Determining of Crystalline Silica in Respirable Dust Samples by Infrared Spectrophotometry in the Presence of Interferences

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Abstract : Determining of Crystalline Silica in Respirable Dust Samples by Infrared Spectrophotometry in the Presence of Interferences: Jun OJIMA. National Institute of Industrial Health—Infrared Spectrophotometry (IR) is now widely used to determine crystalline silica in industrial dust samples. Though the IR method has many advantages when dealing with respirable dust samples, some serious analytical errors are often caused by interference minerals contamination. These minerals have a characteristic absorption band corresponding in position to the analytical peak for crystalline silica. In this paper, six typical interference minerals (Kaolinite, Mullite, Muscovite, Pyrophyllite, Montmorillonite and Amorphous silica) were pre-size controlled to respirable range and their infrared spectra were measured by means of an FT-IR with the well-known potassium bromide tablet technique. The effects of these interference minerals on the Japanese OEL or the administrative control level for respirable dust which depend on the silica content were calculated and expressed in figures. The measured absorption coefficients of the interference minerals and quartz were 1.36–6.98 Abs/mg and 24.46 Abs/mg, respectively. The absorption band height ratios of each interference minerals were also measured. Then the efficiency and applicability of two spectrum correction methods for the interference minerals, absorbance ratio method and difference spectrum method were examined by using artificially mixed samples (standard interference mineral + standard quartz). By comparing the quantifying results for the mixture samples, it was revealed that the interfered spectra were almost corrected successfully when using the difference spectrum method, whereas correction by the absorbance ratio method resulted in apparent negative errors. Furthermore, the difference spectrum method was proven to be superior to the absorbance ratio method in applicability.
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The hazard due to inhalation of respirable crystalline silica has been recognized and now many countries have adopted dust concentration standards in industries which are dependent on crystalline silica content in the dust. In Japan, the administrative control level of respirable mineral dust in the working environment (E) is calculated by the following formula

$$E = 2.9/(0.22Q+1) \quad [\text{mg/m}^3] \quad (1)$$

where

Q: percentage content of crystalline silica in dust [%]

The occupational exposure limit (OEL) of respirable mineral dust recommended by the Japan Society of Occupational Health is also calculated with the same formula provided the silica content in dust is over 10%.

X-ray diffraction and the solution chemistry method (phosphoric acid method) were accepted as official crystalline silica analytical methods at the promulgation of Japanese Working Environment Measurement Standards (Ministry of Labour Notification No.46, 1976) and have been in use since then. Both methods have been constantly undergoing some changes and refinements for the past 25 yr, and infrared spectrophotometry (IR), extensively used in other countries from the 1970s, was belatedly added to the Japanese official methods when the Working Environment Measurement Guidebook[1] was revised in 1998.

Although the IR method is known to be advantageous in analyzing environmental dust samples due to its sensitivity and convenience, some peculiar disadvantages, such as absorption peak interference, have been explicitly mentioned by many foreign researchers. The presence of some clay or mica minerals that have an absorption peak corresponding in position to the analytical peak for silica may increase the apparent silica concentration, and will result in excessive regulation of the administrative control level or the OEL. In order to eliminate such analytical errors caused by spectrum interference, the author examined the effectiveness and applicability of
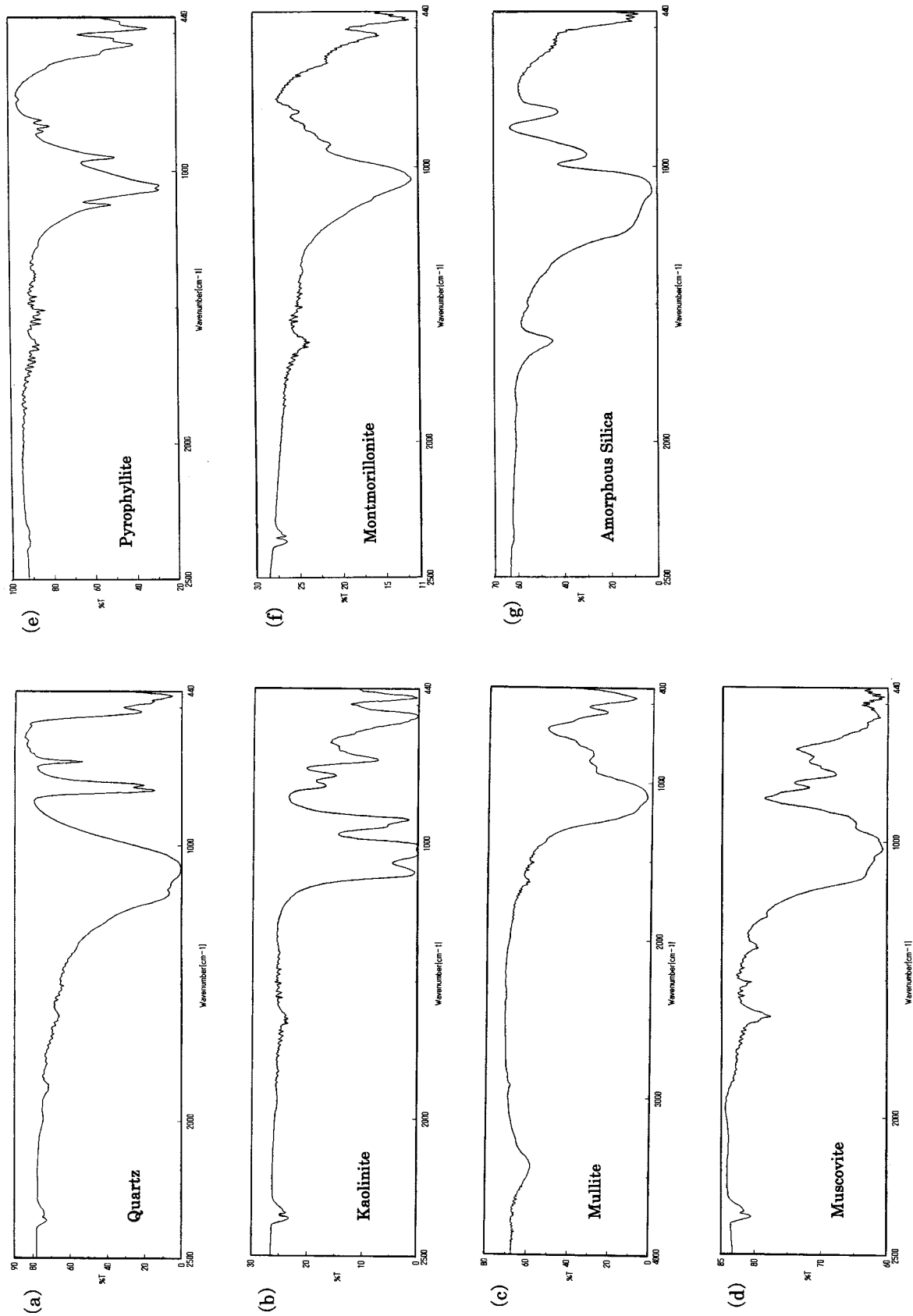
Fig. 1. Infrared absorption spectra of (a)Quartz, (b)Kaolinite, (c)Mullite, (d)Muscovite, (e)Pyrophyllite, (f)Montmorillonite and (g)Amorphous Silica.

