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Silica Content of Dusts from Five Texas Cottonseed Oil Mills

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ABSTRACT

Total dust samples, collected with high-volume samplers, were ashed and then analyzed for aluminum, silicon and silica (SiO_2). Ash and aluminum contents agreed with earlier reported data, but the silicon content was lower. The amounts of silica ranged from 2-7% in dusts from the cleaning rooms to 0.01-0.05% in dusts from the baling rooms. Agreement with silica contents determined by infrared (IR) spectrometry was good. IR spectra indicated silica particle diameters were in the range of 6-8 μm in the cleaning rooms and 10 μm or more in the delintering and baling rooms. Threshold limit values (TLV) calculated on the basis of total silica in the high-volume samples suggest silica values above the limit in 4 of the cleaning rooms, and possibly one at the delintering rooms. Calculation of respirable silica concentrations and TLV for respirable silica was precluded by the sampling method.

INTRODUCTION

Silica is a component of a number of agricultural dusts, including corn (1), wheat, barley, rapeseed and oats (2) and can make up 1.5-17% of these dusts. Small quantities of silica and clays are found in cotton carding room dust by optical microscopy (3) and infrared (IR) spectroscopy (4). Dust generated during cotton ginning can include as much as 16-23% silica (5).

Information on the composition and physiological activity of cottonseed oil mill dust is scant. Data on the organic and ash contents of Egyptian oil mill dusts have been published (6). Jones et al. (7) found a low prevalence (< 6.5%) of chronic airways diseases among 172 employees of 5 American oil mills. A survey of the total and respirable dust levels in 5 Texas cottonseed oil mills was published by Matlock et al. (8). In a companion study, Brown et al. (9) determined the proximate and inorganic compositions of the Texas oil mill dusts. They found variable amounts of silicon and aluminum and suggested these elements were present as silica and silicates. However, no quantitative data on silica or silicates were obtained.

Although reports of silicosis in agricultural workers are extremely rare (10), information on the extent of silica contamination in agricultural dusts is of theoretical interest in light of the National Institute of Occupational Safety and Health (NIOSH) proposed guidelines for occupational exposure to crystalline silica (11). The present Federal standards (12) for exposure to free silica are on an 8-hr time-weighted average: (a) respirable quartz = 10 mg/m^3/(% SiO_2 + 2), and (b) quartz (total dust) = 30 mg/m^3/(% SiO_2 + 3). In this paper we report the silica content of the dusts collected in the 5 Texas cottonseed oil mills and revise some of the silicon and aluminum data reported earlier.

MATERIALS AND METHODS

Methods for collecting the high-volume air samples and recovering the dusts from the filters were described previously (8,9). Samples were from mills processing stripper-harvested cottonseed. Ash was determined gravimetrically after ashing at 750 C. Silicon and aluminum were determined by X-ray fluorescence (9). For silica (α-quartz) analyses, quadruplicate total dust samples (10-100 ± 0.01 mg) were ashed and analyzed by X-ray diffraction after quantitatively transferring the ash to 0.2 μm porosity silver membrane filters as outlined by the NIOSH procedure (11). Diffraction patterns were obtained for blank and silica-laden filters using a Diano Corp. XRD-5 X-ray diffractometer. Quantitative analysis for silica was conducted by setting the instrument at the $2\Theta = 26.70°$ maximum for SiO_2 and averaging the count obtained in 10-sec counting periods. These measurements were corrected for the background by subtracting the signal obtained from similarly prepared blank filters. The widest beam Soller slit (3°) was used to improve the counting statistics. Silica values were obtained by comparison with a standard curve covering the range 0-0.500 mg SiO_2. IR spectra were obtained from disks prepared by pressing ash (1.1-1.2 mg) with KBr (350 mg). Spectra were recorded on a Digilab model FTS 15 Fourier transform IR spectrometer. Standard silica was obtained through the NIOSH Criteria Development and Standards Development Division, Cincinnati, OH. The silica had been wet-sieved to pass a 10 μm porosity sieve and was from the same batch used in developing the NIOSH silica method. Percentage silica in the dusts was calculated from the IR data after converting percentage change in transmittance at 795 cm^{-1} caused by silica and comparing the 795 cm^{-1} absorbance to that of pure silica in KBr. The change in transmittance at 795 cm^{-1} was obtained by difference between a line drawn between the IR shoulders at 850 and 700 cm^{-1} and the 795 cm^{-1} minimum. Corrections were made for differences in the amounts of ash obtained from the samples.

