COMPUTATIONAL FORMULAS FOR TOTAL RELATIVE STANDARD DEVIATIONS OF COMBINED GRAVIMETRIC-ANALYTIC DETERMINATIONS

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Computational Formulas for Total Relative Standard Deviations of Combined Gravimetric-Analytic Determinations

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ABSTRACT

Many analytical methods require multiple analyses to be done using all or part of the same sample. For a gravimetric sample, this could involve determination of the weight of the sample, as well as further analyses of extractables. In this paper the question of interest is this: if the weight of the sample collected corresponds to the limit of quantitation of the gravimetric determination, what is the magnitude of errors for subsequent determinations, e.g. of extractables. Suppose that relative standard deviations for the determinations of the different components of the measurement process, i.e. for sampling, weighing, and analysis, can be obtained from available data. These values can be used in the formulas presented here to calculate the total relative standard deviations of the determinations, which can then be compared to target relative standard deviations, for example, for assessment of accuracy. An application is given for collection of total aerosol on filters, followed by analysis for solvent extractable material and polycyclic aromatic hydrocarbons.

Introduction

In the typical National Institute for Occupational Safety and Health (NIOSH) analytical gravimetric procedure the mass of aerosol collected is determined by the difference between the pre- and post-sampling weight of the filter. Sometimes the fraction of collected mass that can be extracted by a solvent (e.g., benzene) may also be determined. The filter containing the aerosol sample is washed with the solvent. Then an aliquot of the entire sample wash of the solution containing the solvent extractables is generally placed in a preweighed cup and evaporated to dryness. Following evaporation to dryness, the cup is reweighed and the difference in weights is used to determine the solvent extractables. Sometimes the solvent-extactable fraction is further analyzed by injection of an aliquot into a liquid chromatograph to determine the amount of polycyclic aromatic hydrocarbon (PAH) in the extracted material. This is done by reconstituting all or part of the extracted material in solution for injection into an analytical instrument (generally a liquid chromatograph); alternatively, the mother liquor may be used, if available, for this purpose. A flowchart representing each of these contingencies is shown in Figure 1.

In this paper, we consider the sources of variability, in each of the above determinations, at the limits of quantitation of the aerosol gravimetric procedure. We address how these estimates may be pooled together to obtain an overall estimate of the variability of the entire procedure, including all gravimetric and chromatographic analyses. Included in this estimate is a consideration of the variances of the ratios of these measurements. Upper and lower bounds are provided to take into account uncertainty about the form of

the variance for pump and sampling variability. Bounds on the total variability are obtained that can be used in the assessment of whether 25% accuracy is attained at the limit of quantitation. A practical application of these sources of variability to a "real-world" sampling situation is provided. The formulas presented can be generalized so that they apply when total mass collected is at mass other than the limit of quantitation.

Components of Variability

In order to determine the mass of a particulate aerosol, the following measurements are made (see Figure 1):

a.) The filter is weighed before sampling,

$$m_{tb} = \mu_{tb} + \epsilon_{w,tb} \ , \qquad (1)$$

where m_{tb} denotes the mass determinations on the filter before sampling, determined by weighing. The true mass of the blank filter is μ_{tb} and $\epsilon_{w,tb}$ denotes the error associated with weighing.

b.) The filter is weighed after sampling,

$$m_{t1} = \mu_{tb} + \alpha_t + \epsilon_{p,t} + \epsilon_{s,t} + \epsilon_{w,t1} \ , \qquad (2)$$

where m_{t1} denotes the total mass after sampling, determined by weighing. The true total mass collected by sampling is α_t, and $\epsilon_{p,t}$ and $\epsilon_{s,t}$ are, respectively,

the pump and sampling errors. The difference m_{t1}-m_{tb} estimates the total aerosol mass, as shown in the first row of Figure 1.

c.) Next, the filter is washed to remove extractable material, and an aliquot of the solution is placed in an evaporation cup. It is also possible that the extractable material will be extracted both from a filter and from a sorbent set up in tandem with the filter. This device is weighed initially, yielding $m_{eb} = \mu_{eb} + \epsilon_{w,eb}$, and reweighed after evaporation of the solution of extractables. If all extractable material has been deposited on the evaporation cup, the second weight can be described by

$$m_{e1} = \mu_{eb} + \alpha_e + \epsilon_{p,e} + \epsilon_{s,e} + \epsilon_{w,e1} + \epsilon_{ext,e}. \qquad (3)$$

