

IH for the CSP 3: Equivalent Exposure of a Mixture Or Constant Pressure Air Sampling

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Abstract

In industry, employees seldom have exposure to one single contaminant. Instead, there is a mixture of contaminants in workroom air. When a number of chemicals attack the same target organ in a similar manner, their effects must be considered additively. Although each contaminant may be well below the permissible exposure limit, PEL, or threshold limit value, TLV, the additive effect of all contaminants combined could be quite hazardous. The equivalent exposure of the mixture, E_m , is calculated to assess the additive effect of chemicals.

Generally the analytical method for different contaminants will not allow them to be collected on the same filter or sorbent tube. Constant pressure mode air sampling allows one pump to draw air through several sorbent tubes simultaneously.

Constant Pressure Mode

Low flow pumps can operate in either of two modes, constant flow, or constant pressure. In the constant flow mode, elements of design in the pump sense changes in the flow rate, and respond to keep the volume flow rate constant even when pressure differentials across the pump may change. In the constant pressure mode, the pump senses the pressure at the outlet of the pump and responds to changes to keep the pressure constant even though the flow rate may change. Medium flow pumps can come with attachable modules to allow sampling at low flow rates. Separate modules are available for constant pressure and constant flow modes.

Constant flow modes provide for the most precise determination of flow rates. That is, the flow rate is most nearly the rate determined by calibration. When one sorbent tube is replaced by another, there will always be some slight difference in the resistance to air flow. Further, as air is drawn through the sampling media it will become loaded and more resistant to flow. The pump, however, while in the constant flow mode, will compensate for these differences, pull harder against the resistance, and the volume flow rate will remain constant.

Low flow pumps operated in the constant pressure mode are not as precise. Slight changes in the resistance to flow will result in slight changes in the flow rate. The constant pressure mode operation is still considered accurate, however. The actual flow rate will sometimes be higher than the calibrated value, sometimes lower, but on the average, the calibrated flow rate will describe flow rates during sampling. The constant pressure mode is said to be less precise only because the flow rate is not as

well tied down. In other words, there is more uncertainty in the actual flow rate when the constant pressure mode is used.



The figure above illustrates the difference between Accuracy and Precision.

The constant pressure mode has one great advantage; the pump may be used to draw air through more than one sorbent tube at a time. Suppose two sorbent tubes were attached to one low flow pump in constant flow mode. As one becomes loaded, or worse clogged, the volume flow rate through that tube lessens or stops. The pump will continue to draw the same total volume flow rate, however. Therefore, the flow rate through the other tube must increase. A relatively small change in the resistance to flow in one sorbent tube could cause a relatively large change in the flow rate through the other. In the constant pressure mode, both sorbent tubes will always have the same pressure differential across them. A change in the resistance to flow in one sorbent tube will have little effect on the other.

Whenever a pump is used to draw air through more than one sorbent tube at a time, the pump must be operated in a constant pressure mode.

The desired flow rate, time of sampling, number of samples, and the required sampling media are determined for each analyte (contaminant being tested) based on the analytical technique as dictated by the laboratory processing the samples, and the time available for sampling. This is done for each analyte separately.

Before calibrating, or measuring the flow rates through the sorbent tubes, the proper operation of the constant pressure mode must be checked. This must be done according to the manufacturer's recommendations. Generally, however, there are two tests to be sure the constant pressure mode is operating properly. First the pressure across the pump (pressure relative to atmosphere at the inlet of the pump) is measured under conditions of no flow. The pump can be attached directly to a pressure measuring device, such as an aneroid barometer, or digital or inclined manometer, or the pump may be attached to the pressure sensing device using a "T" union with the third end closed (or leading to a closed valve). The pressure must be within tolerance of the manufacturer's nominal value. Pressures are usually given in "H₂O, or inches of

water. For example, assume the manufacturer indicates the pressure should be 18 "H₂O and that a deviation of ± 2 "H₂O is allowed. If the pressure reads greater than 20 "H₂O or less than 16 "H₂O the pump has failed the test, and can not be used until the problem is corrected.

