All results prior to this were discarded due to uncertainties in some aspects of the procedure.

The precision is reasonably good which indicates that the filters are homogeneous. Only one value, namely that for filter No. 410 appears to be out of line and it was not included in the average.

The accuracy of the values is still uncertain. It will be noted that the average value is about 3/4 of that expected. It is difficult to understand why the samples deviated that much from the target values. It would be easy to conclude that the problem arises from partial solution of the very fine fraction of  $\text{SiO}_2$  during the phosphoric acid leach. However, four gravimetric determinations of the amount of  $\text{SiO}_2$  remaining after leaching 1 mg samples of "Min-u-sil 15" with phosphoric acid indicated losses of 2, 15, 6, and 2 percent, respectively, hence this explanation does not seem reasonable.



Table 1  
Summary of Results

<u>Sample Number</u>	<u>μg SiO<sub>2</sub></u>	<u>Average SiO<sub>2</sub></u>	<u>Expected Value, μg</u>
124	2 )		0
155	trace)		0
127	trace)	0	0
138	0.2 )		0
239	25)		30
250	24)		30
227	24)	23	30
247	20)		30
360	63)		80
315	62)	62	80
333	62)		80
410	156		200
460	137)		200
428	136)	135	200
440	133)		200

NBS 97a Clay + 0.1 μl gum + 47 mm filter

314 μg	2		0
420 μg	2		0
320 μg	trace		0
371 μg	2		0

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