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Proficiency Analytical Testing (PAT) Silica Variability, 1990–1998

Industrial hygiene laboratories use one of three analytical techniques (X-ray diffraction spectrometry, infrared absorption spectrometry, and colorimetric spectrophotometry) for the quantitative determination of crystalline silica. Interlaboratory variability historically has been high for these analyses (~25–35% relative standard deviation). Agreement between laboratories, as measured by the American Industrial Hygiene Association Proficiency Analytical Testing program over the period April 1990 through April 1998, was studied. Analysis of over 11,000 data points (laboratory/sample/round combinations) showed some significant differences between analytical methods in their relative recovery and precision, although overall mean recoveries were similar for the three techniques. Relative recovery of colorimetric results (but not those of the X-ray or infrared results) was significantly affected by sample loading in the range 40–170 μg silica per sample. Differences on the order of 5–10% were produced in some intermatrix comparisons for infrared and colorimetric recoveries, but not for those of X-ray. X-ray and infrared techniques were both more precise than colorimetric. Small differences, on the order of 2–5%, were observed in the interlaboratory and intralaboratory relative standard deviations between different matrices for X-ray and infrared analyses, but not for the more variable colorimetric results.

Keywords: colorimetric, infrared, PAT program, quartz, silica, X-ray diffraction

Inhalation of dusts containing crystalline silica can cause chronic lung disease (silicosis), and the polymorphs are suspected human carcinogens.(1) The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 0.05 mg/m^3 time-weighted average. The typical 8-hour occupational sample using current sampling methods may contain on the order of a few tens of micrograms of silica. The American Industrial Hygiene Association (AIHA) conducts the Proficiency Analytical Testing (PAT) program to improve the accuracy of analytical results on occupational samples. Samples of asbestos fibers, organic solvents, metals, and silica (as alpha-quartz) are provided to participating laboratories four times per year. Performance limits for samples in the program are determined by the mean and precision of results of designated reference laboratories for that round.(2) [Note: As of Round 132, reference laboratories are no longer used in the PAT program. The reference value will be replaced by the mean of all participating laboratories.]

For silica the reference laboratories comprise a majority of all participating laboratories, and performance limits have been wider than those for most of the other PAT analytes. The number of participants analyzing for silica reached a peak of 134 laboratories in 1984 (PAT Round 78), and has been declining since that time (Figure 1).

In a previous study the accuracy and precision of laboratories in PAT silica rounds from 1972 to 1990 were analyzed.(3) The samples in those rounds were prepared by three different organizations, using many combinations of different quartz sources, background matrices, collection filters, and methods of generation. Also, the analytical methods used by the participating laboratories varied widely over the period of the study. The effect of these multiple variables was to obscure any differences in performance between PAT laboratories with respect to time, sample loading, sample matrix, or analytical methods used. For example, the particle size of the quartz used in Rounds 16 through 62 (Min-U-Sil 10 or Min-U-Sil 15) was larger than

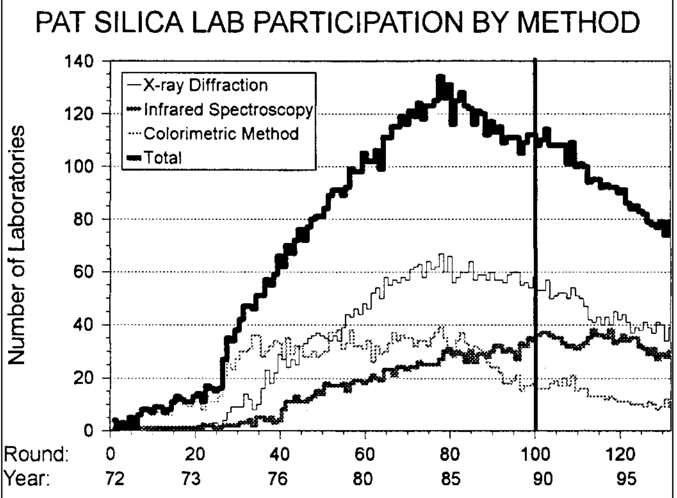

FIGURE 1. Distribution of analytical methods for silica used by participating laboratories in PAT Rounds 101–132 (April 1990–January 1998)

that in other rounds, including the current study. The effects of a shift to smaller particles depend on the analytical technique used. Sensitivity of X-ray diffraction (XRD) is reduced for smaller particles, while that of infrared absorption is enhanced relative to analyses of larger particles. Colorimetric methods typically include a precisely timed heating step in phosphoric acid to dissolve amorphous silica species, in which some of the smaller crystalline silica particles may be lost.