two spectrum corrections, the absorbance ratio method and difference spectrum. The absorbance ratio method is prescribed in the latest Japanese Guidebook[1] as an effective interference correction method though it was originally used for an outdated double beam grating IR by NIOSH (National Institute for Occupational Safety and Health, U.S.A.) more than 20 yr ago. Unlike the obsolete absorbance ratio method, difference spectrum is the prevailing method and thought to be effective in spectrum correction. It is a spectrum processing function commonly equipped with a current Fourier transform IR (FT-IR) and depends on a high-precision He-Ne laser for FT-IR. Owing to the high precision, the spectrum of one component in a sample can be subtracted from the spectrum of a mixture instantaneously. In this study, the author intends to prove the effectiveness of the difference spectrum in the interfered spectrum correction, and to propose it as a substitute for the absorbance ratio method.

Materials and Methods

In this study, infrared spectra were acquired by means of a Herschel FT/IR-410 model with a DLATGS detector (JASCO, Japan) at a resolution of 4 cm^{-1}. The apodization function was the cosine. The number of scans was set at 16–64 to meet each sample spectrum S/N ratio. A quartz sample of respirable range was made from commercially available standard quartz powder (JAWE451, Japan). Samples for investigation, except standard quartz, were grounded in a laboratory vibration ball mill (Yoshida Manufacturing, Japan) and particle size was controlled within respirable range by the liquid sedimentation technique[2] with an Andersen pipette. It was then homogenized in spectroscopic grade potassium bromide (KBr) in an agate mortar and pressed into 3 mm diameter pellets with a hand press. The mixing time was set at 5 min because excess grinding in the agate mortar may destroy the crystalline structure of the quartz[3]. The pellets were weighed with an electric micro balance readable to 10^{-3} mg (model HA-202M, A&D Co.,Ltd., Japan).

In order to obtain calibration curves of crystalline silica, quartz samples of respirable range were used as the standard. Although crystalline silica has several polymorphs such as cristobalite and tridymite, it is reasonable to use quartz as the standard because the other forms of silica are usually not present in significant amounts in industrial hygiene samples[4–6].

The absorbance ratio method was carried out according to the Guide book[1]. The difference spectrum was obtained by operating the initially installed program with the FT-IR. In obtaining difference spectrum, the appropriate factor by which a component spectrum should be multiplied was interactively determined by visually observing remaining spectrum deformation on the CRT display of the FT-IR.
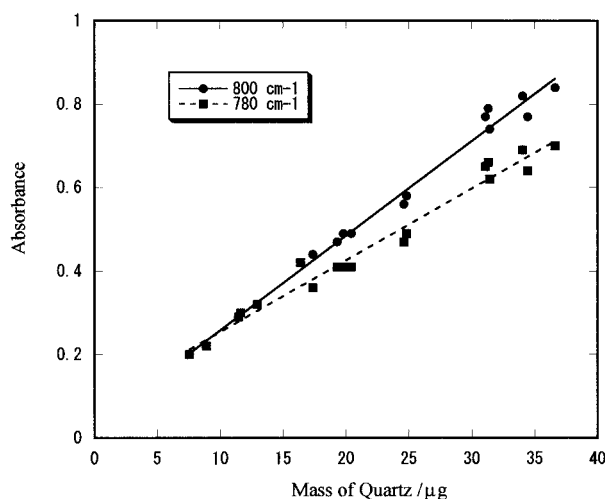

Fig. 2. Infrared calibration curves for the standard Quartz peaks at 780 cm^{-1} and 800 cm^{-1}.

