

ON THE DETERMINATION OF CRYSTALLINE  
SILICA IN THE PRESENCE OF AMORPHOUS  
SILICA

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## INTRODUCTION

Infrared spectroscopy and X-ray diffraction are the methods most widely used for characterising and analysing crystalline silica in samples of interest for occupational hygiene. Analytical ranges, sensitivities and some of the sources of interference are described in detail for both techniques in the "NIOSH Manual of Analytical Methods 1975-1977". In the section devoted to the infrared technique for analysing quartz in coal dust it is explicitly stated that amorphous silica is not a source of interference. This is not so, and it is the purpose of this communication both to draw attention to this error and to demonstrate that a combination of infrared spectroscopy and X-ray diffraction is capable of yielding amorphous as well as crystalline silica contents in mixtures containing the two. We report here the results of such a combined study.

## EXPERIMENTAL

Three amorphous silica samples were studied: (a) fumed silica collected from the furnace smoke of a ferrosilicon plant, (b) precipitated silica, (c) uncalcined diatomaceous silica. Standard samples of crystalline silica were prepared from the Scandinavian standard  $\alpha$ -quartz (Fyle-quartz). All samples were sedimented to particle size  $\leq 5 \mu\text{m}$  using the procedures described by Jahr (1970).

### Infrared spectroscopy

Infrared analyses were carried out using a JASCO-IRA2 spectrometer and the potassium bromide disc procedure. Amorphous and crystalline standards were prepared by mixing the appropriate silica (1.0 mg) with spectrograde potassium bromide

(0.3 g). The areas under the absorption region at 700-900  $\text{cm}^{-1}$  were obtained by integrating over 10  $\text{cm}^{-1}$  intervals.

### X-ray diffractometry

Samples for X-ray diffraction analysis were prepared by dissolving in water the potassium bromide discs used in the infrared analyses and filtering the released dust through 25 mm Nuclepore filters (pore size 0.8  $\mu\text{m}$ ). This has the advantage of presenting the same sample to both analytical techniques and of avoiding different weighing errors.

The analytical measurements were carried out by placing the filters on top of a silver reference filter in a sample holder which was then introduced into a Philips diffractometer equipped with a broad - focus copper anode X-ray tube (operated at 30 mA; 50 kV) and graphite crystal monochromator. The samples were rotated during analysis and the intensities of the  $\alpha$ -quartz (100), (101) and (112) reflections measured by counting over a peak while scanning at  $1/2^\circ$   $2\theta/\text{min}$ , and subtracting the background which was measured by averaging counts before and after the peak. The silver (111) and (200) reference reflections were measured in the same manner and used to correct for instrumental drift, and for mass absorption by using the equation developed by Aftree-Williams (1977, and references therein). A number of standard samples containing light  $\alpha$ -quartz loadings (40 - 500  $\mu\text{g}$ ) were prepared by filtering aqueous suspensions of known concentrations through Nuclepore filters. For such small quantities a linear relationship between X-ray line intensity and weight of quartz was observed thereby confirming that mass absorption effects were negligible. The line intensities from these standards were used to calculate the quartz calibration constants for each line.

In order to check the absorption correction procedure, which is essential for heavy loadings ( $> 500 \mu\text{g}$ ), an additional series of standards consisting of mixtures of quartz and aluminium oxide in varying ratios was prepared, each sample containing either 1.0 or 2.0 mg dust. These were analysed by infrared spectroscopy (1.0 mg samples) and X-ray diffraction. Table 1 contains the results of this comparison.

#### Characterisation of fumed silica

The fumed silica sample was analysed for all elements heavier than fluorine by means of energy dispersive X-ray spectrometry. The only detectable element found in this industrial waste product was silicon. In addition, the sample was examined in a scanning electron microscope and found to consist mainly of spherical particles of diameter  $\leq 5 \mu\text{m}$ . The spherical form is consistent with the condensation process that the sample had undergone and with the material being amorphous.

#### RESULTS AND DISCUSSION

One can differentiate between two types of silica: crystalline silica as represented by the low and high forms of quartz, tridymite and cristobalite; and amorphous silica which may be subdivided into three categories, namely, colloidal, precipitated and fumed silica. In addition, amorphous silica, often contaminated with crystalline silica ( $< 5\%$ ), occurs naturally in diatomaceous earths. Crystalline silica, like all crystalline materials, possesses intrinsic internal symmetry and accordingly diffracts X-rays. On the other hand, amorphous silica is a dehydrated, polymerised silica in which the internal arrangement does not exhibit long range order, and therefore the material does not diffract X-rays.