The present study was undertaken to analyze recent PAT silica results since 1990 for relative recovery of silica and precision as functions of sample loading (mass of silica per filter), sample matrix, and the analytical methods used by the reporting laboratories. Over this time period, Rounds 101 through 132, few changes in PAT sample generation occurred and all samples contained Min-U-Sil 5, generated and sampled in aerosol form at one facility, using predominantly one brand of collection filter. This makes the identification of differences in laboratory performance easier than in the previous PAT study.

PAT DATA, ROUNDS 101–132

The PAT silica results from individual laboratories for the past 8 years (Round 101, April 1990, through Round 132, January 1998) are tabulated by matrix in Table I. For statistical analysis the results reported by individual laboratories on each round were grouped by analytical method. There were 11,566 observations (32 rounds × 4 filters per round × $\sim$90 laboratories per round) available for analysis by the SAS® General Linear Models Procedure.

For Rounds 101 through 132, except for Round 130, which had no background matrix, the matrix applied to the filters (in addition to the Min-U-Sil 5) was rotated regularly in the following order: calcite, talc, talc + coal mine dust, and coal mine dust (CMD). At least seven replications of each matrix occurred during the time period studied. The filter loading (as measured by the reference values(2)) over the period studied ranged from 38 to 173 µg silica, as Min-U-Sil 5.

Figure 1 shows the number of laboratories using XRD, infrared spectroscopy (IR), or colorimetric (CO) methods in these rounds. For example, out of a total of 78 laboratories that participated in Round 132, 39 laboratories (50%) used XRD, 30 (38%) used IR, and 9 (12%) used colorimetry.

TABLE I. PAT Silica Samples for Rounds 101–132

Round	Matrix[A]	Filter	QC CV[B]	RefLab CV[C]
101	calcite	FWS-B	0.172	0.255
102	talc	FWS-B	0.065	0.230
103	talc + CMD	FWS-B	0.111	0.225
104	CMD	FWS-B	0.095	0.228
105	calcite	GLA-5000	0.118	0.245
106	talc	GLA-5000	0.146	0.226
107	talc + CMD	GLA-5000	0.162	0.193
108	CMD	Omega	0.199	0.201
109	calcite	FWS-B	0.194	0.273
110	talc	FWS-B	0.160	0.242
111	talc + CMD	FWS-B	0.152	0.235
112	CMD	FWS-B	0.164	0.233
113	calcite	FWS-B	0.123	0.228
114	talc	FWS-B	0.158	0.273
115	talc + CMD	FWS-B	0.151	0.253
116	CMD	FWS-B	0.120	0.239
117	calcite	FWS-B	0.161	0.240
118	talc	FWS-B	0.166	0.236
119	talc + CMD	FWS-B	0.121	0.213
120	CMD	FWS-B	0.170	0.229
121	calcite	FWS-B	0.176	0.223
122	talc	FWS-B	0.158	0.209
123	talc + CMD	FWS-B	0.133	0.204
124	CMD	FWS-B	0.160	0.223
125	calcite	FWS-B	0.156	0.218
126	talc	FWS-B	0.166	0.253
127	talc + CMD	FWS-B	0.133	0.235
128	CMD	FWS-B	0.111	0.208
129	calcite	FWS-B	0.166	0.243
130	none	FWS-B	0.093	0.213
131	talc	FWS-B	0.150	0.246
132	talc + CMD	FWS-B	0.137	0.175
Mean			0.145	0.229

[A] Background matrix added to Min-U-Sil 5; CMD = coal mine dust.
[B] CV of 13 replicate determinations by IR at one laboratory, pooled over 4 samples per round
[C] CV pooled over 4 samples per round and pooled over reference laboratories

QUALITY CONTROL

The quality control (QC) results (analyses by IR using NIOSH Method 7603 and muffle furnace ashing on 13 replicates of each of the 4 filters per round by the generating laboratory prior to release of the samples to the PAT laboratories)(4) were compared with the reference values (the mean values reported by designated reference laboratories) subsequently obtained for each round. (Beginning with Round 132 the mean values of all reported laboratories replace the reference values; thus, reference laboratories will no longer be used.) Overall, as might be expected, the QC results by the generating laboratory agreed well (r^2=0.856; n=128) with subsequent PAT reference values. High correlation coefficients were found between the QC values and the reference values separately for each matrix (no separate regression was done for Round 130, with no background matrix, since only four mean results were generated):

talc + CMD (r^2=0.970; n=32), calcite (0.922; 32),
talc (0.906; 32), and CMD (0.864; 28).

