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QUARTZ POWDER OF INDIAN ORIGIN**

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# **Trace Element Characterisation and Purification of Quartz Powder of Indian Origin**

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## **1. Abstract**

Analytical methodologies for the trace element characterisation and purification of quartz powder of Indian origin have been described. Metallic impurities (11 elements) in ~ 700 quartz samples have been analysed using different instrumental techniques. The values are cross-validated by American and British analytical laboratories. A special multi channel vapour phase digestion (MCVPD) chamber has been designed to reduce the process blank levels for the determination of ultra trace impurities in high purity silicon matrix. In this vessel 21 samples can be digested at a time in a period of 8hrs at normal pressure and low temperature (~80°C). Analytical methodologies for the determination of non-metals (phosphorus, boron and chloride) at very low levels (<1ppm) have also been described. A highly cost effective, single step, room temperature purification procedure is developed based on chemical leaching. Around 300 raw quartz powders (3-4N) from various mines have been purified to 5N pure (optical grade).

## **2. Introduction**

Silica in its various crystalline and amorphous forms has wide spectrum of industrial applications. Its use ranges from a simple raw material for the manufacture of glasses to highly technical applications such as quartz oscillators and optical waveguides used in the long distance telecommunication industries. Large deposits of quartz are found in various parts of our country,

from which it is mined and exported to various countries. Its cost in international market depends upon the levels of impurities present in it. Metallic impurities affect the optical property of quartz. Therefore, accurate determination of these impurities in quartz powder is essential. Quartz is also used in the manufacture of silicon rubber for which levels of water leachable ions are important. Presence of impurities like chloride and fluoride in quartz powder corrodes moulding apparatus used in the manufacture of TV picture tube. The electrophysical properties of silicon compounds essentially depend on levels of boron and phosphorus and hence determination of these impurities is also necessary.

This report describe the methods developed for the determination of metallic and non-metallic impurities in raw and purified quartz, effectiveness of MCVPD technique in decreasing the process blank levels and purification of raw quartz to 5N pure quartz.

### **3. Experimental**

#### *3.1. Instruments and apparatus*

1. Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) Model JY 2000 2. Flame Atomic Absorption Spectrometer (FAAS) Model GBC 932 AA 3. UV-Visible Spectrophotometre Model U-3210/U-3410. MCVPD apparatus has been designed and prepared at CCCM.

#### *3.1. Physical processing*

Physical processing has been carried out by M/s Gimpex, Chennai, a quartz exporting company using the following procedure. Naturally occurring quartz (lump size 30-35mm) was crushed to 6mm-grain size by jaw and crusher-mill. Magnetic particles were seperated by rare earth plate magnet. Non-magnetic fractions were again grained to -16mesh by agate mortar and taken for analysis.

### 3.2. Analytical procedures

#### 3.2.1. Determination of traces of metal impurities

a) Open digestion: About 1g of (raw/purified) quartz powder was taken in a 50ml wide mouth screw cap plastic container, 48% HF (1ml/100mg of quartz powder) and 0.5ml of con. H<sub>2</sub>SO<sub>4</sub> were added. The mixture was allowed to react at room temperature overnight. After complete dissolution, the solution was evaporated on a water bath (until 0.5ml of H<sub>2</sub>SO<sub>4</sub> remains in the container) and made up to required volume and analysed by ICP-AES, FAAS.

#### b) Multi Channel Vapour Phase Digestion (MCVPD)

The quartz samples (~1g each) were weighed into the PFA vials, 0.2ml of H<sub>2</sub>SO<sub>4</sub> was added to each quartz sample. The PFA vials were then placed in the grooves of the sample rack. 250 ml of pure / GR grade HF were carefully poured in to the reagent reservoir. The vessel was capped and placed on a water bath located in fume hood for digestion. When the dissolution was complete, the MCVPD assembly was allowed to cool to room temperature. The PFA vials were then heated at approximately 100°C on a ceramic top hot plate to remove HF. After evaporation made upto required volume and analysed by ICP-AES and ICP-MS.