RESULTS AND DISCUSSION

Fourier transform IR spectra of the standard silica and ashed dust samples from the cleaning room, delintering room and baling room of Mill D are shown in Figure 1. The absorptions stem from metallic oxides and thermally stable salts. Sulfates, phosphates, silica and silicates absorb strongly in the region 900-1130 cm^{-1}; medium-to-weak bands are in the region 600-800 cm^{-1} (13).

The spectra represent samples containing from 1% silica (Fig. 1 D) to 100% silica (Fig. 1 A). Tuddenham and Lyon (14) found that the pair of bands recorded in KBr pellet spectra of many minerals near 790 and 770 cm^{-1} are specific for quartz, that the ratio of the 790/770 intensities can be used to estimate particle size and that the intensity of the 790 band can be used for quantitative analysis. In our spectra, the minima for the silica doublet were recorded at 795-797 and 775-779 cm^{-1}. The small discrepancies from the band positions reported by Tuddenham and Lyon

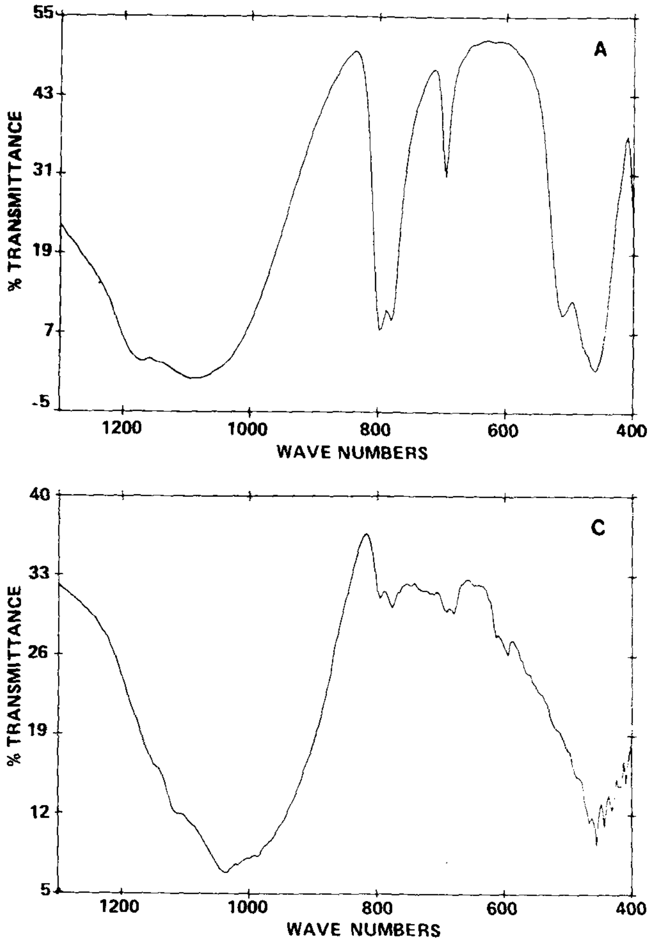

FIG. 1. Infrared spectra of (A) pure silica, (B) mill D cleaning room dust, (C) mill D delintering room dust, and (D) mill D baling room dust.

probably result from differences in instruments and calibrations. The minimal quantity of silica which could be detected by Fourier transform IR spectroscopy was less than 0.01%.

The size of the silica particles in the dusts from Mill D can be estimated from the ratio of the absorbancies of the 790 and 770 cm^{-1} bands shown in Figure 1. Silica particles in the ranges of 1 and 2-4 µm yield ratios of ca. 1.40 and 1.20, and the ratio for 6-8 µm diameter particles is ca. 1 (14). The band ratio from the wet-sieved silica standard (1.03) indicates particle diameters of ca. 5-6 µm. The ratio from the cleaning dust (1.00) indicates particle diameters in the range of 6-8 m. The 790/770 ratios from the delintering dust (0.95) and baling dust (0.85) indicate that most of the particles in these samples exceeded 10 µm diameter.