The mean ratio of QC value to reference value for Rounds 101–132 was 1.009, (range 0.59–1.45). The ratio was not a function of sample loading or round. The mean coefficient of variation (CV) of the QC values over all rounds was 0.145, compared with 0.229 for the mean reference laboratory CV (Table I).

DIFFERENCES BETWEEN LABORATORIES ATTRIBUTABLE TO ANALYTICAL METHODS

To obtain a measure of relative recovery by a laboratory on a given sample, the relative recovery ratio, R_{ij}, of the silica mass reported by the laboratory to the mean mass of silica reported by all laboratories for that filter was calculated (using 11,566 data points):

$$R_{ij} = (\text{mass reported by laboratory i on filter j}) \div (\text{all-laboratory mean mass for filter j})$$

On a given round, the mean of all laboratories using one of the three analytical techniques was calculated:

$$R_{kj} = (\text{mean mass for method k on filter j}) \div (\text{all-laboratory mean mass for filter j})$$

Thus, there were 128 values of R_{kj} (32 rounds × 4 filters per round), yielding information that can be stated as, for example: "The mean recovery by XRD on Round 128 (CMD matrix) was 1.007, with a between-laboratory standard deviation (STD) = 0.012."

The distributions of R_{kj} by analytical method are shown in Figures 2a–2c. Over the 32 rounds, this ratio varied from 0.847 to 1.084 for laboratories using XRD, 0.843 to 1.170 for IR, and 0.763 to 1.359 for the colorimetric methods (Table II). There were no significant differences between the overall mean recoveries of the three methods.

When plotted against sample loading, a significant difference between methods is apparent. The XRD (Figure 3c) and IR (Figure 3b) recoveries are independent of sample loading over the range studied, but the ratio, as reported by the colorimetric methods, was strongly dependent on the mass of silica present (Figure 3a). At low loadings in the range 40–60 μg silica, a positive bias of as much as 20% is evident for colorimetric analyses. However, for loadings in excess of 140 μg silica, negative biases of 5–20% occurred. It is well known that the colorimetric method has a limited linear range, and that significant blank values (20 μg silica or higher) are common.(5–7) Both of these factors may contribute to the observed dependence of colorimetric method recovery on filter loading. The dependence of recovery on loading and high intralaboratory variability (up to about twice as high as XRD or IR) of the colorimetric methods was also noted in the study of the PAT results up to Round 101.(3)

DIFFERENCES BETWEEN LABORATORIES BECAUSE OF SAMPLE MATRIX

An analysis of variance (ANOVA by SAS Linear Models Procedure) was performed using as dependent variable the mean recovery for the four filters on a round by all laboratories (Round 130, having no background matrix, was excluded). There were 2828 observations (31 rounds × ~90 laboratories per round), of which 1378 observations were XRD, 1036 were IR, and 414 were colorimetric. The independent variable was matrix (calcite, talc, talc + CMD, and CMD).