#### 3.2.2. Determination of Non-Metals

a) Boron: The quartz samples were dissolved using HF (48%) in screw capped plastic container at room temperature. After dissolution required quantity of mannitol [mannitol to boron ratio > 10 (w/w)] was added prior to evaporation to dryness, made upto required volume and analysed by ICP-MS [1].

b) Phosphorus: About 1g of quartz powder was dissolved by vapour phase digestion [2]. The sample solution was treated with 0.5ml each of H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>. After removing HClO<sub>4</sub> it was taken in H<sub>2</sub>SO<sub>4</sub> medium (keeping ~0.4N by required dilution) for spectrophotometric determination using the following procedure.

Sample solution was taken in a separating funnel (after maintaining the acidity at 0.4N and volume at around 40ml). Two ml of ammonium molybdate solution (2.5% in 3%HNO<sub>3</sub>) was

added and mixed thoroughly for 1 minute, 5ml of n-butyl acetate was added to this mixture and vigorously shaken for 1 minute, to extract the molybdophosphate complex. After discarding the aqueous phase, 10ml of acidified dye solution (9 ml of 0.008% of crystal violet + 1ml of 5N HNO<sub>3</sub>) was equilibrated with the organic phase for the formation of ion-pair of molybdophosphate with crystal violet. The aqueous phase was discarded and the organic phase containing the ion-pair was washed twice with 5ml of 0.5N HNO<sub>3</sub>. The organic phase was drained into a dry 10ml flask and the inner wall of the separating funnel was washed with a few ml of acetone to collect back any traces of the ion-pair sticking to the funnel wall and finally the solution was made upto 10ml with acetone. The absorbance of the solution was measured at 593nm after filtering the organic layer through Whatmann 540 filter paper to remove any aqueous traces.

c) Chloride: The sample (~0.5g) was fused with NaOH and the fusion mixture was leached with warm water. Then ~ 3ml of HNO<sub>3</sub> was added to precipitate out silica as silicic acid, filtrate was made up to required volume. To aliquot of the sample solution, 2ml of 0.25M ammonium ferric sulphate in 9M HNO<sub>3</sub> followed by 2ml of saturated mercuric thiocyanate in ethanol was added and made upto 25 ml. After 10 minutes, the absorbance was measured at 460nm.

### 3.2.3. Determination of water leachable-ions (Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, F<sup>-</sup>, Na<sup>+</sup>, K and Fe<sup>3+</sup>)

After leaching the quartz powder with water, these ions were determined in the leachate by the following analytical / instrumental technique. Chloride was determined both by ion selective electrode and by spectrophotometric method (section 3.2.3c). Fluoride by spectrophotometric method using Zirconium-Xylenol orange complex and cross-validated by ion-selective electrode. Phosphate was determined using the procedure mentioned in section 3.2.2.b. Metallic ions were determined by ICP-AES.



### *3.3. Purification of raw quartz powder by chemical leaching*

#### *3.3.1. Three step process at elevated temperature (Routine process)*

Raw quartz powders (obtained after magnetic separation) were subjected to purification by sequential chemical leaching using dilute mineral acid solution ( $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ) in presence of dilute  $\text{HF}$ . Quartz sample (10g) and equal volume of acid mixture solutions were taken in a LDPE container, kept on water bath in a closed condition for two hrs with periodical shaking at an interval of 15 minutes. After the scheduled time the reactants were drained off and washed twice with Millipore water and the quartz was passed to the next leaching process with other two mineral acid mixtures as done by earlier leaching process. After final leaching, quartz powder was washed by Millipore water until washed solution becomes neutral. After heating it at  $200^\circ\text{C}$  for 4hrs, quartz powder was taken for analysis. As required by Gimpex Ltd., purification by mineral acid leaching has been carried out in our laboratory for ~ 300 samples.

