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HEALTH AND SAFETY COMMISSION

ADVISORY COMMITTEE ON TOXIC SUBSTANCES (ACTS)

MEASURING LOW MASSES OF RESPIRABLE CRYSTALLINE SILICA (RCS) AT PROPOSED WORKPLACE EXPOSURE LIMITS

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Action: from ACTS/MIN/01/2006 (3 May 2006) item 4.1.2: HSL to prepare a paper for the next ACTS meeting setting out progress on its work on measurement of exposures in the field.

Issue

What is measurable?

The main analytical techniques used to measure RCS are x-ray diffraction (XRD) and infra-red (IR) analysis. XRD measures the intensity of the radiation reflected by the crystal structure of silica and assumes the dust is deposited as a thin layer and infra-red measures the absorbance infra-red energy by Si-O vibrations that are also found in other silicate minerals. In ideal conditions, in a single laboratory, on laboratory test samples, the lowest limit of detection (LOD) that is theoretically achieved, when measuring pure RCS with the methods and techniques currently available is about 5 – 10 µg, which is equivalent to an air concentration of 0.005 – 0.01 $mg.m^3$ for an 8-hr sample at 2.2 $l.min^{-1}$. In theory, all laboratories should be able to achieve these limits of detection. However, there are several factors that raise the LOD in real samples and increase the variability of results obtained by different laboratories.

- The reported LODs assume that silica is the only substance present on the filter. In real samples confirmatory evidence is needed, so the most sensitive calibration is not always used until a threshold value is reached that is usually higher than the reported LOD.
- Quantification in the presence of interferences increases the potential error in analysis because additional measurements have to be made or a less precise result reported.
- Components that affect the background, such as the fluorescence of iron in x-ray diffraction or very dark samples in infrared analysis will also increase the LOD.
- Few samples are taken for the full 8-hr period, which reduces the amount measured on the filter and increases the limit of detection.
- It is difficult to obtain reliable calibration test samples with a mass of dust standard that is less than 30 µg when preparing filters following MDHS 101 [1] and using a 6-figure balance, because the method used to prepare the calibration filters is approaching its limit of quantification at about 25µg This creates greater uncertainty in the reported LOD's.
- Bias in the calibration relationship from the 'true' mass on the filter can introduce differences between laboratories, especially if different calibration dusts are used or different corrections applied for the amount of crystalline silica. The responses from XRD and IR measurements are influenced by the particle size of the dust being measured, so it is important that the particle size of the dust standard used is similar to the dust being measured.

These have a corresponding affect on what we are able to confidently quantify.

HSL is currently involved in a project to assess the performance of array detectors used in XRD that offer in an increase in counts on a sample. In theory the increased counts should reduce the noise of the background and so improve the signal to noise ratio and the limit of detection. However, initial research does not yet show any improvement when compared with the performance of the proportional detectors used for silica measurement with XRD.

How good are laboratories at measuring this?

Measurements between laboratories need to be consistent to reduce the possibility of different interpretations being made when assessments are made at the same site and to reduce potential disputes arising from enforcement action. Both HSE in the United Kingdom and the American Industrial Hygiene Association in United States operate proficiency testing schemes so that laboratories and regulators have a tool through which they are able to assess the reliability of these measurements. In the UK proficiency testing program the Workplace Analysis Scheme for Proficiency (WASP), the variation of results between laboratories, when measuring replicate test samples of pure α-quartz at about 300µg (~0.3 mg.m^{-3} for an 8 hr sample at 2.2 l.min^{-1}) is about 6 % but this increases to between 10 % and 15 % at about 80µg (~0.08 mg.m^{-3} for an 8 hr sample at 2.2 l.min^{-1}). The scheme has shown that similar levels of accuracy are obtained by XRD or IR techniques. This is a satisfactory level of agreement for a WEL of 0.1 mg.m^{-3}, however, a linear extrapolation to about 50µg suggests that the relative uncertainty of results is in excess of 20 % (95 % confidence level assuming a normal distribution) for an 8hr sample before taking into consideration further uncertainty due to the interferences present, additional analytical measurements or from sampling. This level of precision may be satisfactory in a survey where the working day is only 5 or 6 hrs but there are various reasons why samples are only taken for shorter periods. For example, workers may not remain on one particular task on the day of sampling or commercial pressure and travel time may only allow hygienist a limited opportunity on site. It is difficult to predict the between-laboratory precision in situations, where measurement levels lower than 50µg are expected, because of difficulties in preparing validated replicate samples at very low masses; the lowest loading used in the WASP scheme is 60 µg and error can result if the relationship is extrapolated too far. A model based on an exponential equation suggests that the percentage relative standard deviation (% RSD) of measurements will increase significantly for small changes in the mass measures below 0.05 mg.m^3 and that the analytical precision in many laboratories is likely to exceed the European requirement EN482 [2], that stipulates that the maximum expanded uncertainty of occupational hygiene measurements, including the variation in measurement attributable to the sampling apparatus, must not be greater than ± 30 % (0.5 – 2x exposure limit). This suggests that the absolute error is constant as the mass is reduced below this value and that the analysis is approaching its limit of quantification. As part of HSE's involvement in an International Organisation for Standardisation working group collaborating in this field, data from WASP was supplied to our colleagues in the Occupational Safety and Health Administration (OSHA), who are involved in a project to estimate the precision of measurements using the Horwitz equation [3]. The Horwitz equation is an empirical expectation for the median spread of results based on data obtained from a wide range of collaborative testing programmes in the Association of Official Analytical Chemists in the United States. A linearised version of the Horwitz equation [4] was applied to the WASP data and the predicted percentage variation of results are shown in Figure 1. The values determined from the Horwitz equation are more optimistic than were derived from other studies however they suggest that between 50 – 25 µg the 95 % confidence level of the precision of the measurement, not including sampling, is between 23 – 36 % and confirm the reduced reliability of these measurements at these levels.