The second test is to measure the pressure drop across the pump at some specified flow rate, e.g. 750 cc/min (0.750 lpm). The pump is attached to a pressure sensing device and to a flow restricting valve using a "T" union. The inlet to the flow restricting valve is attached to a volume flow rate calibrator. The valve is slowly opened until the flow rate through the pump is 750 cc/min. As air is allowed to flow through the pump, the pressure across the pump must drop slightly. The pressure across the pump with a flow rate of 750 cc/min may be no further below the pressure drop at no flow than an amount specified by the manufacturer. As an example, suppose the manufacturer indicates that the change in the pressure drop may not exceed 2 "H₂O. If the pressure drop at no flow was observed to be 20.0 "H₂O (just passing the first test) and the pressure at 750 cc/min was observed to be 17.9 "H₂O, the pump has failed and can not be used until the problem is corrected. Notice, even though the pressure across the pump is now very close to the nominal value specified by the manufacturer, the pump failed because the pressure was not "constant" when the load (flow rate) changed.

Once the pump has passed the two tests for constant pressure mode operation, the actual calibration, or setting and measuring of the volume flow rate may be done. The sorbent tube holders are attached together at the base. This is referred to as a parallel configuration because the same air does not flow through any two holders. The set of sorbent tube holders is attached to the pump inlet using an appropriate length of tubing. It is often convenient to number the sorbent tube holders, usually starting with the tube holder closest to the pump. The sorbent tube holder to be used for each contaminant, or analyte, should be clearly recorded on a field worksheet. Sorbent tubes are then placed in the holders for calibration. Care must be taken to be sure the proper sampling media is placed in each tube holder for the analyte to be tested later using that holder.

The set screw on the pump was used only to set the pump speed at a level to drive the constant pressure mode. It may not be used to adjust the actual volume flow rate. The volume flow rate is adjusted for each sorbent tube by a set screw in the base of the sorbent tube holder, usually covered by a knurled cap. The inlet of a single sorbent tube holder is attached to the calibrator. The flow rate is measured and adjusted as necessary. Once the desired flow rate for that sorbent tube is attained, the protective cap is placed over the sorbent tube set screw, the calibrator is removed from the first sorbent tube holder, and is attached to the second. The volume flow rate through the second sorbent tube holder is measured and adjusted as was the first. This process is repeated for all sorbent tube holders in the set.

Because the pressure at the inlet of the pump will vary slightly with volume flow rate (as seen in the constant pressure tests), the flow rate through all sorbent tubes must be set before the final measurement of flow rates is done. After the flow rates of all sorbent

tubes have been set, five readings of volume flow rate are taken for each using the calibrator. The mean, standard deviation, and coefficient of variance are calculated for each sorbent tube. Readings and calculations are recorded on the field worksheets. Care must be taken to associate each set of readings with the appropriate sorbent tube holder. It is often most convenient to use a separate field worksheet for each sample tube holder and staple together worksheets referring to the same pump (and the same employee sampled). Paper is cheap. Mistakes are costly. Be sure to note the target analyte (contaminant to be tested) for the sorbent tube in question on the appropriate worksheet.

For best results, **leave the pump running**. Flow rates can vary significantly from the calibrated value when pumps are turned off after calibration and then turned back on for sampling.

Time-weighted averages, TWA's, are calculated separately for each individual contaminant by,

$$TWA = \frac{C_1 t_1 + C_2 t_2 + C_3 t_3 + \dots + C_n t_n}{t_1 + t_2 + t_3 + \dots + t_n} \quad 1$$

The uncertainty in the time-weighted average concentration, ΔTWA , for each analyte (contaminant) is also calculated,

$$\Delta TWA = SAE (TWA) \quad 2$$

Often, parallel sampling is done for contaminants with additive effects. In an additive effect, two or more chemicals attack the same target organs and cause the same effect. The effect of exposing the employee to the second contaminant in addition to the first is the same as exposing the employee to a higher concentration of the first contaminant alone. If all chemicals had the same effect at the same concentration, determining the additive effect would be easy, concentrations could simply be added.

Different chemicals, however, do not produce the same effect at the same concentration. This is why different chemicals must have different permissible exposure limits, PEL's. Xylene and acetone affect the body in similar ways. Exposure to acetone at 1000 ppm, however, will have little to no effect on most workers, while exposure to xylene at 1000 ppm can very hazardous.