Although X-ray diffraction cannot be used to identify amorphous materials it can establish that a sample is amorphous. Thus, the amorphous natures of the precipitated and fumed silicas are revealed unequivocally by the absence of reflections peaks in their diffractograms (Fig. 1). Figure 1 also shows the diffractogram of the diatomaceous earth. The peaks contained in the latter diffractogram are characteristic of  $\alpha$ -quartz. However, the low intensities of these reflections together with the absence of other crystalline phases when related to the relatively large amounts of material examined (5.0 mg) indicate that the major part of the sample is amorphous. In contrast with X-ray diffractometry, infrared spectroscopy registers amorphous as well as crystalline silica. The line profiles (Fig. 2), which are characteristic for  $\alpha$ -quartz with particle sizes  $< 5 \mu\text{m}$  in mean diameter (see below) and amorphous silica, overlap thereby clearly demonstrating that amorphous silica does interfere with the infrared analyses of crystalline silica. This is shown quantitatively by comparing the X-ray and infrared analyses of the sedimented diatomaceous earth already shown to contain a small amount of quartz. The infrared result (30.1(2)%), based on the  $\alpha$ -quartz calibration, is considerably higher than that (1.4(2)%) obtained from X-ray diffraction. The infrared spectrum is consistent with most of the silica being amorphous and the analytical result when based on the amorphous silica calibration is  $> 95\%$  amorphous silica.

At this point, it should be noted that resolution of the  $\alpha$ -quartz absorption bands at  $780 \text{ cm}^{-1}$  ( $12.5 \mu\text{m}$ ) and  $800 \text{ cm}^{-1}$  ( $12.8 \mu\text{m}$ ) is particle size dependent (e.g. Tuddenham and Lyon (1960)), with the first band being particularly sensitive to absorption by quartz particles. Resolution

of these two bands, which is maximum for particles  $< 2 \mu\text{m}$  in average diameter, progressively decreases with increasing particle size until for particles ca  $8 \mu\text{m}$  the bands are almost completely merged. The absorption envelope then resembles that of amorphous silica and accordingly, cannot be used to ascertain whether or not all of the silica in dust samples of unknown particle size is crystalline.

In order to establish the reliability of the X-ray result it should be pointed out that in our experience X-ray diffraction and infrared spectroscopic analyses of quartz, in the absence of interfering phases, are generally consistent to within  $\pm 2.5\%$  absolute for sedimented dust samples. Some typical industrial samples consistent with this are shown in Table 2.

In conclusion, the key to quantifying the amorphous and crystalline silica contents in mixtures is to combine the X-ray and infrared results. X-ray diffraction yields the crystalline silica content whereas the infrared technique provides information on the total silica content. By combining both analyses and using the appropriate amorphous and crystalline silica calibration constants one has enough information to be able to extract the amorphous silica content. In this connection, it is relevant to refer to the method proposed by S.L. Nieto (1978, and references therein) for deconvoluting the infrared spectra of multicomponent mixtures.

Acknowledgement: We thank Mr. Jørgen Jahr for his interest in the problem.

## REFERENCES

Altree-Williams, S. (1977) Analyt. Chem. 49, 429-432

Jahr, J. (1970) Staub Reinhaltung der Luft 30, 27-31

Nieto, J.L. (1978) Analyst 103, 128-133

NIOSH Manual of Analytical Methods (1975), (1977)

Tuddenham, W.M. and Lyon, R.J.P. (1960) Analyt. Chem. 32,  
1630-1634

TABLE 1

Check of calibration contained in absorption correction programme. X-ray samples (1 - 5) prepared by dissolving IR - KBr discs in water and filtering released dust through Nuclepore filters. This permits direct comparison of IR vs X-ray.

Nominal % $\alpha$ -SiO <sub>2</sub> in SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mixtures	% $\alpha$ -SiO <sub>2</sub> IR	% $\alpha$ -SiO <sub>2</sub> ( $\sigma$ ) X-ray (not corrected for absorption)	% $\alpha$ -SiO <sub>2</sub> ( $\sigma$ ) X-ray (cor- rected for absorption)
5 (1.0 mg)	(9.3)	4.1(1)	4.98(1)
15 (1.0 mg)	17.4	12.36(6)	15.15(7)
30 (1.0 mg)	29.8	25.8(6)	31.7(7)
50 (1.0 mg)	47.0	41.03(2)	49.65(2)
75 (1.0 mg)	70.3	60.67(4)	74.17(5)
100 (1.0 mg)	--	77.08(3)	92.70(5)
100 (1.0 mg)	--	78.71(5)	98.80(5)
100 (2.0 mg)	--	77.8(5)	102.8(6)
100 (2.0 mg)	--	76.9(4)	101.8(6)



TABLE 2

Comparison of infrared and X-ray analyses (% quartz) of some industrial samples (1.0 mg).