#### *3.3.2. Single step process at room temperature (Developed process)*

About 10g of quartz powder was taken in a LDPE container and equal volume of diluted acid mixtures ( $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{HF}$ ) was added, shaken well and kept it at room temperature in a closed condition for 48 hrs. After the scheduled time the reactants were drained off and washed by Millipore water until washed solution becomes neutral. After heating it at  $200^\circ\text{C}$  for 4hrs, quartz powder was taken for analysis.

## **4. Result and Discussion**

### *4.1. Determination of traces of metal impurities*

Quartz and silicon metal powders are usually dissolved using  $\text{HF}/\text{HF}:\text{HNO}_3$  mixture. But these acids contain many impurities and also the quantity of acids used is much greater than the quantity of sample taken, the reagent blank becomes unacceptably high for the determination of trace impurities in high purity quartz. Sub-boiled acids can be used to control the process blank

levels. But preparation of sub-boiled acids is time consuming, needs special equipment and leads to contamination risk while storing in a container. To control blank levels, a simple low temperature, low pressure and multi channel vapour phase digestion (MCVPD) system is designed which enabled the determination of impurities at ultra trace levels in quartz and silicon metal powder. This MCVPD procedure has been applied for determination of trace impurities in purified quartz powder. Our department is also involved in the process of producing high purity silicon upto 6N+. This method can also be applied for determining trace impurities in such samples.

The determination of Na, K and Li has been carried out by FAAS/FAES after addition of cesium buffer (around 100 times of total alkali metal present in the solution) to suppress the ionisation, the same amount of buffer has been added to the standard solutions. As the level of Li in majority of quartz samples contained at ppb levels, its determination is carried out by FAES using Suprapur CsCl as ionizing buffer and the values are cross validated by ICP-MS and ICP-AES.

During the routine analysis of raw quartz sample, it is observed that some samples did not dissolve completely by HF and HNO<sub>3</sub> medium. Such samples are brought into solution by HF-HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> and in some cases by HF- HNO<sub>3</sub>-HClO<sub>4</sub> depends upon the amount of Ca and K present in the sample. Alkali digestion has also been carried out to dissolve some of the quartz samples that contain resistant mineral phases. After suitable dilution, the sample solutions are analysed by ICP-AES and FAAS.

#### *4.2. Multichannel Vapour Phase Digestion (MCVPD)*

Sample decomposition of high purity quartz powder requires Suprapur grade (E.Merck) HF to reduce the blank level as the analytes are in parts per billion levels. To obviate the need of costly Suprapur grade HF, a novel apparatus has been fabricated where, in a single batch 21 high purity quartz samples can be digested at a time by keeping it for 8hrs on water bath. Commercially available polypropylene vessel (capacity 5 liters) has been used for this purpose.

Significant decreases (20-1000 times) in trace metal process blank concentrations (18 trace impurities) from impure grade HF is observed. Comparison of process blank values of conventional digestion and MCVPD procedure is presented in Table-1.

#### *4.3. Determination of Non-Metals*

A method has been developed for determination of traces of B in purified quartz powder using ICP-MS [1]. The loss of B due to volatilisation during removal of silica matrix is eliminated by adding mannitol. The recovery of boron is established by comparing the values obtained by external calibration with those obtained by isotope dilution. Using this method boron concentration can be determined at ppb levels. A simple vapour phase decomposition (VPD) of quartz powder has been developed for the determination of phosphorus [2]. Phosphorus contamination by reagents (HF, HNO<sub>3</sub>) has been drastically reduced (around 250 times) compared to conventional dissolution procedure. Phosphorus is determined by spectrophotometry as an ion pair of molybdophosphate with crystal violet. Limit of Detection is 0.066µg/g. A method has been developed for the determination of chloride in quartz powder by reaction of the analyte with Hg(SCN)<sub>2</sub>-Fe<sup>3+</sup> reagent. After NaOH fusion, the extract is neutralised with HNO<sub>3</sub>. Below a pH of 1.5 of this extract, the tendency of the solution is towards the polymerisation of excess silica and ultimately aggregates to form a precipitate of silicic acid. After filtration, the chloride is determined by Hg(SCN)<sub>2</sub>-Fe<sup>3+</sup> method. Cross validation has been done by turbidimetric (AgNO<sub>3</sub>) method. All the results are shown in Table 2.