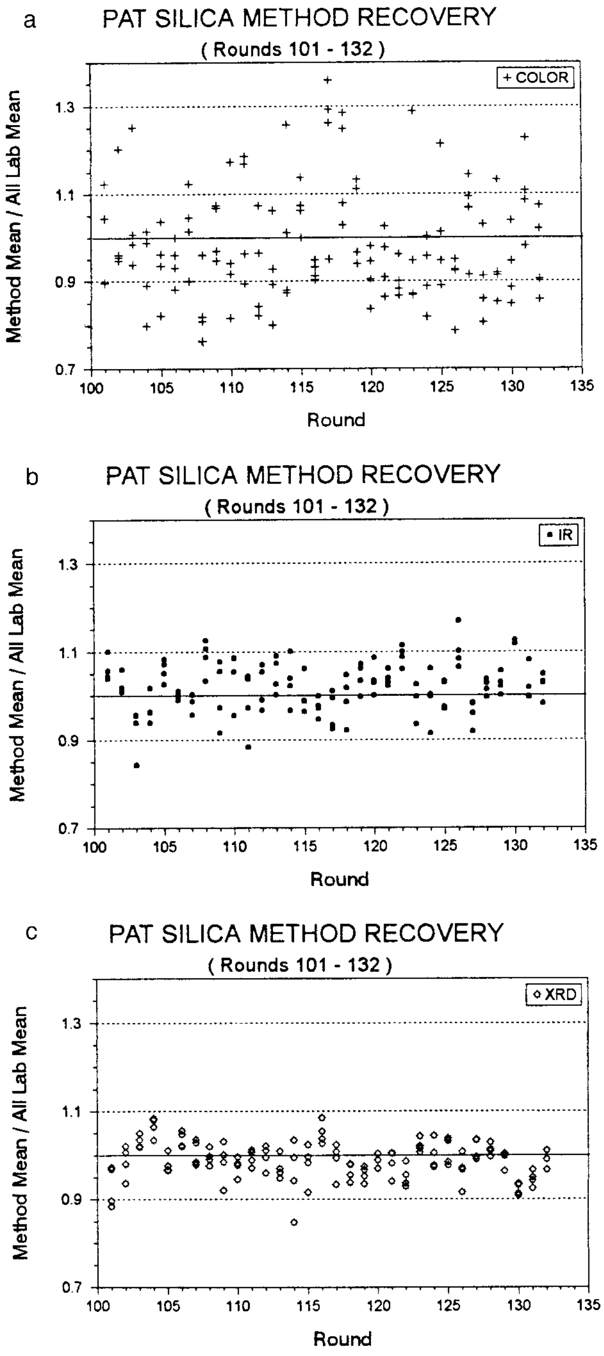

FIGURE 2. Relative recovery (mean mass of silica found by all laboratories using a given method for a given sample divided by the corresponding mean of all laboratories for 128 filters) for 32 PAT rounds, with 4 filters per round. (a) colorimetric, (b) infrared, (c) X-ray diffraction

TABLE II. Relative Recovery (Method Mean/All-Lab Mean), Rounds 101–132

Method	Matrix	N	Mean	Min	Max
X-ray	all	128	0.987	0.847	1.084
Infrared	all	128	1.021	0.843	1.170
Colorimetric	all	128	0.984	0.763	1.359