Infrared	X-ray (corrected for absorption)
21.9	18.2(6)
2.4	6.5(2)
10.8	11.3(6)
16.8	18.9(2)
5.6	5.8(2)

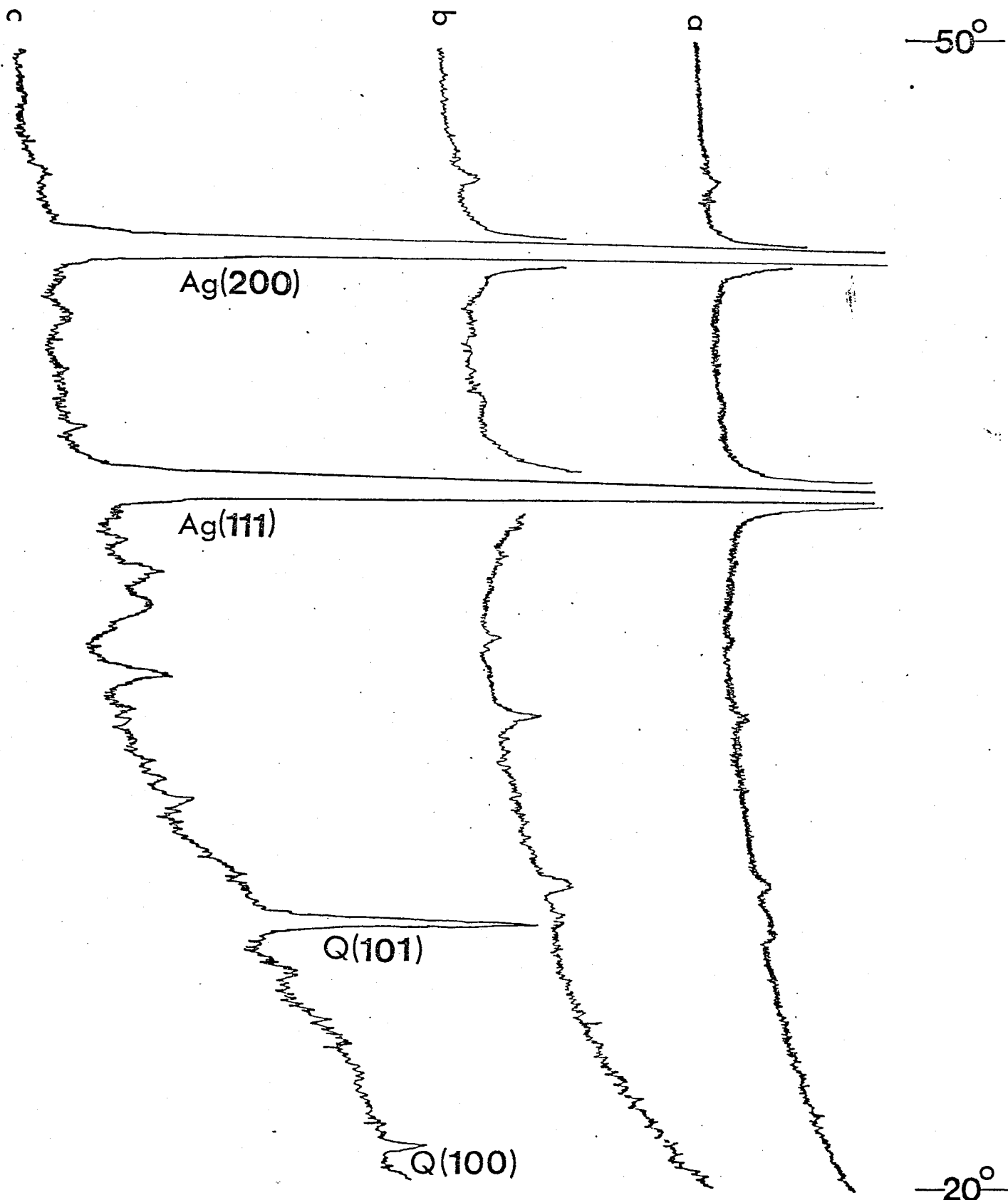
FIGURE CAPTIONS

FIGURE 1 Superimposed diffraction scans of

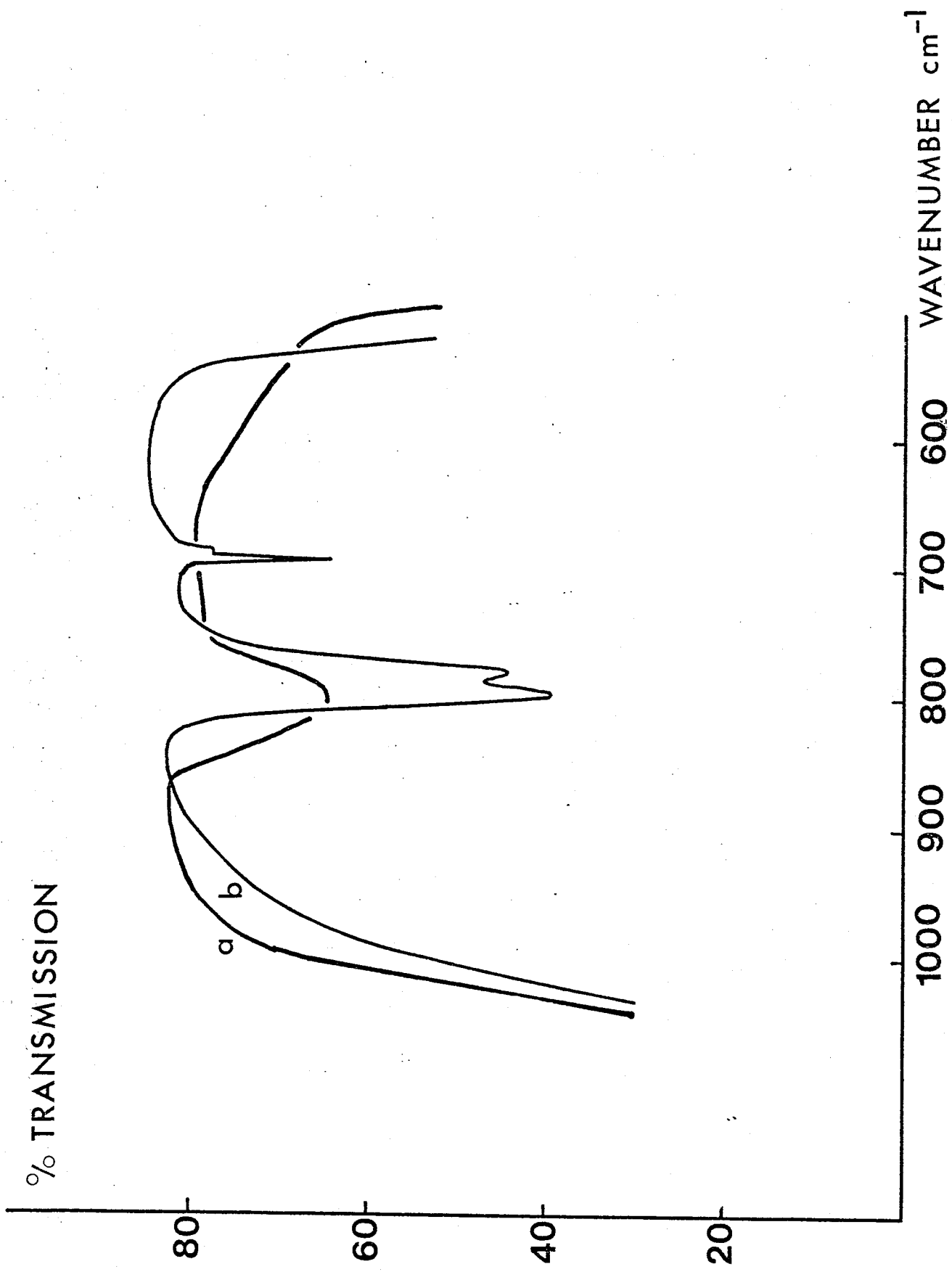
- (a) precipitated silica (2.0 mg); (b) fumed silica (2.0 mg);
- (c) diatomaceous silica (5.0 mg) with  $\alpha$ -quartz reflections (Q). Full scale deflection = 2000 c/s; time constant 2s)

FIGURE 2 Superimposed infrared spectra of

- (a) diatomaceous silica; (b) standard  $\alpha$ -quartz



**FIGURE 1**



**FIGURE 2**