The values obtained for water leachable ions are given in Table 3.

#### *4.4. Purification of raw quartz powder by a single step process at room temperature (Developed process)*

The results obtained are compared with the routine procedure, (Table-4) which showed the same factor of purification and in some cases got better purification. Advantages of the developed procedure compared to the routine procedure are:

1. This does not require any expensive reactor vessels, as HDPE containers are adequate.

2. No need for heating, therefore this reduces power consumption.
3. Consumption of acid and Millipore water is reduced by 66%.
4. No need for highly skilled operator.
5. Since the amount of acid consumption is, less waste treatment cost is also reduced.
6. Since purification method requires inexpensive HDPE containers, large number of containers can be handled at a time to increases production.

## **5. Application**

As application of the methods developed ~ 700 quartz samples have been analysed for M/S.Gimpex Ltd., Chennai, one of the quartz exporting companies in India. They were using the analytical services of foreign laboratories (American and British laboratories) before approaching CCCM. After cross checking the values obtained using our procedures with American and British Laboratories they have been utilising our services for the past 3-4 years. Purification of raw quartz powder ( ~ 300 ) has also been carried out using the procedure developed at CCCM. Values obtained for a set of 5 samples both before and after purification were given in Table 4.

## **6. Conclusion**

The developed methodology (MCVPD) for the determination of ultra trace impurities in high purity silicon matrix does not require costly imported digestion vessel. Using this vessel, large number of samples of (upto 6N+ pure) can be analysed on routine basis using AR grade HF. This vessel can also be used for digesting any other high purity samples, which can be digested by low boiling point acids (HF, HCl, and HNO<sub>3</sub> etc.,). Single stage room temperature purification procedure is developed is cost effective with respect to energy consumption and reactor vessel.

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Table-1. Comparison of process blank values of conventional digestion and MCVPD procedure for 1g of quartz powder ( $\mu\text{g}/\text{kg}$ )

Element	Conventional (using pure grade, n=2)	MCVPD (using pure grade, n=5)	Conventional (using GR grade, n=2)	MCVPD (using GR grade, n=5)	Conventional (using suprapur grade)
Na	20000	$60 \pm 12$	640	$70 \pm 13$	$120 \pm 16$
K	15000	$60 \pm 16$	280	$60 \pm 16$	$90 \pm 20$
Ca	5000	$45 \pm 8$	800	$50 \pm 9$	$100 \pm 30$
Ti	800	$40 \pm 10$	260	$40 \pm 8$	$40 \pm 10$
Fe	12000	$60 \pm 10$	680	$70 \pm 12$	$70 \pm 12$
Li	40	$1.5 \pm 0.2$	5	$1.5 \pm 0.4$	$1 \pm 0.2$
Mg	1200	$13 \pm 2.3$	360	$12 \pm 2.5$	$10 \pm 3$
Al	1600	$50 \pm 12$	300	$40 \pm 10$	$30 \pm 11$
V	1000	$1.0 \pm 0.2$	4	$0.9 \pm 0.2$	$2 \pm 0.4$
Cr	80	$7 \pm 0.6$	30	$6 \pm 0.5$	$8.2 \pm 1.1$
Mn	400	$6 \pm 0.3$	220	$7 \pm 0.5$	$7.4 \pm 0.3$
Co	20	$0.5 \pm 0.2$	7	$0.7 \pm 0.3$	$0.9 \pm 0.2$
Ni	300	$3.8 \pm 0.8$	50	$3.3 \pm 0.8$	$15 \pm 1.5$
Cu	1500	$3 \pm 1.2$	16	$4.0 \pm 1.4$	$2.3 \pm 0.3$
Zn	1000	$6 \pm 1.5$	140	$5.0 \pm 1.4$	$9.6 \pm 0.2$
Mo	160	$4 \pm 0.3$	12	$2.0 \pm 0.2$	$3.0 \pm 0.4$
Cd	10	$0.4 \pm 0.2$	3.8	$0.8 \pm 0.3$	$0.4 \pm 0.1$
P #	7500	$11 \pm 7$	5000	$11 \pm 7$	$200 \pm 15$