Figure 1: % RSD of laboratories in the WASP programme, the predicted fit from the Horwitz-like equation and the 95 % confidence interval of the distributions of % RSD.
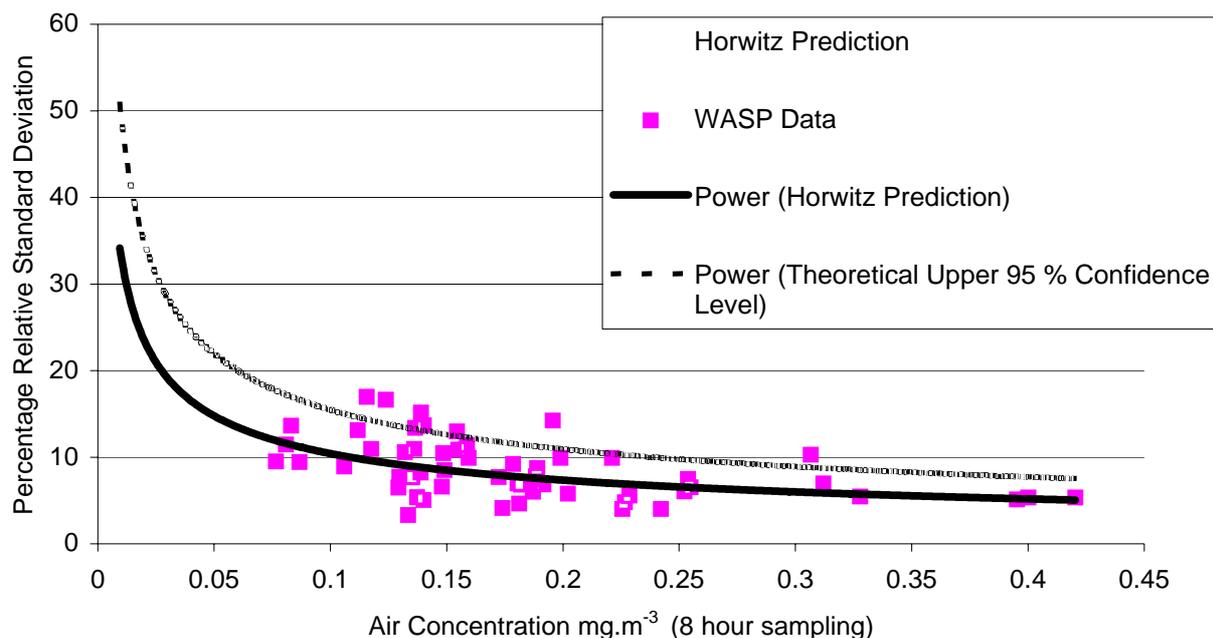
The figure shows that at 0.025 mg.m^{-3} (26 µg) the median precision for 95 % of results is estimated as ± 39 % (10 µg). The results reported by laboratories are likely to range from 16 (close to the expected LOD of 10 µg) to 36µg or 0.030 – 0.068 mg.m^{-3} for a 4 hr sample at 2.2 l/min. If the result is reported at the lower end of the range then the hygienist may conclude that a problem did not exist when further measurements are needed to confirm the situation. The 99 % confidence level would include the LOD. The situation described by the Horwitz model is poorer when:

- Laboratories measure identical samples with interferences. In the Proficiency Analytical Testing (PAT) program, where test samples with interferences are included, the average between-laboratory percentage RSD (~30 %) [5] is twice that found in the WASP program for similar loadings.