The ash, aluminum, silicon and silica content and the respective standard deviations obtained for the dust samples from the oil mills are reported in Table I. Statistical agreement (95% confidence limit) between the ash values in Table 1 and those reported earlier (9) was satisfactory, except for the dust from the cleaning room at Mill B. Aluminum percentages agreed less well; the new data indicated an average of 50% more aluminum. However, the differences in aluminum content were statistically significant only for the dust from the Mill B cleaning room, 0.83 vs 0.43%, and for the dust from the Mill D baling room, 0.48 vs 0.03%.

The silicon contents of the mill dusts in our earlier report (9) were extrapolated from a set of standards that generally contained much lower quantities of silicon than were found in the samples. The data in Table I were obtained when silicon was redetermined by replicate analysis of the dusts and are based on a set of silicon-microcrystalline cellulose standards that included the range of silicon concentrations found in the samples. The new silicon values were decreased on the average by 36% and in 13 of the 19 samples the differences were statistically significant at the 95% level of confidence.

Most of the ashed dust samples contained an interfering substance that had the same diffraction angle as the fluorite internal standard. The identity of the interfering substance is unknown. Consequently, the silica data had to be calculated from a standard curve relating instrument counts vs mg silica. The relationship between counts and mg silica was linear (the origin at 0), a correlation of $r = 0.960$ and a standard error of estimate of 0.0509.

The silica content of the total dust samples is shown in Table I. Cleaning dust contained 2.33-6.82% silica, delintering dust 0.05-2.77%, hulling dust 0.01-0.05% and baling dust 0.01-0.97%. The highest percentages of silica in dusts from cleaning, delintering and baling rooms were found in the samples from Mill D. The highest percentage of silica in a hulling room dust was found at Mill C.

The percentage of silica in the dusts collected at Mill D was calculated from the IR spectra shown in Figure 1. The results were: (a) cleaning 5.9%, (b) delintering 2.2%, and (c) baling 0.47%. The lower silica values obtained from the IR data probably resulted because the silica particles in the samples tended to be much larger than those in the standard, because increasing particle size results in a pronounced decrease in the absorbance of silica at 770 and 790 cm^{-1} (14,15). We conclude that, when the differences in particle size are taken into consideration, the silica values determined by IR analysis corroborate the X-ray diffraction results and support the conclusion that oil mill dust can contain appreciable percentages of silica.

The average total dust levels (8) and concentrations of airborne silica found in the various work areas of the mills are shown in Table II. Total dust concentrations are based on 4 replicates and silica concentrations were obtained by multiplying the total dust levels by the corresponding silica percentage (Table I).

The highest concentrations of airborne silica were found in the cleaning rooms and ranged from 0.271 mg/m^3 to 3.05 mg/m^3 at Mill E, where the dust-suppression system was inoperable during the samplings. The atmospheres within the delintering rooms at Mills C and D contained 0.065 mg/m^3 and 0.288 mg/m^3, respectively. Silica levels in all hulling areas were low and the only baling area with a relatively high level of airborne silica was at Mill D, 0.114 mg/m^3.