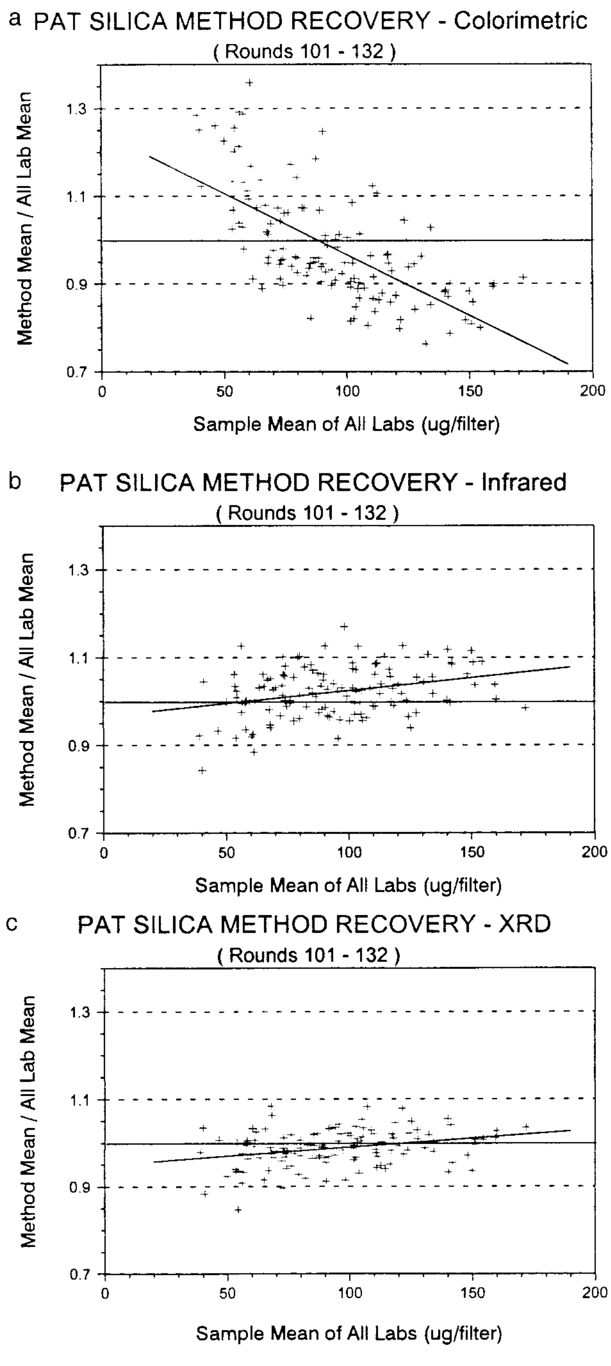

FIGURE 3. Relative recovery (mean recovery by laboratories using a given analytical method for each of 128 filters) as a function of sample loading and analytical method used. (a) colorimetric, (b) infrared, (c) X-ray diffraction

The results are shown in Table III. There were no significant differences in recovery of the XRD methods between the different matrices. The mean recovery by IR methods in talc matrix was significantly higher (by about 5%) than in talc + CMD. Samples containing CMD matrix gave significantly lower recovery by colorimetric methods than those having talc (9.7% difference) or talc + CMD (9.3% difference).

Within some of the matrices, dependence of recovery on sample loading was observed for each of the analytical techniques. Small, positive correlations (i.e., increasing recovery with increasing loading) occurred between XRD recovery and loading in talc + CMD ($r^2=0.21$), calcite ($r^2=0.17$), and talc ($r^2=0.07$). Similarly, small, positive correlations of recovery with sample loading for IR methods were observed in talc + CMD ($r^2=0.41$) and CMD matrices ($r^2=0.28$). The strong dependence, similar to that in Figure 3a, of colorimetric recovery on sample loading was also observed separately in all matrices.

INTRALABORATORY PRECISION

An estimate of intralaboratory precision of IR methods in the current study can be derived from the CV of the 13 replicate determinations of QC samples for each of the 4 samples prepared for each round. Pooled values for each round, given in Table I, column 4, range from 0.065 (Round 102) to 0.199 (Round 108). This CV for individual samples had a mean of 0.142, a range from 0.046 (Round 102, Sample 2) to 0.237 (Round 129, Sample 3), and exhibited a tendency to rise at low sample loading as did other estimates of inter- and intralaboratory variability (Figure 4).

The earlier study of PAT data estimated intralaboratory precision of analytical methods for Rounds 63–101 by separately pooling results in high and low sample loading ranges, obtaining CV values of 0.186 for XRD, 0.165 for IR, and 0.198 for colorimetric methods.(3)

For this study, estimates of precision by analytical technique were obtained by calculating the STD of the recovery ratio, R_{ij}, of the four filters reported by the laboratories on that round:

$$\mathrm{STD}_i = [\mathrm{Sum}_{j=1}^{4} (R_{ij} - R_i)^2/3]^{1/2}$$

Approximately 2900 data points were available for analysis (32 rounds × ~90 laboratories per round). This definition does not allow for sensitive analysis of dependence of precision on sample loading, as the range of sample loadings was roughly similar from round to round, but it allows comparison of the relative precision of PAT results as affected by methods and matrices. Precision was not a significant function of round in this study.

The ANOVA results are shown in Table III. The overall CV for XRD methods was 0.165, and a significantly higher CV was observed in calcite matrix than in talc + CMD. Significant differences by matrix were also observed for IR methods, for which within-laboratory results were more variable for calcite and talc matrices. Colorimetric results were so variable as to obscure any dependence of precision on matrix.

In a previous collaborative test of XRD and IR methods, the intralaboratory CV found for specific XRD (NIOSH P&CAM 259; similar to current NIOSH 7500) and IR (MSHA P-7) methods was 0.07–0.10.(8) The controlled conditions of the collaborative test as compared with the present data probably account for the lower CVs in the former.