# Absolute process blank value of phosphorus in ng for 0.5g of quartz powder (by Spectrophotometry)

Table-2. Determination of Chloride by mercuric thiocyanate and turbidimetric method

All values are in mg/kg

Sample No	Mercuric thiocyanate method	Turbidimetric method
B-449	122	83
B-450	78	62
B-451	289	277
B-452	90	106
B-453	88	80
B-454	-	21
B-455	29	44
B-456	49	44
B-457	30	44
B-458	130	110

Table-3. Determination of water leachable ions in quartz powder

All values are in mg/kg

Sample number	Na	Fe	K	$PO_4^{3-}$	$F^-$	$Cl^-$
B-640	1.6	0.10	0.7	0.11	<0.5	6.7
B-641	1.6	0.05	0.4	0.07	<0.5	9.4
B-642	1.7	0.07	0.5	0.09	<0.5	14.4
B-643	1.7	0.07	0.4	0.22	<0.5	15.3
B-645	0.7	0.12	0.4	0.07	<0.5	2.6
B-646	0.2	0.07	0.2	0.13	<0.5	1.4
B-647	0.4	0.04	0.3	0.01	<0.5	3.8
B-648	0.4	0.04	2.9	0.11	<0.5	4.4
B-650	0.4	0.03	0.4	0.16	<0.5	7.6



Table-4. Comparative result of purification of quartz powder by different procedure

All values are in mg/kg

Samp	Fe	Mn	Mg	Cu	Ti	Zr	Ca	Al	Na	Li	K
Raw	5.5	<0.05	0.8	1.0	2.5	<0.05	11	285	104	1.4	307
Pfq.1	0.9	<0.05	0.3	<0.05	2.5	<0.05	0.7	13	0.4	1.1	2.1
Pfq.2	0.4	<0.05	<0.1	<0.05	2.6	<0.05	<0.2	11	0.4	1.2	1.0
Raw	26	0.07	2.4	1.4	4.2	<0.05	15	103	12	1.1	24
Pfq.1	1.7	<0.05	0.5	<0.05	3.2	<0.05	1.3	18	0.6	1.2	4.4
Pfq.2	1.6	<0.05	<0.1	<0.05	3.4	<0.05	<0.2	13	0.3	1.1	13
Raw	76	0.88	11.6	1.6	3.4	<0.05	18	250	26	1.4	143
Pfq.1	7	0.10	1.5	<0.05	4.2	<0.05	1.4	39	0.8	1.4	20
Pfq.2	5	0.10	0.6	<0.05	4.0	<0.05	<0.2	20	0.6	1.3	7.5
Raw	8.3	<0.05	1.6	1.4	3.6	<0.05	24	62	8	0.6	15
Pfq.1	0.3	<0.05	0.3	<0.05	3.4	<0.05	1.1	10	0.6	0.6	1.6
Pfq.2	0.2	<0.05	<0.1	<0.05	3.2	<0.05	<0.2	10	0.6	0.5	1.2
Raw	11	0.15	1.9	1.1	4.2	<0.05	10	98	20	0.7	51
Pfq.1	1.3	0.05	0.3	<0.05	3.5	<0.05	<0.2	50	1.0	0.6	3.2
Pfq.2	1.8	<0.05	0.2	0.07	3.6	<0.05	<0.2	18	0.9	0.6	6.7

Pfq.1 – Routine procedure (three step at elevated temperature)

Pfq.2 – Developed procedure (single step at room temperature)