The additive effect of different chemicals is quantified by calculating the equivalent exposure of the mixture, E_m . The equivalent exposure of the mixture is given by,

$$E_m = \frac{TWA_1}{PEL_1} + \frac{TWA_2}{PEL_2} + \dots + \frac{TWA_N}{PEL_N} , \quad 3$$

where TWA_i is the time-weighted average concentration of the i^{th} chemical, and PEL_i is the permissible exposure limit for the i^{th} chemical. It should be observed that the equivalent exposure of the mixture can be calculated based on ceiling concentrations, short term exposure limits (STEL's), or threshold limit values, TLV's, or any other recommended limits, as well as on PEL's.

The equivalent exposure of the mixture can be thought of as the fraction of the allowable exposure represented by the mixed exposure in question. For example, the PEL for acetone is 1000 ppm. If an employee were exposed to acetone at a time-weighted average of 500 ppm, this would represent half, 0.50 or 50%, of the allowed exposure. The PEL for xylene is 100 ppm. If an employee were exposed to xylene at a time-weighted average of 25 ppm, this would represent one quarter, 0.25, of the allowed exposure. These exposures combined represent $0.50+0.25=0.75$, or three quarters of the allowed exposure. The equivalent exposure of the mixture is 0.75 or 75%.

If the equivalent exposure of the mixture is greater than one ($E_m > 1.00$ or 100%), then an overexposure was observed.

The uncertainty in the equivalent exposure of the mixture can be calculated from the uncertainties in the time-weighted averages. When uncertainties add absolutely (not in quadrature), the uncertainty in the equivalent exposure of the mixture, ΔE_m , is given by,

$$\begin{aligned} \Delta E_m &= \frac{\Delta TWA_1}{PEL_1} + \frac{\Delta TWA_2}{PEL_2} + \dots + \frac{\Delta TWA_N}{PEL_N} \\ &= \frac{SAE_1 TWA_1}{PEL_1} + \frac{SAE_2 TWA_2}{PEL_2} + \dots + \frac{SAE_N TWA_N}{PEL_N} , \quad 4 \end{aligned}$$

where ΔTWA_i is the uncertainty in time-weighted average of the i^{th} contaminant, and SAE_i is the standard analytical error for the i^{th} contaminant.

The lower confidence limit for the equivalent exposure of the mixture, LCL, is given by,

$$LCL = E_m - \Delta E_m .$$

There is 95% confidence that the true equivalent exposure of the mixture is above this value. If the lower confidence limit is above one, then it can be stated with confidence that the equivalent exposure of the mixture was greater than one ($LCL = E_m - \Delta E_m > 1.00$ or 100%), and it can be stated with 95% confidence that an overexposure was observed.

The upper confidence limit for the equivalent exposure of the mixture, UCL, is given by,

$$UCL = E_m - \Delta E_m \quad .$$

There is 95% confidence that the true equivalent exposure of the mixture is below this value. If the upper confidence limit is below one, then it can be stated with confidence that the equivalent exposure of the mixture was greater than one ($UCL = E_m + \Delta E_m < 1.00$ or 100%), and it can be stated with 95% confidence that an overexposure was not observed.

Unfortunately, sometimes results are in the undetermined range ($UCL > 1.00 > LCL$) when uncertainties are added absolutely. When this occurs, uncertainties must be added in quadrature. There is no uncertainty in the PEL. The uncertainty in E_m , is therefore given in quadrature by,

$$\begin{aligned} \Delta E_m &= \left[\frac{\Delta TWA_1^2}{PEL_1^2} + \frac{\Delta TWA_2^2}{PEL_2^2} + \dots + \frac{\Delta TWA_N^2}{PEL_N^2} \right]^{1/2} \\ &= \left[\frac{SAE_1^2 TWA_1^2}{PEL_1^2} + \frac{SAE_2^2 TWA_2^2}{PEL_2^2} + \dots + \frac{SAE_N^2 TWA_N^2}{PEL_N^2} \right]^{1/2} \quad . \quad 3 \end{aligned}$$

Notice, uncertainties in the time-weighted averages are **not** calculated in quadrature as you would expect. When different sorbent tube holders are used to sample for the different contaminants, addition of uncertainties in quadrature is rigorously justifiable. When a single sorbent tube is used, but analyzed for multiple chemicals, addition in quadrature is not really justified by sound experimental theory. But it is still the practice in industrial hygiene to do so. Just do it.