INTERLABORATORY PRECISION

The observed relative standard deviation (RSD = CV × 100%) of the reported mass of silica, pooled across the four samples in each round and pooled across laboratories, was used as a measure of interlaboratory precision. Figure 5 shows the trends in RSD over time, and the QC variability (Table I, column 4) is plotted for comparison. The reference laboratory pooled RSD (Table I, column 5), along with its XRD and IR components, did not change significantly over the period studied. However, a measurable improvement in the precision of colorimetric methods

TABLE III. ANOVA of Method Recovery Means and CV by Matrix

Response Variable	No. Data Points	Grand Mean	ANOVA P-Value	Significant Difference[A]
XRD recovery	1378[B]	0.985	0.03	none
IR recovery	1036[C]	1.012	0.06	$R_{talc} > R_{talc + CMD}$ by 0.051
CO recovery	414[D]	0.959	0.02	$R_{talc} > R_{CMD}$ by 0.097 $R_{talc + CMD} > R_{CMD}$ by 0.093
XRD intralab CV	1378[B]	0.165	0.04	$CV_{calcite} > CV_{talc + CMD}$ by 0.025
IR intralab CV	1036[C]	0.166	0.03	$CV_{calcite} > CV_{talc + CMD}$ by 0.032 $CV_{talc} > CV_{talc + CMD}$ by 0.024
CO intralab CV	414[D]	0.204	NS[F]	none
XRD interlab CV	124[E]	0.249	0.09	$CV_{calcite} > CV_{talc + CMD}$ by 0.029
IR interlab CV	124[E]	0.253	0.03	$CV_{calcite} > CV_{talc + CMD}$ by 0.047 $CV_{calcite} > CV_{CMD}$ by 0.037 $CV_{talc} > CV_{talc + CMD}$ by 0.032
CO interlab CV	124[E]	0.276	NS[F]	none

Note: Intralaboratory CV = coefficient of variation of relative recovery of the 4 filters per round within laboratories; interlaboratory CV = coefficient of variation of means of relative recovery between laboratories.

[A] At the 95% confidence level

[B] 31 Rounds × ~44 laboratories per round

[C] 31 Rounds × ~33 laboratories per round

[D] 31 Rounds × ~13 laboratories per round

[E] 31 Rounds × 4 samples per round

[F] Not significant

seems to have occurred, and typical values of colorimetric RSD fell from the 35–40% range in early rounds to less than 30% recently. Of interest is the fact that the number of laboratories using colorimetric methods in PAT rounds has declined by approximately 50% during this same period.

Interlaboratory RSDs for all laboratories ranged from 20 to 45% during Rounds 101–132 and varied inversely with sample loading, being significantly lower at sample loadings above about 60 μg silica per sample (Figure 6). A similar relationship, displaced to lower RSDs by approximately five to eight percentage points, is observed for the reference laboratories (Figure 7). This dependence on analyte concentration is typical of many analytical techniques at the lower ends of their working ranges (i.e., between the limits of quantitation and detection).(9)

ANOVA results for interlaboratory precision are shown in Table III. Significantly poorer precision in calcite matrix was observed for both XRD and IR methods compared with talc + CMD; in addition, IR precision suffered in calcite versus CMD and in talc versus talc + CMD. No dependence of precision on matrix could be observed for colorimetric methods.

The effects of sample loading on interlaboratory precision of each analytical technique are shown in Figure 8. The three regressions have similar shapes, and the colorimetric methods exhibit significantly poorer precision than XRD or IR at all sample loadings.

CONCLUSIONS AND RECOMMENDATIONS

(1) The overall precision of PAT silica results depends on sample loading, improving above loadings of 60–80 μg silica per sample. The observed interlaboratory variability has not changed significantly over the past 8 years and remains above RSD = 20%.

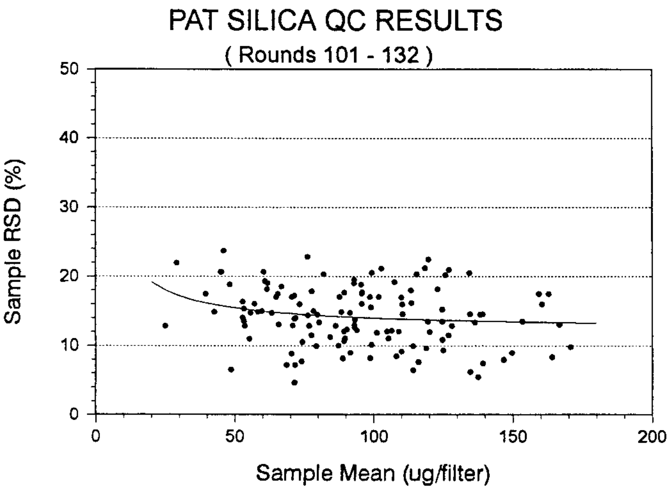

FIGURE 4. Variability of QC results as a function of sample loading (13 replicate determinations by one laboratory using IR on each of 4 filters per round)