Results

Analytical peaks and calibration curves

The infrared spectrum of quartz is shown in Fig. 1-(a). The main characteristic absorption bands of the quartz occur at 1,085, 800, 780, 695, 514 and 462 cm^{-1}. Among these bands, the absorption at 800 cm^{-1}, which is due to Si-O-Si symmetrical stretching vibration[7, 8], is generally accepted as the most suitable band for analytical peak measurement and is commonly used for silica determination[9, 10]. The 780 cm^{-1} band is able to be the complement of 800cm^{-1} in some cases[11], whereas the band at 1,085 cm^{-1} is too broad to secure a reliable peak measurement. The bands occurring at 462 cm^{-1} and 514 cm^{-1} that are assigned to mixed Si-O-Si and O-Si-O bending mode[12] are seldom used because they are common to many silicate minerals[13]. Therefore, an ordinary calibration curve is expressed as the graph of absorbance of 800 cm^{-1} vs. μg quartz in a sample pellet as shown in Fig. 2. The calibration curve obtained from the 780 cm^{-1} peak is also shown in Fig. 2. The regression equations of the calibration curves are

$$\text{800 cm}^{-1}: Y=0.0227\ X+0.0321 \quad (r=0.995) \quad (2)$$
$$\text{780 cm}^{-1}: Y=0.0172\ X+0.0831 \quad (r=0.988) \quad (3)$$

Spectrum measurement of interference minerals

The interference minerals which are known to have a band close to 800 cm^{-1} are listed in Table 1[5, 11, 13–23]. In this study, six minerals in Table 1, Kaolinite, Mulite, Muscovite, Pyrophyllite, Montmorillonite and Amorphous silica, were selected as typical interference minerals for investigation. Among the fourteen minerals in the Table, these six minerals are most often quoted as the interference minerals for quartz determination in past IR studies[5, 11, 13, 16, 17, 20–23]. They are commonly used as

Table 1. Position of the main absorption bands for minerals that commonly interfere in crystalline quartz analysis

	Wave number [cm^{-1}]
Kaolinite	3694, 3650, 3620, 1114, 1032, 1010, 936, 912, **790**, 752, 693, 537, 468, 430
Mullite	3445, 2925, 1634, 1514, 1087, 908, **822**, 556, 468
Muscovite	3640, 1065, 1020, 920, 822, **799**, 538, 472, 410
Pyrophyllite	3685, 1118, 1065, 1047, 948, 850, 830, **814**, 620, 573, 535, 515, 477, 457, 415
Montmorillonite	3629, 3437, 2926, 2360, 2341, 1634, 1507, 1385, 1044, 918, **797**, 668, 526, 470, 427
Amorphous Silica	3447, 1636, 1088, 958, **800**, 464
Adamite	3520, 3400, 1620, 880, 820, **795**, 730, 530, 510, 470
Gedrite	1086, 1015, 982, **795**, 780, 700, 535, 498, 463, 400
Albite	1157, 1105, 1039, 1005, **788**, 746, 726, 652, 614, 598, 535, 477, 465, 432, 418, 402
Daphnite	991, **798**, 771, 667, 610, 539, 467, 429
Orthoclase	1140, 1046, **788**, 767, 745, 728, 649, 593, 540, 464, 435
Talc	3676, 3460, 1168, 1079, 1014, 985, **797**, 778, 668, 641, 620
Anthophyllite	3675, 1095, 1020, 979, 910, **785**, 755, 712, 690, 666, 550, 532, 495, 450, 368
Vermiculite	1070, 995, 955, **810**, 755, 685, 510, 450

Table 2. The absorption coefficients of each interference mineral at the peaks which overlap the characteristic 800 cm^{-1} quartz absorption band

	Production region	Wave number [cm^{-1}]	Coefficient of absorption* [Abs/mg]
Kaolinite	Unidentified**	790	5.83 ± 0.36
Mullite	Synthetic	822	6.88 ± 0.43
Muscovite	Ibaragi Pref.	799	1.36 ± 0.33
Pyrophyllite	China	814	6.79 ± 0.56
Montmorillonite	Unidentified**	797	3.84 ± 0.18
Amorphous Silica	Synthetic	800	6.98 ± 0.54

*: Values are the mean ± SD (n=10), **: Reagent : NAKARAI brand

industrial materials and therefore thought to come into existence in many working environments. The spectra of the abovementioned interference minerals are shown in Fig. 1-(b)–1-(g). Their absorption coefficients at the peaks which will interfere with the analytical peak are shown in Table 2.

Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), known as a hydro-thermally altered mineral in volcanic rock and a common component of coal mine dust, exhibited an absorbance of Si-O-Al vibration at 790 cm^{-1}. It is the only example of interference mineral prescribed in the current Guidebook[1]. Mullite (Al$_4$OSi$_2$Al$_2$O$_{12}$), usually synthesized from kyanite, andalusite or sillimanite[23], is one of the most common ceramics now used in industry. As shown in Fig. 1-(c), a relatively broad band around 800 cm^{-1} was observed. Muscovite (K$_2$Al$_4$(Si$_6$Al$_2$)O$_{20}$(OH, F)$_4$), generally used for insulating parts in electrical appliances because of its non-conductance of electricity, exhibited a weak peak that completely overlaps the analytical peak of 800 cm^{-1}. Although the coefficient of absorption of muscovite was

rather small in comparison with that of the other minerals, it has been thought to cause significant interference at the 800 cm^{-1} peak[3, 17, 20, 21]. Pyrophyllite (Al$_2$O$_3$•4SiO$_2$•H$_2$O), a well-known raw material for chinaware and refractory, exhibited a peak at 814 cm^{-1} due to Si-O-Al vibration. Montmorillonite ((Al$_{2-y}$Mg$_y$)Si$_4$O$_{10}$(OH)$_2$•M$_y$nH$_2$O), commonly used for casting sand, manure components, pesticide binders and drilling mud for petroleum rigs, exhibited a peak at 797 cm^{-1}. Although this peak was a shoulder of an absorption band, Gade and Luft noted that the main interference with quartz absorption was produced by kaolinite and montmorillonite[24]. Amorphous Silica (SiO$_2$•H$_2$O) is one of the polymorphs of silica[6], and can easily transform from quartz at high temperature or often occurs naturally in diatomaceous earth. It has been excluded from the silica mineral group defined by the current Japanese regulation because Amorphous Silica does not diffract X-rays. As shown in Fig. 1-(g), Amorphous Silica exhibited a relatively strong peak at 800 cm^{-1} which can hardly be distinguished from the band
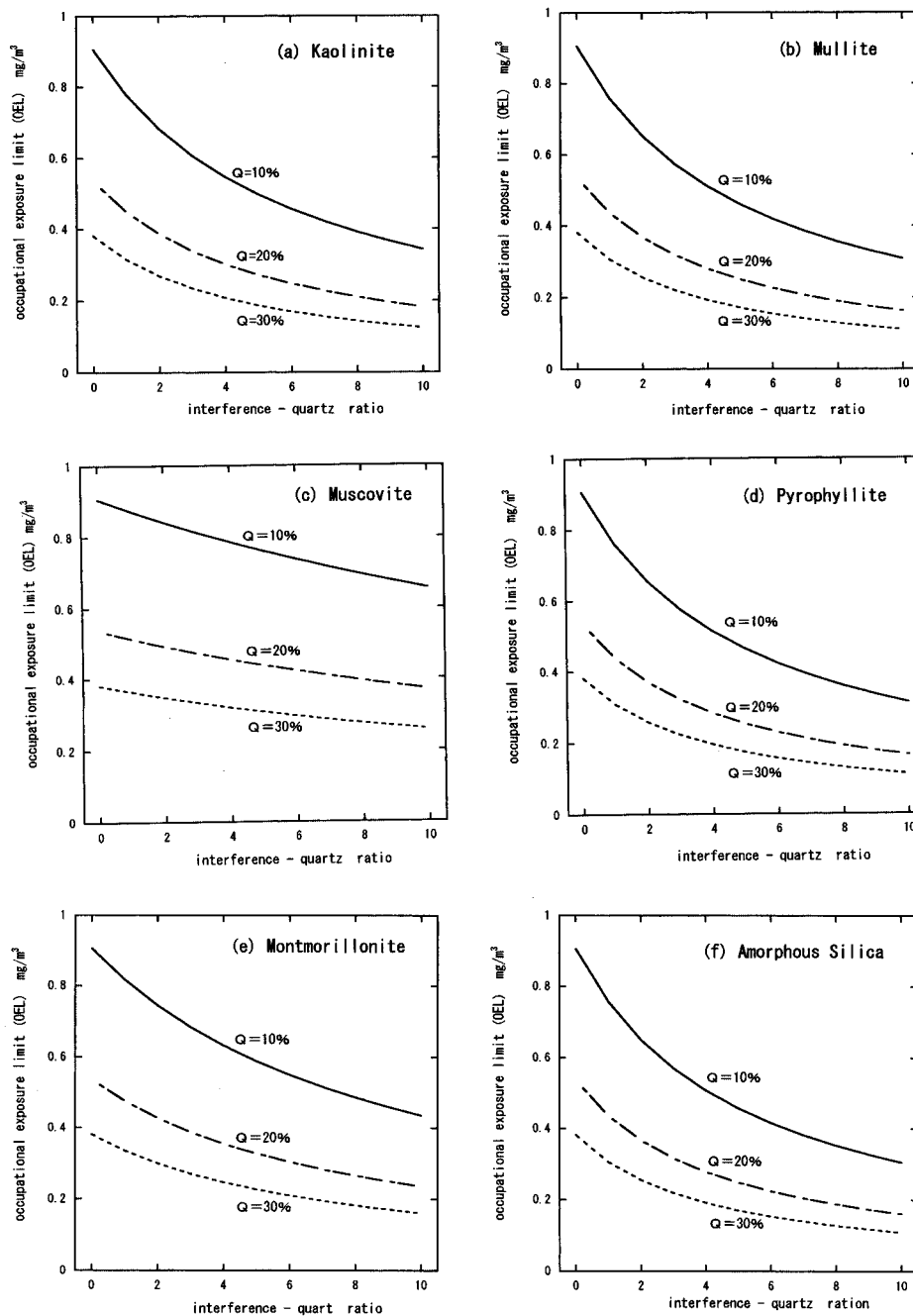
Fig.3. Relationship between occupational exposure limit and interference mineral contamination of (a)Kaolinite, (b)Mullite, (c)Muscovite, (d)Pyrophyllite, (e)Montmorillonite and (f)Amorphous Silica.

of crystalline silica without any spectrum processing.