The difference (m_{e1} - m_{eb}) is a measure of the extractable material. The variance components (subscripted ϵs) have analogous meanings to the components described in b.) above. This description of extractable material is a simplification. In fact, all material may not be extracted from the total mass. Also, since extraction will, in general, add variability to the determination, there could be another component associated with total variability. However, we assume that these components are negligible ($\epsilon_{ext,e}$=0). We will consider the case that only an aliquot of the solution of extractable material will be used in the section, "Correction Factors to Analyze a Fraction of a Sample." Note that Figure 1 allows either of these possibilities, weighing of a portion or of all the extractable material.

d.) An aliquot of solution containing the extractable material is analyzed chromatographically to determine its PAH content. If the liquid sample

containing all of the PAH (after reconstitution from the extractable material) were injected into the chromatograph, then:

$$m_{pah} = \alpha_{pah} + \epsilon_{p,pah} + \epsilon_{s,pah} + \epsilon_{a,pah} + \epsilon_{ext,pah}, \quad (4)$$

where m_{pah} denotes the mass of PAH material, and α_{pah} is the true PAH mass (choice [b] in Figure 1). The component $\epsilon_{a,pah}$ refers to the analytical errors associated with use of the chromatograph. The same comments given in c.) about extraction efficiency and variability apply here. The situation where only a portion of the extracted sample is injected into the chromatograph ([a] in Figure 1) is discussed below ("Correction Factors to Analyze a Fraction of a Sample").

The operations described in c.) and d.) may be performed differently if the amount of extractable material is so small that the entire solution of extractable material must be evaporated to dryness in the evaporation cup. The residue must then be reconstituted into another solution for injection into the chromatograph. This treatment introduces other sources of variability in the present PAH determinations, and also may involve correlation among the errors of measurements of extractable material and of PAHs.

For the above determinations, there are several components of variability, each of which is denoted by ϵ with subscripts. The subscripts beginning with "p" denote variability in a mass determination resulting from variability in the pump flow rate that draws the air sample through the filter. The subscripts beginning with "s" denote variability in mass determination

resulting from sampling variability. This includes variability among samplers or variability associated with use of the same sampler, in either case under the same conditions at which the original sample was taken. The subscripts beginning with "w" denote variability associated with the weighing process. The single subscript beginning with "a" denotes the analytical variability associated with the chromatographic analysis. For each mass determination made above, the different types of error are treated as statistically independent of each other. Thus, the pump errors are treated as statistically independent of the sampling errors, the weighing errors, and the chromatographic errors. Similar assumptions are made about the sampling errors with respect to the other errors, and about the weighing errors and the chromatographic errors. These assumptions seem reasonable, since different instrumentation is required for different functions, whether that be pumping air, sampling material, weighing mass, or making a chromatographic determination. Because of the statistical independence, the variances associated with these different components will add together to form the total, without including a term for covariances among these errors. Although no assumption of normal distribution of the errors is made here, this assumption may be appropriate in many situations. The above assumption that different kinds of error are statistically independent says nothing about correlation between the errors in different fractions of the same sample, say, between the extractable and non-extractable material on the same sample. This is discussed in the following two sections.

In the notation used above, any quantity of the form m_y refers to a measurement either by weighing or by chromatography. It is useful to have another set of variables, x_c, each of which refers to the nonanalytical (non-

weighing and non-chromatographic) component of m_c, after removal of the mean of the blank. Thus,

$$m_{t1} = \mu_{tb} + x_{t1} + \epsilon_{w,t1}.$$

This new set of variables is useful because the sum of the components x_c of the total collected mass is total collected mass, x_{t1}. Such a summation does not apply to the components of m_{t1} or to the components of $(m_{t1} - \mu_{tb})$ because not all components are analyzed individually. In terms of extractables (e) and non-extractables (ne) $x_{t1} = x_e + x_{ne}$, or

$$x_{t1} = (\alpha_e + \alpha_{ne}) + (\epsilon_{p,e} + \epsilon_{p,ne}) + (\epsilon_{s,e} + \epsilon_{s,ne}). \qquad (5)$$

Thus, not only do the means of the components add, but also each type of error adds. An analogous relationship holds for any components of $x_{t1} = x_{c1} + x_{c2}$.