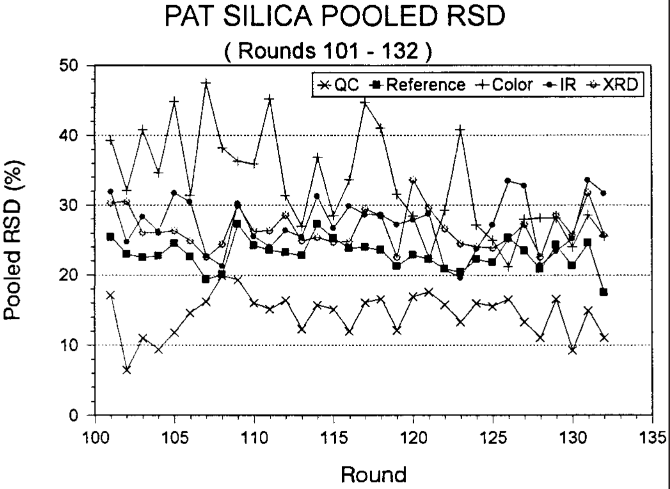

FIGURE 5. Interlaboratory variability of PAT reference laboratory results overall and by analytical method used by round. RSD of QC samples (13 replicates per sample by 1 laboratory) are also plotted.

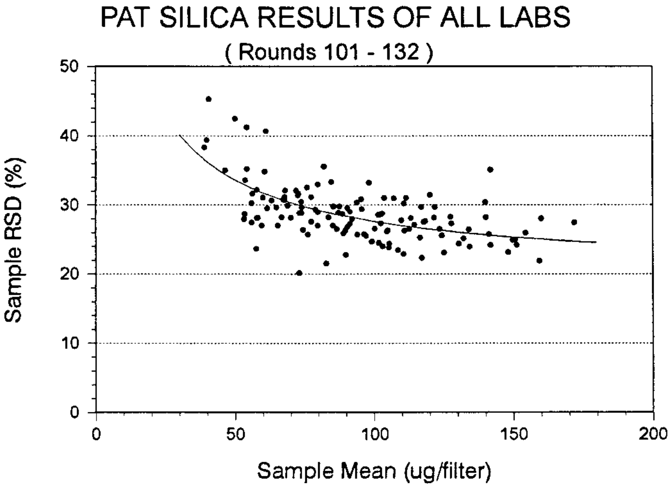

FIGURE 6. Interlaboratory RSD of all participating laboratories as a function of sample loading (mean mass of silica found by all laboratories)

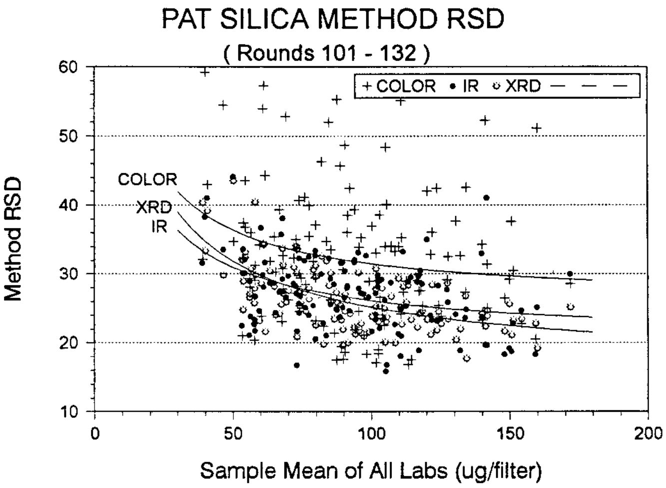

FIGURE 8. Interlaboratory RSD of all participating laboratories by analytical method used as a function of sample loading (mean mass of silica found by all laboratories)

(2) Estimates of the intralaboratory component of variability are in the range 16–20% RSD, and suggest that considerable improvement may be possible through standardizing analytical methods used by participating PAT laboratories, including the use of a common silica reference material.