Effects of interference on occupational exposure limits

The peak interference results in an overestimation of silica content, and will lead to stricter occupational exposure limits for respirable dust because of equation (1). Fig. 3-(a)–3-(f) show the decline of calculated occupational exposure limits to the interference/quartz ratio from 0 to 10 in respirable dust. Three curves (one solid line and two dotted lines) shown in each figure represent the cases in which the genuine silica content in dust is assumed to be 10, 20 and 30% respectively. Cases over 30% were not calculated since the silica percentages in an air sample from general industry are usually below 30%[25]. As shown in these figures, the effects of peak interference on the exposure limits grew significantly with

Table 3. Absorption band height ratio of each mineral *

Kaolinite	Abs (912 cm⁻¹)/Abs (790 cm⁻¹)	0.20 ± 0.01
Mullite	Abs (1,087 cm⁻¹)/Abs (822 cm⁻¹)	4.28 ± 0.21
	Abs (908 cm⁻¹)/Abs (822 cm⁻¹)	1.05 ± 0.01
	Abs (556 cm⁻¹)/Abs (822 cm⁻¹)	1.29 ± 0.03
	Abs (468 cm⁻¹)/Abs (822 cm⁻¹)	2.52 ± 0.11
Muscovite	Abs (1,020 cm⁻¹)/Abs (799 cm⁻¹)	7.33 ± 1.24
	Abs (822 cm⁻¹)/Abs (799 cm⁻¹)	0.96 ± 0.09
	Abs (538 cm⁻¹)/Abs (799 cm⁻¹)	4.55 ± 0.73
	Abs (472 cm⁻¹)/Abs (799 cm⁻¹)	4.63 ± 0.77
Pyrophyllite	Abs (948 cm⁻¹)/Abs (814 cm⁻¹)	4.52 ± 0.29
	Abs (830 cm⁻¹)/Abs (814 cm⁻¹)	1.29 ± 0.02
	Abs (535 cm⁻¹)/Abs (814 cm⁻¹)	5.60 ± 0.33
	Abs (477 cm⁻¹)/Abs (814 cm⁻¹)	6.08 ± 0.89
	Abs (415 cm⁻¹)/Abs (814 cm⁻¹)	2.20 ± 0.11
Montmorillonite	Abs (1,634 cm⁻¹)/Abs (797 cm⁻¹)	0.83 ± 0.07
	Abs (1,044 cm⁻¹)/Abs (797 cm⁻¹)	6.38 ± 0.25
	Abs (918 cm⁻¹)/Abs (797 cm⁻¹)	1.80 ± 0.04
	Abs (526 cm⁻¹)/Abs (797 cm⁻¹)	3.80 ± 0.13
	Abs (470 cm⁻¹)/Abs (797 cm⁻¹)	5.22 ± 0.28
Amorphous	Abs (1,636 cm⁻¹)/Abs (800 cm⁻¹)	0.88 ± 0.02
Silica	Abs (1,088 cm⁻¹)/Abs (800 cm⁻¹)	6.34 ± 0.41
	Abs (958 cm⁻¹)/Abs (800 cm⁻¹)	1.42 ± 0.03
	Abs (464 cm⁻¹)/Abs (800 cm⁻¹)	3.28 ± 0.21

*: Values are the mean $\pm$ SD (n=10)

the reduction of silica content in dust.

Corrections of interference

The absorbance ratio method is a conventional method in which correction of the measured absorbance at 800 cm⁻¹ is applied by calibration with a standard sample of the interference mineral. For example, the absorption around 800 cm⁻¹ due to Kaolinite is able to be estimated by referring to the pre-measured ratio of (absorbance at 912 cm⁻¹) / (absorbance at 790 cm⁻¹). Then the net absorbance due to silica is derived by subtracting this amount of absorbance from the sample absorbance at 800 cm⁻¹. The absorbance ratios of the interference minerals that were essential for this method are shown in Table 3. In this study, the absorbance ratio of Kaolinite was obtained from 912 cm⁻¹ peak and 790 cm⁻¹ peak, and was applied to correction in conformity to the Guidebook specifications[1]. For the other interference minerals, several ratios for each were observed and their applicability to the correction was examined.

The difference spectrum method is based on the principle of spectrum subtraction. Although the principle of the absorbance ratio method is almost the same as that of the difference spectrum in essence, the practical procedures for each method are quite different since the difference spectrum command can subtract one spectrum from another without time-consuming measuring of the absorbance ratio.

The comparative merits of both correction methods were evaluated by applying them to mixture sample analyzing. The mixture samples are artificial mixtures of quartz and interference mineral that were prepared by weighing appropriate amounts of each compound and mixing them in a mortar. The nominal quartz contents in the mixture samples were varied within the range of 6.2% to 52.5% in accordance with the each interference's coefficients of absorption (Table 2).