- When the other commonly encountered polymorph of silica, cristobalite, is measured the repeated measurement of a single filter containing 23 µg of this material in a single laboratory has a precision of about 41 % RSD when using x-ray diffraction to measure the main 101 reflection [6]. In this situation the 95 % confidence interval of measurements for half shift samples at a proposed WEL of 0.05 mg.m^{-3} will coincide with the confidence interval of measurements at the LOD for cristobalite (~20µg), and so it would be difficult to prove, with repeated measurement on the same sample, the conclusion that the WEL was exceeded. It is important to remember that the WEL is for all forms of RCS and that the quartz polymorph is only the most frequently encountered.

- When half shift (4hr) samples are collected the volume and mass of quartz analysed is half that for a full shift sample and the precision is corresponding poorer.

Individual laboratories may achieve a better within-laboratory precision than is predicted but without participation in proficiency testing they may not necessarily take into consideration any bias.

These issues are of international concern and HSL is involved in work with colleagues in the International Organisation for Standardisation (ISO) working group for silica measurement to agree best practice. A draft standard is almost complete. This international working group also intends to

bring instrument manufacturers together to create a dialogue with them and bring to their attention the need for better instrumentation.

Why not sample more?

The mass collected and measured is limited by the flow rate used to sample the air. The size selector devices used to obtain the respirable size fraction operate at specific flow rates (usually 1.7 – 2.2 l.min^{-1}) so if the WEL is reduced the mass measured at the WEL is also reduced because the size selector cannot sample at a higher rate. The masses measured on a filter at three exposure levels from a size selector, operating at 2.2 l/min, are shown in Table 1.

Table 1: Mass measured of silica measured on the filter		
Exposure Limit mg.m-3	8- hr sample µg	4 – hr sample µg
0.1	106	53
0.05	53	26
0.025	26	13

Newer samplers, such as the GK 2.69, have higher flow rates of 4.2 litres/minute that allow twice the usual sampling volume to be taken and others that use foam pads such as the CIP 10 sampler can use much higher flow rates (10 l.min^{-1}). However, as these samplers produce more heavily loaded filters the samples become opaque to the infrared beam, and matrix and sample absorption effects will increase for x-ray diffraction. The x-ray diffraction technique measures the reflected radiation from the surface of the sample and assumes the dust is deposited as a thin layer. The calibration line starts to leave the linear relationship when about 3 mg of dust is deposited because of the depth or absorption effect. Overloading of the sample is also a problem for other methods including the indirect analysis approach (such as NIOSH 7500 [7]) where the dust is recovered from the air sample filter and deposited onto another filter for analysis. Pre-treatments of the sample may reduce the amount of dust present but they are not always successful. Silicate minerals such as feldspars are insoluble in the strong and potentially hazardous acids that are used and there is always the danger of dissolving the quartz itself.

HSL is working to adapt the GK2.69 for use in short-term sampling and to verify its suitability for the direct on-filter analysis method MDHS 101.

Conclusion

In most situations, the current instrumentation and methods used for the measurement of RCS will not be able to demonstrate compliance if a WEL is established at or below 0.05 mg.m^{-3}. The LODs reported for RCS are not applicable to all matrices and are often optimistic of what is achievable. The evidence suggests that measurements of 0.025 mg.m^{-3} and short term measurement of samples (~ 4 hrs) at the proposed WEL of 0.05 mg.m^{-3} are beyond the limit of what can be reliably measured using the existing methods and techniques; before taking into consideration the additional uncertainty of results because of interferences and the variability of the sampling/instrument environment. The challenge is to develop a system and techniques to support measurement, that would tackle the issues discussed above, with;

- A more flexible approach to the use of different sampling apparatus to suit the dust concentrations,
- The introduction of minimum sampling periods for a working shift in some industries with lower levels of silica in materials.
- The investigation of new software techniques to help measurement to cope with interferences

- The requirement for the participation of laboratories in proficiency testing or accreditation to encourage the consistency of results and to monitor their performance.

The implementation of a lower WEL before measures are in place to support the analysis may lead to a greater ambiguity of results, an inconsistency in their interpretation and a reduction in confidence in the control/enforcement process.

Action

ACTS members are asked to note the information provided in this paper.

References

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