(3) The colorimetric methods for silica are significantly less precise than either the infrared or the X-ray method. However, the number of laboratories using colorimetric methods has decreased by nearly 50% over the past 8 years, during which time the precision of the colorimetric results has improved by about 20%. The recovery of the colorimetric method is a strong function of sample loading, exhibiting positive bias at low loadings and negative bias at high loadings. Strict adherence to standardized procedures (e.g., those given in Reference [10]) are necessary to produce precise results.

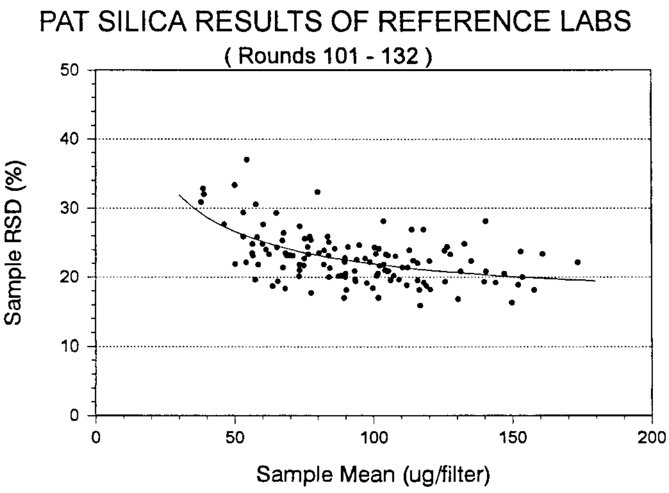

FIGURE 7. Interlaboratory RSD of PAT reference laboratories as a function of sample loading (mean mass of silica found by all laboratories)

(4) Further research into the actual practices and method variations used by laboratories may be useful in standardizing analytical methods and in identifying important analytical variables with the aim of reducing interlaboratory variability. Laboratory personnel are urged to communicate with PAT program personnel concerning analytical problems that arise during analysis of PAT samples.

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REFERENCES

1. **National Institute for Occupational Safety and Health (NIOSH):** *Recommendations for Occupational Safety and Health: Compendium of Policy Documents and Statements* [DHHS (NIOSH) pub. no. 92–100]. Cincinnati, OH: U.S. Department of Health & Human Services, Public Health Service, Centers for Disease Control, NIOSH, 1992.
2. **Esche, C.A., J.H. Groff, P.C. Schlecht, and S.A. Shulman:** *Laboratory Evaluations and Performance Reports for the Proficiency Analytical Testing (PAT) and Environmental Lead Proficiency Analytical Testing (ELPAT) Programs* [DHHS (NIOSH) pub. no. 95–104]. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, NIOSH, 1994.
3. **Shulman, S.A., J.H. Groff, and M.T. Abell:** Performance of laboratories measuring silica in the Proficiency Analytical Testing Program. *Am. Ind. Hyg. Assoc. J. 53*:49–56 (1992).
4. **Parish, H.:** *Quarterly Analytical Report to AIHA, Proficiency Analytical Testing Program* (AIHA, 1990–1998; unpublished).
5. **Talvitie, N.A.:** Determination of free silica: Gravimetric and spectrophotometric procedures applicable to air-borne and settled dusts. *Am. Ind. Hyg. Assoc. J. 25*:169–178 (1964).
6. **Talvitie, N.A.:** Determination of Quartz in the presence of silicates using phosphoric acid. *Anal. Chem. 23*:623–626 (1951).

7. **Talvitie, N.A., and F. Hyslop:** Colorimetric determination of siliceous atmospheric contaminants. *Am. Ind. Hyg. Assoc. J. 19*:54–58 (1958).
8. **Anderson, C.C., and M.T. Abell:** *Collaborative Tests of Two Methods for Determining Free Silica in Airborne Dust* [DHHS (NIOSH) pub. no. 83–124]. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, NIOSH, 1983.
9. **Taylor, J.K.:** *Quality Assurance of Chemical Measurements.* Chelsea, MI: Lewis Publishers, 1987. p. 82.
10. **National Institute for Occupational Safety and Health (NIOSH):** Crystalline silica by visible colorimetry: method 7601. In *NIOSH Manual of Analytical Methods,* 4th rev. ed., P.M. Eller and M.E. Cassinelli (eds.) [DHHS (NIOSH) pub. no. 94–113]. Cincinnati, OH: U.S. Department of Health & Human Services, Public Health Service, Centers for Disease Control and Prevention, NIOSH, 1994.