Table 4 shows the results of quantifying quartz content in the mixture samples with and without the corrections. The measured absorbance of the mixture sample spectrum was calibrated by equation (2) when it was corrected by the absorbance ratio method, whereas the absorbance of the same spectrum was calibrated by equations (2) and (3) when it was corrected with the difference spectrum. In processing difference spectrum command, one can simultaneously obtain the net absorbance at 800 cm⁻¹ and 780 cm⁻¹ due to quartz very easily, and it is normal practice to quote the mean results for these two peaks[11, 21]. As shown in Table 4, amounts of quantified quartz in the mixture samples were certainly overestimated without the corrections. The amount of this overestimation which surely depends on the interference's coefficient of absorption decreased with the increase in nominal quartz content. It was recognized that the correction with the

Table 4. Correlation of quartz determinations for the mixture samples (quartz + interference mineral) in the conventional absorbance-ratio method and spectrum subtraction

Interference mineral	Nominal quartz cont. (%)	Measured quartz cont. (%)		
		uncorrected	corrected by absorbance-ratio**	corrected by spectrum subtraction
Kaolinite	21.1	38.6 ± 0.7	17.0 ± 0.5 (Abs912 cm⁻¹/Abs790 cm⁻¹)	22.9 ± 1.1
	26.7	42.5 ± 0.4	22.3 ± 0.3 (Abs912 cm⁻¹/Abs790 cm⁻¹)	29.5 ± 1.1
	36.1	49.6 ± 0.8	31.3 ± 0.6 (Abs912 cm⁻¹/Abs790 cm⁻¹)	33.7 ± 1.0
	47.2	52.9 ± 0.3	38.2 ± 0.3 (Abs912 cm⁻¹/Abs790 cm⁻¹)	44.9 ± 1.9
Mullite	22.9	50.6 ± 1.0	19.0 ± 0.5 (Abs556 cm⁻¹/Abs822 cm⁻¹)	19.7 ± 0.3
	28.8	55.6 ± 0.8	25.1 ± 0.2 (Abs556 cm⁻¹/Abs822 cm⁻¹)	27.7 ± 1.0
	32.2	56.6 ± 0.8	28.4 ± 0.3 (Abs556 cm⁻¹/Abs822 cm⁻¹)	30.0 ± 0.6
	52.5	68.8 ± 0.7	–	53.3 ± 0.5
Muscovite	6.2	10.8 ± 2.2	4.9 ± 1.9 (Abs1,020 cm⁻¹/Abs799 cm⁻¹)	2.7 ± 0.3
			3.8 ± 0.4 (Abs822 cm⁻¹/Abs799 cm⁻¹)	(4.4 ± 0.2)***
			5.4 ± 1.8 (Abs538 cm⁻¹/Abs799 cm⁻¹)	
			4.2 ± 1.7 (Abs472 cm⁻¹/Abs799 cm⁻¹)	
	8.9	13.3 ± 1.4	7.0 ± 1.2 (Abs1,020 cm⁻¹/Abs799 cm⁻¹)	5.6 ± 0.2
			6.2 ± 0.4 (Abs822 cm⁻¹/Abs799 cm⁻¹)	(7.3 ± 0.1)***
			7.9 ± 1.1 (Abs538 cm⁻¹/Abs799 cm⁻¹)	
			6.1 ± 1.0 (Abs472 cm⁻¹/Abs799 cm⁻¹)	
	11.5	15.8 ± 3.7	9.4 ± 3.1 (Abs1,020 cm⁻¹/Abs799 cm⁻¹)	9.3 ± 0.6
			9.3 ± 0.5 (Abs822 cm⁻¹/Abs799 cm⁻¹)	(10.6 ± 0.5)***
			10.4 ± 2.8 (Abs538 cm⁻¹/Abs799 cm⁻¹)	
	17.7	22.0 ± 1.0	–	14.9 ± 0.2
				(16.3 ± 0.2)***
Pyrophyllite	24.0	27.7 ± 0.5	4.9 ± 0.3 (Abs948 cm⁻¹/Abs814 cm⁻¹)	23.4 ± 0.5
			9.7 ± 0.1 (Abs830 cm⁻¹/Abs814 cm⁻¹)	
			6.5 ± 0.8 (Abs535 cm⁻¹/Abs814 cm⁻¹)	
			5.8 ± 1.9 (Abs 477 cm⁻¹/Abs814 cm⁻¹)	
			6.5 ± 0.4 (Abs415 cm⁻¹/Abs814 cm⁻¹)	
	30.1	33.6 ± 1.1	11.5 ± 0.8 (Abs948 cm⁻¹/Abs814 cm⁻¹)	30.6 ± 0.5
			16.2 ± 0.5 (Abs830 cm⁻¹/Abs814 cm⁻¹)	
			12.7 ± 1.0 (Abs535 cm⁻¹/Abs814 cm⁻¹)	
			9.6 ± 1.9 (Abs477 cm⁻¹/Abs814 cm⁻¹)	
			13.2 ± 0.8 (Abs415 cm⁻¹/Abs814 cm⁻¹)	
	41.3	43.3 ± 1.0	24.0 ± 0.7 (Abs948 cm⁻¹/Abs814 cm⁻¹)	42.4 ± 0.7
			28.3 ± 0.4 (Abs830 cm⁻¹/Abs814 cm⁻¹)	
			24.9 ± 0.9 (Abs535 cm⁻¹/Abs814 cm⁻¹)	
			17.5 ± 2.2 (Abs477 cm⁻¹/Abs814 cm⁻¹)	
			25.4 ± 0.6 (Abs415 cm⁻¹/Abs814 cm⁻¹)	
	48.3	49.9 ± 1.2	31.9 ± 0.9 (Abs948 cm⁻¹/Abs814 cm⁻¹)	48.8 ± 0.9
			35.6 ± 0.6 (Abs830 cm⁻¹/Abs814 cm⁻¹)	
			32.9 ± 1.0 (Abs535 cm⁻¹/Abs814 cm-⁻¹)	
			26.5 ± 2.2 (Abs477 cm⁻¹/Abs814 cm⁻¹)	
			32.6 ± 1.0 (Abs415 cm⁻¹/Abs814 cm⁻¹)	
Montmorillonite	15.3	24.2 ± 1.2	10.9 ± 0.6 (Abs918 cm⁻¹/Abs797 cm⁻¹)	12.1 ± 0.3
	23.5	34.6 ± 0.7	22.3 ± 0.3 (Abs918/ cm⁻¹/Abs797 cm⁻¹)	22.1 ± 0.6
	28.6	38.1 ± 1.0	–	26.5 ± 1.2
	33.8	42.8 ± 0.9	–	31.3 ± 0.9
Amorphous Silica	25.3	48.1 ± 0.9	18.1 ± 0.4 (Abs958 cm⁻¹/Abs800 cm⁻¹)	28.8 ± 0.9
	32.0	51.3 ± 1.1	22.4 ± 0.5 (Abs958 cm⁻¹/Abs800 cm⁻¹)	35.0 ± 1.5
	40.2	57.4 ± 1.0	27.2 ± 0.5 (Abs 958 cm⁻¹/Abs 800 cm⁻¹)	42.9 ± 0.9
	49.7	62.8 ± 1.2	–	52.5 ± 1.6