Also, the nature of the sampling variability may be different for the extractable material, compared to the non-extractable sample, since the entire sampling device may consist of drawing the air through a filter followed by a sorbent. The non-extractable material will be collected mostly by the filter, and the extractable (including PAH) may be on both the filter and the sorbent. Some implications of the two-stage collection procedure are mentioned in the section below, "Reasonableness of the Assumption of Constant Pump and Sampling RSDs, and Relation to Correlation of Errors."

It may seem more appropriate to use concentration (mass/unit volume) as the measurement variable in the above models. For instance, the pump variability

leads to error in the amount of air that is drawn through the sampler. Thus, the denominator in the concentration of analyte may differ from that used, based on the assumption of constant flow rate of the pump. However, the variability in the pump flow rate also enters into the mass measurements if these are viewed as mass measurements at a fixed concentration for a fixed period of time. The same is true of the sampling variability.

Assumptions about Variances and Covariances

There are some important differences in the assumptions made concerning the variances that correspond to these different sources. The pump and sampling standard deviations are usually assumed to be a constant fraction of the amount of material collected. Thus, the relative standard deviations (RSD) are usually assumed to be constant, whatever that mass of material is. Thus, $RSD_p(x)$, which denotes the relative standard deviation at a collected mass x because of the pump variation, is assumed to be a constant value, say RSD_p, independent of the mass x. The same assumption is made for RSD_s, which is assumed to have some value RSD_s for any mass. Also, for the analytical variability, such an assumption is made, and the corresponding RSD is denoted by RSD_a. In the next section, the reasonableness of the assumption of constant pump and sampling RSD is discussed.

The variability associated with weighing is different. For small masses of material, the masses m_{tb} and m_{tl} will not differ much. Their standard deviations, $\sigma_w s$, will be approximately constant, since the mass of the filter is so much more than the mass of what has been collected. Thus, the absolute

standard deviation of determination is constant, rather than the relative standard deviation.

Of interest here is the RSD_{wt} associated with determinations at the limit of quantitation (LOQ). The definition of LOQ does not include sources of variability associated with sampling, such as pump or sampling variabilities. According to the NIOSH DPSE Standard Operating Procedure 018 [1], the limit of quantitation (LOQ) "is the lowest mass that can be reported with acceptable precision." The LOQ is the larger of: (a) the mass corresponding to the mean blank signal + 10 * standard deviation of the blank signal, " or (b) the mass above which recovery is >= 75%." For the weighing process only, definition "a" applies. For a blank filter, the signal corresponding to the difference of post- and pre-weighings is $x_{Ba} - x_{Bb}$. The standard deviation of the blank signal will be denoted by σ_{wt}. If the limit of quantitation is assumed to be that mass at which the total analytical precision (RSD) is 10%, then the following relationships apply:

$$\text{mean blank signal} + \text{LOQ} = \text{mean blank signal} + 10\sigma_{wt}, \text{ or}$$

$$\text{std. dev. blank signal} / \text{LOQ} = 1/10$$

and the LOQ is $10*\sigma_{wt}$, the mass corresponding to 10*standard deviation of a blank signal. Notice that the above definitions require adjustment for the mean blank signal, as well as an estimate of the standard deviation of the blank signal. The latter may be obtained in a variety of ways, either as the estimated standard deviation of the differences $(x_{Ba}-x_{Bb})$ from field blanks, or as the standard deviation of $(x_{Ba}-x_{Bb})$, or $\sqrt{2}*\hat{\sigma}_{Bb}$, when the variances of x_{Bb} and of x_{Ba} are assumed to be approximately equal.

We shall be interested in the variability at the LOQ. Define $RSD_{wt} = \sigma_{wt}/\alpha_t$, which is 0.10 for α_t equal to LOQ. For any component mass collected on a filter (true mean α_c) and determined by the differencing technique assumed here, RSD_{wt} $(m_{c1}-m_{cb})$ will be σ_{wt}/α_c, or $RSD_{wt}/(\alpha_c/\alpha_t)=RSD_{wt}/(\alpha_c/LOQ)$ for α_t=LOQ. The above remarks also apply to the masses m_{eb} and m_{e1}, the two weighings of the evaporation cup. It is unclear whether the weighing variance σ^2_{wt} of the filter is equal to that of the evaporation cup (Figure 1). If they are equal, then $RSD_{wt}(m_{e1}-m_{eb})$ equals $RSD_{wt}/(\alpha_e/\alpha_t)$. If the evaporation cup is much heavier than the filter, it may be that the variance of the measured weight of the former is larger than the measured weight of the latter. However, since the filter can absorb moisture from the air and the evaporation cup cannot, this possibility increases the variance of the filter weight relative to that of the evaporation cup. Reference [2] contains work related to filter weighing variability, and the experiment described there could be adapted to study evaporation cup weighing variability. We will denote