Several threshold limit values (TLV) for occupational

TABLE I

Ash, Aluminum, Silicon and Silica Content of Total Dust Samples from Oil Mills

		Percentage and standard deviation of constituent in sample			
Mill	Processing area	Ash SD	Aluminum SD	Silicon SD	Silica SD
A	Cleaning	18.00 ± 1.29	0.67 ± 0.24	3.42 ± 0.15	2.33 ± 0.36
	Delintering	7.73 ± 1.00	0.03 ± 0.03	1.91 ± 0.44	0.30 ± 0.10
	Hulling	6.52 ± 0.22	0.063 ± 0.090	0.28 ± 0.11	0.0097 ± 0.0082
	Baling	9.81 ± 0.20	0.082 ± 0.018	1.51 ± 0.17	0.097 ± 0.019
B	Cleaning	21.4 ± 0.59	0.83 ± 0.15	7.30 ± 1.53	3.29 ± 1.28
	Delintering	24.2 ± 1.10	0.62 ± 0.28	4.83 ± 0.62	1.24 ± 0.22
	Hulling	6.71 ± 0.15	0.145 ± 0.038	0.58 ± 0.024	0.012 ± 0.022
	Baling		(Baling area shared with mill A)		
C	Cleaning	33.95 ± 1.67	1.10 ± 0.45	7.54 ± 0.18	5.16 ± 1.21
	Delintering	10.15 ± 0.21	0.29 ± 0.17	1.84 ± 0.32	0.37 ± 0.052
	Hulling	7.17 ± 0.79	0.070 ± 0.121	0.57 ± 0.15	0.031 ± 0.023
	Baling	5.57 ± 0.23	0.097 ± 0.137	0.57 ± 0.24	0.0071 ± 0.018
D	Cleaning	39.45 ± 1.55	1.12 ± 0.37	10.0 ± 1.34	6.82 ± 1.08
	Delintering	23.98 ± 1.47	0.73 ± 0.31	6.40 ± 0.78	2.77 ± 0.64
	Hulling	9.60 ± -	0.26 ± -	2.66 ± -	Not determined
	Baling	15.81 ± 0.47	0.48 ± 0.16	3.74 ± 0.12	0.92 ± 0.25
E	Cleaning	26.05 ± 1.65	1.11 ± 0.38	8.26 ± 1.34	3.51 ± 0.70
	Delintering	9.59 ± 0.23	0.19 ± 0.11	1.81 ± 0.13	0.049 ± 0.015
	Hulling	6.74 ± 0.53	0.10 ± 0.068	0.51 ± 0.040	0.048 ± 0.042
	Baling	9.60 ± 0.26	0.15 ± 0.19	1.56 ± 0.66	0.040 ± 0.013

SD = standard deviation.

TABLE II

Average Total Dust and Silica Concentrations Found in Total Dust Samples from Five Texas Cottonseed Oil Mills

Mill	Processing area	Dust concentration (mg/m^3)[a,b]	Silica concentration (mg/m^3)
A	Cleaning	11.61	0.271
	Delintering	8.46	0.025
	Hulling	12.21	0.001
	Baling	26.99	0.026
B	Cleaning	26.72	0.888
	Delintering	4.31	0.053
	Hulling	11.88	0.001
	Baling	(Baling area shared with Mill A)	
C	Cleaning	12.92	0.667
	Delintering	17.48	0.646
	Hulling	17.67	0.055
	Baling	4.93	Tr[c]
D	Cleaning	14.09	0.961
	Delintering	10.39	0.288
	Hulling	17.28	Not determined
	Baling	12.37	0.114
E	Cleaning	86.77	3.046
	Delintering	11.77	0.057
	Hulling	6.94	0.003
	Baling	3.73	0.015

[a] Source: Matlock et al. (8).

[b] Averages from 4 replicate samples.

[c] Tr = trace.

exposure to dusts containing silica and the corresponding formulas for calculating the TLV have been proposed (11,16). The TLV for respirable silica prescribed by the Occupational Safety and Health Administration (OSHA) is based on the concentration of silica that is capable of penetrating to the gas exchange region of the lungs (12). The upper size limit of particles that can penetrate that deeply into the lungs is ca. 5 μm aerodynamic diameter (16). The dust levels and silica concentrations reported in Table II cannot be directly related to the respirable dust TLV because a large but unknown proportion of the silica in our samples (collected with high-volume samplers) exceeded the 5-μm limit.

The respective OSHA 8-hr time-weighted average TLV for exposure to total airborne silica in the dusts can be estimated (16) using the formula:

$$\mathrm{TLV} = \frac{30}{\%\ \mathrm{quartz} + 3}$$

The formula yields an upper permissible limit for total dust exposure of 10 mg/m^3 when the quartz content is ca. 0 and a maximal permissible total dust exposure limit of 0.3 mg/m^3 when the quartz content approaches 100%. The respective quantities of total silica which could be allowed in the dust from each work area can be calculated by multiplying the total dust TLV by the percentage of silica in the dust (15). These calculations yield a maximal permissible silica exposure limit of 0.3 mg/m^3, which occurs in dusts containing 97% silica.