*: Values are the mean ± SD (n=10), **: the wave numbers of bands are given in parentheses, ***: calibrated with the equation for the 800 cm⁻¹ peak

absorbance ratio would produce an underestimated result.

For Kaolinite mixing, it was necessary to correct the absorption at 800 cm^{-1} provided the quartz content was below 50%. Although both correction methods were passably effective for the Kaolinite interference, the difference spectrum method was more effective than the absorbance ratio method.

For Mullite mixing, only the 556 cm^{-1} band could be applied to the absorbance ratio method because the other bands, 1,087 cm^{-1} and 468 cm^{-1}, completely overlapped the quartz characteristic bands of 1,085 cm^{-1} and 462 cm^{-1}, respectively, whereas the 908 cm^{-1} band was too weak to be detected. Nevertheless, the absorbance ratio method was not invariably effective for Mullite interference since the absorption at 556 cm^{-1} was hardly able to be measured with a quartz content of over 50%. In contrast, the difference spectrum could be effective without regard to the quartz content.

For Muscovite mixing, the absorbance ratio of 538 cm^{-1}/ 799 cm^{-1} was found to be most suitable for the correction when compared to the other ratios but the 538 cm^{-1} band could not be measured with a quartz content of over 17.7%. On the other hand, the difference spectrum could be operated independently of the quartz content. Unlike for the other interference minerals, difference spectrum correction was more reasonable without the combined use of the 780 cm^{-1} calibration curve. It was proved that relatively remarkable negative errors were caused in the difference spectrum when the mean results for the 800 cm^{-1} band and the 780 cm^{-1} band were quoted.

For Pyrophyllite mixing, correction by the absorbance ratio method was thought to be ineffective. Although the five bands (948, 830, 535, 477 and 415 cm^{-1}) were examined, none of them could fulfil the absorbance ratio correction successfully. In contrast to this, almost completely accurate quartz contents could be acquired with the difference spectrum correction.

For Montmorillonite mixing, five characteristic bands except 918 cm^{-1} were concealed by quartz bands and could not be detected. The ratio 918 cm^{-1}/797 cm^{-1} was applicable unless the quartz content exceeded 23.5%. The quartz contents determined with the difference spectrum correction were almost equal to the nominal values.

For Amorphous Silica mixing, only the ratio 958 cm^{-1}/ 800 cm^{-1} was barely applicable to the correction whereas the bands at 1,636, 1,088 and 464 cm^{-1} were close to the quartz bands and could not be measured. Although it has been stated in some research that Amorphous Silica does not act as interference material, obvious interference at 800 cm^{-1} was recognized[26] as shown in Table 4. With the absorbance ratio method, the quantified quartz contents were relatively underestimated, but satisfactory results were obtained with the difference spectrum correction.