$$RSD_{wt}(m_{e1}-m_{eb})=RSD_{wt,cup}/(\alpha_e/\alpha_t)=RSD_{wt,cup}/F_e, \text{ for } F_e=\alpha_e/\alpha_t. \quad (6)$$

Another important difference between the weighing variability and the pump and sampling variability concerns possible correlations in the errors made on determinations on the same filter. Weighings are done at different times, and it is proper to treat the errors in these mass determinations as statistically independent. Although pump, sampling, weighing, and chromatographic errors are assumed to be independent of each other, pump errors on components of the same sample need not be statistically independent. A similar remark applies to sampling errors. The pump errors that affect the m_{t1}, m_{e1}, and m_{pah} determinations from material collected on the same filter are parts of common

pump error terms, through the variables x_{t1}, x_{e1}, and x_{pah}. If the variability in the pump flow rate leads to oversampling, all components of the sample would be expected to be oversampled -- total mass, nonextracted mass, extracted mass, and PAH. An analogous statement is true for the sampling errors if a particular sampler were to collect more than the true average amount of mass. Thus, the pump errors of all determinations on the same filter should be positively correlated with each other. The sampling errors, too, should be positively correlated with each other.

Reasonableness of the Assumption of Constant Pump and Sampling RSDs, and Relation to Correlation of Errors

In this document, the assumption of constant RSD is extended as follows. Suppose that the total mass has several components, say extractable and non-extractable, and that the pump and sampling errors have several components, say, $\epsilon_{p,t}=\epsilon_{p,e}+\epsilon_{p,ne}$, and analogously for the sampling errors. The pump RSD of the total mass is defined by

$$RSD^2_{p,t}=\text{Variance}(\epsilon_{p,t})/\alpha_t^2, \qquad (7)$$

and the RSDs of the components are defined analogously. We will always express the relative variance or relative standard deviation relative to the mean of the component under discussion.

The statistical models used here and the assumption of constant RSD_p and RSD_s have implications for the covariances among the pump errors (and sampling errors) of components of the total mass. The assumption of constant RSD is

equivalent to the assumption that the variance is proportional to α_c^2 for the component c of the total mass. Since

$$\epsilon_{p,t1} = \epsilon_{p,e} + \epsilon_{p,ne},$$

the corresponding equation in terms of variances and covariances is

$$\sigma^2_{p,t1} = \sigma^2_{p,e} + \sigma^2_{p,ne} + 2Cov(\epsilon_{p,e},\epsilon_{p,ne}), \text{ or} \qquad (8)$$

$$\sigma^2_{p,t1}/\alpha_t^2 = (\sigma^2_{p,e}/\alpha_e^2)*F_e^2 + (\sigma^2_{p,ne}/\alpha_{ne}^2)*(1-F_e)^2 + (2/(\alpha_t)^2)*Cov(\epsilon_{p,e},\epsilon_{p,ne}), \text{ or}$$

$$RSD_p^2=RSD_p^2*(1 - 2F_e + 2F_e^2) + (2/\alpha_t^2)*Cov(\epsilon_{p,e},\epsilon_{p,ne}), \text{ where } F_e=\alpha_e/\alpha_t=1-\alpha_{ne}/\alpha_t=1-F_{ne},$$

from which it follows that

$$Cov(\epsilon_{p,e},\epsilon_{p,ne})=\alpha_t^2*(F_e-F_e^2)*RSD_p^2 = \alpha_e*\alpha_{ne}*RSD_p^2, \text{ and}$$

$$Cov(\epsilon_{p,e},\epsilon_{p,t})=Var(\epsilon_{p,e})+Cov(\epsilon_{p,e},\epsilon_{p,ne})=(\alpha_e^2+\alpha_e\alpha_{ne})*RSD_p^2=\alpha_e\alpha_t RSD_p^2.$$

These are the extreme values for the covariance of $\epsilon_{p,e}$ and $\epsilon_{p,ne}$, and of $\epsilon_{p,e}$ and $\epsilon_{p,t}$, since they correspond to correlation 1. Analogous results hold for the sampling errors.