Dust levels in the 5 cleaning rooms exceeded the 10 mg/m^3 TLV in their delintering rooms, 3 in their hulling rooms and 2 in their baling rooms. In addition, our data suggest that excessive silica was contained in the atmosphere within 4 and possibly all 5 of the cleaning rooms. The concentration of airborne silica in one of the delintering rooms also may have been excessive. It is important to note that since the time these samples were collected, all 5 of the mills have taken steps to control their dust levels.

A significant difference exists in the dust content of cottonseed harvested by stripper and spindle harvesters (17). A bale of stripped cotton may contain 5 times as much trash as a bale of spindle-picked cotton. Cottonseed from gins processing stripped cotton generally contains more foreign matter than cottonseed from spindle-picked cotton and it is logical that an oil mill processing cleaner cottonseed will have less dust in its work environment (17). The mills in this survey were processing stripper-harvested cottonseed. Therefore, the data in this paper should be interpreted to mean that dust generated in oil mills processing stripper-harvested cottonseed could contain regulatorily significant quantities of silica. As precautions, oil mill operators need to use well-cleaned cottonseed and make every reasonable effort to minimize dust levels. The most critical areas are apparently in the cleaning and baling rooms.

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REFERENCES

1. Jaremin, B., and W. Szczekocki, Bull. Inst. Marine Med. 26:43 (1975).
2. Farant, J.P., and C.F. Moore, Am. Ind. Hyg. Assoc. J. 39:177 (1978).
3. Hersh, S.P., T.G. Rochow, P.A. Tucker and F.W. Farwell, Text. Res. J. 46:743 (1976).
4. Brown, D.F., E.R. McCall, B. Piccolo and V.W. Tripp, Am. Ind. Hyg. Assoc. J. 38:107 (1977).
5. Khasanov, V. Kh., Gig. Sanit. 5:96 (1975).
6. Noweir, M.H., Y. El-Sadek and A.A. El-Dakhakhny, Arch. Environ. Health 19:99 (1969).
7. Jones, R.N., J. Carr, H. Glindmeyer, J. Diem and H. Weill, Thorax 32:281 (1977).
8. Matlock, S.W., L.R. Wiederhold and C.B. Parnell, Jr., Proc. Am. Soc. Agric. Eng. Meet., Dec. 1975, Chicago, IL, Paper No. 75-5536.
9. Brown, D.F., B. Piccolo, V.W. Tripp and C.B. Parnell, Jr., JAOCS 54:255 (1977).
10. Chan-Yeung, M., M.J. Ashley and S. Grzybowski, Can. Med. Assoc. J. 118:1271 (1978).
11. National Institute for Occupational Safety and Health, "Criteria for a Recommended Standard . . . Occupational Exposure to Crystalline Silica," U.S. Dep. Health, Education and Welfare, Publ. Health Serv., Publ. No. (NIOSH) 75-120, Washington, DC, 1974, 121 pp.
12. Occupational Safety and Health Administration, U.S. Department of Labor, Air Contaminants, 29CFR, Part 1910.93 Federal Register 39 (125):23541 (1974).
13. Hunt, J.M., M.P. Wishard and L.C. Bonham, Anal. Chem. 22:1478 (1950).
14. Tuddenham, W.M. and R.J.P. Lyon, Anal. Chem. 32:1630 (1960).
15. Mangla, A., Anal. Chem. 47:927 (1975).
16. Williams, C.J., and R.E. Hawley, Am. Lab. 7:20 (1975).
17. Parnell, C.B., Jr., OSHA Cotton Dust Standard–Cottonseed Oil Mills, in "Proceedings Third Special Session on Cotton Dust Research," edited by P.J. Wakelyn, Beltwide Cotton Production Research Conference, Phoenix, Jan. 9-10, 1977, National Cotton Council America, Memphis, TN, 1979, pp. 52-54.

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