Table 5. Detection limit of quartz in the sample which includes the interference mineral

interference mineral	calibration curve	
	780 cm^{-1}	800 cm^{-1}
	[μg quartz]	
Kaolinite	13	14
Mullite	10	11
Muscovite	1	3
Pyrophyllite	17	18
Montmorillonite	7	9
Amorphous Silica	17	18

Sensitivity of the difference spectrum method

The limits of detection of the amount of quartz by means of the difference spectrum method are shown in Table 5. The detection limit in each case was defined as the amount of quartz in the mixture sample which had the minimum absorption reading in this study. From the experiments it was proved that the sensitivity of the difference spectrum method varied according to the type of interference mineral. No relationship between the detection limit and the interference mineral content in the sample was found. Generally, the detection limit was increased with the increase in the absorption coefficient of the interference mineral (Table 2). With the co-existence of Muscovite (1.36 Abs/mg), 1 or 3 micro grams of quartz in the KBr tablet was clearly detectable by subtracting the interference spectrum, whereas 18 micro grams of quartz was barely discernible together with Pyrophyllite (6.79 Abs/mg) or Amorphous Silica (6.98 Abs/mg). In addition, the sensitivity seemed to be affected by the location of the interference absorption band. In this study, the peak location of Pyrophyllite (814 cm^{-1}) was closer to the 800 cm^{-1} band than that of Mullite (822 cm^{-1}). Although the coefficient of Mullite was practically equal to that of Pyrophyllite, the detection limit in the Mullite mixture sample was plainly smaller. The option of the calibration curve may also influence sensitivity. As shown in Table 5, the minimum detection limit of quartz was relatively small when the calibration curve of the 780 cm^{-1} absorption peak was applied, but the difference was very small, and thought to be negligible in fact.

Discussion and Conclusion

Since the occupational exposure limits of respirable dust are apparently decreased by contamination with interference minerals, the spectra of the samples which contain these interferences have to be corrected properly.

In most cases, the presence of the interference minerals in a sample can be predicted after learning their chemistry, mineralizing process, geological geneses and derivation.

And the knowledge of the location (wave numbers) of their characteristic bands ought to be helpful in judging the presence interference. Besides the minerals listed in Table 1, there are several other minerals such as Illite[17, 22], Clinoenstatite[14], Nontronite, Antlerite and Chloritoid, which may have an absorption band around 800 cm⁻¹. Although these minerals are not listed in Table 1, their typical standard spectrum data will be available in commercial research libraries for infrared analysis (e.g. Sadtler Standard Spectra, The Aldrich Library of Infrared Spectra, Wyandotte-ASTM Punched Card Index to Infrared Spectral Absorption Data, etc.). At present, some of the spectral libraries or databases can be served by the Internet. In referring to these libraries, it should be noticed that the crystallinity of a natural mineral differs according to its production region, and may cause slight variation in the spectrum.

The most suitable ratios for the absorbance ratio method are ascertained to be 912 cm⁻¹/790 cm⁻¹ (Kaolinite), 556 cm⁻¹/822 cm⁻¹ (Mullite), 538 cm⁻¹/799 cm⁻¹ (Muscovite), 918 cm⁻¹/797 cm⁻¹ (Montmorillonite) and 958 cm⁻¹/800 cm⁻¹ (Amorphous silica). This knowledge might still be helpful in using an outdated but economical double beam grating IR. Nevertheless, except for Pyrophyllite interference, the absorbance ratio method led to minor but obvious negative errors. Furthermore, the absorbance ratio method was less appropriate when the interference was present in large amounts compared to the quartz whereas difference spectrum was free from such restriction. Therefore, it was shown that the absorbance ratio method was inferior to the difference spectrum method in convenience, applicability and accuracy of result.

In this study, only Muscovite interference could not be corrected properly with the difference spectrum if the calibration curve of (3) was employed with the curve of (2). This might be due to the discrepancy between particle size distribution of standard Muscovite and that of Muscovite in the mixture samples. In infrared analysis in the KBr tablet technique, the coefficient of absorption and the spectrum pattern are remarkably affected by the particle size of the samples. Unfortunately, precise particle size control was practically impossible for Muscovite because it was difficult to crush it into normal particles.

Another countermeasure for spectrum interference is ashing, an indispensable sample preparation procedure for the on-filter analysis method[27]. It is known that the interference due to Kaolinite, Muscovite and Illite can be eliminated substantially by pre-heating of samples at 650 ± 25°C for 10–30 min[17]. Sample preparation with a muffle furnace, which may be employed in the on-filter analysis procedure[27] ought to be useful for this countermeasure.

Unlike the abovementioned interference, there are other types of interferences that may lead to an underestimation in quartz determination. Graphite, corundum, silicon carbide, calcite, iron oxide and other highly absorbing phases are thought to affect the baseline seriously[19, 28], thus preventing precise spectrum measurements. Although it is difficult to correct such negative errors efficiently by means of difference spectrum, the least square method[19, 29] or the multivariate calibration method[30] will successfully correct such interfered spectra and will secure an accurate crystalline silica analysis.

The practicability of an analytical method in dealing with industrial hygiene samples is considerably dependant on analytical sensitivity. Compared with other instrumental analyses for quartz determination, the IR method exceeds in sensitivity. According to the NIOSH's analytical manual[9], the minimum limits of determination in the X-ray diffraction method and the colorimetric method (visible absorption method) are 20 micro grams while that in the IR method is 10 micro grams. Furthermore, a detection limit of a few micro grams has been accomplished with the aid of recent FT-IR. For example, Tuchman[31] reported that only 2 micro grams of quartz could be detected with a DTGS FT-IR detector. In this study, 1–3 micro grams of quartz could be quantified even though the measured spectrum was interfered with Muscovite, and 17–18 micro grams of quartz could be determined with the presence of Amorphous silica. These results prove that the difference spectrum does not degrade the analytical sensitivity of the IR method substantially.

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