Although positive correlation might be expected between two component errors or between a component error and the whole, correlation 1 is not expected. It seems more reasonable to assume it for the pump errors than for the sampling errors, since sampling errors might affect different aspects of the same sample in different ways. Other assumptions about the variances of the

measurements lead to different results for the covariances. For instance, if the variance of the pump error is assumed constant, regardless of the amount collected, then

$$\sigma^2_{p,t}=\sigma^2_{p,e} + \sigma^2_{p,ne} + 2Cov(\epsilon_{p,e},\epsilon_{p,ne}),$$

or

$$\sigma^2_p=\sigma^2_p + \sigma^2_p + 2Cov(\epsilon_{p,e},\epsilon_{p,ne}), \text{ or } Cov(\epsilon_{p,e},\epsilon_{p,ne})=-\sigma^2_p.$$

Since we might expect pump errors of the components to be positively correlated, this seems to be an unreasonable assumption. Alternatively, if the variance($\epsilon_{p,t}$) is proportional to α_c, then the relationship among the variances becomes :

$$\alpha_t\sigma^2_p= \alpha_e\sigma^2_p + \alpha_{ne}\sigma^2_p + 2Cov(\epsilon_{p,e},\epsilon_{p,ne}), \text{ or } Cov(\epsilon_{p,e},\epsilon_{p,ne})=0.$$

Since it seems reasonable to assume positive correlation between the errors on distinct components, it makes sense to assume that, for whatever mass α_c is collected for component c, the variance($\epsilon_{p,c}$) is proportional to α_c^q, for $1\le q\le 2$. Since the interest here is in concentrations of total mass α_t near the limit of quantitation (LOQ), we will assume $RSD^2_{p,LOQ}=Var(\epsilon_{p,LOQ})/LOQ^2=RSD^2_p$ is a fixed value, whatever the form of the variance($\epsilon_{p,t}$).

When $Var(\epsilon_{p,c}) \propto \alpha_c$, then $Var(\epsilon_{p,c})=\alpha_c LOQ*RSD^2_p$.

When $Var(\epsilon_{p,c}) \propto \alpha_c^2$, then $Var(\epsilon_{p,c})=\alpha_c^2\ RSD^2_p$.

When $Var(\epsilon_{p,c}) \sim \alpha_c^q$, then $Var(\epsilon_{p,c}) = \alpha_c^q LOQ^{2-q} RSD_p^2 = (\alpha_c/LOQ)^q LOQ^2 RSD_p^2$,

$1 \leq q \leq 2$, which is a non-increasing function of q, since $\alpha \leq LOQ$. By making the choice that $\sigma_{p,1}^2 = LOQ\ RSD_p^2$, we find that in order to have positive correlation between $\epsilon_{p,c2}$ and $\epsilon_{p,c3}$ for any of the components c2 and c3 of the total mass, the components ci must satisfy

$$\alpha_{ci}\ LOQ\ RSD_p^2 \geq Var(\epsilon_{p,ci}) \geq (\alpha_{ci})^2\ RSD_p^2,$$

Also, for $1 \leq q \leq 2$, (9)

$$\alpha_{ci}\ LOQ\ RSD_p^2 \geq \alpha_{ci}^q\ LOQ^{2-q}\ RSD_p^2 \geq \alpha_{ci}^2\ RSD_p^2,$$

where the middle member in the above expression results when it is assumed that $Var(\epsilon_{p,ci}) \sim \alpha_{ci}^q$, and $\alpha_{ci} \leq LOQ$ for any component ci of the mass. The above inequalities are useful for placing bounds on the variances of the measurements of interest, for those variance assumptions that are consistent with the covariance assumptions of the errors, when RSD_p is assumed to have a common value at the LOQ, regardless of the form of the variance assumption.

Analogous relationships can be written for the sampling errors, although the correlations among the sampling errors of the components might be expected to be lower than among the pump errors. For instance, the sampling errors associated with dust particles can vary by particle size. Since different components of the same sample may have different particle size distributions, correlations among the errors in the components will probably be less than 1. It may be that the extractable material will be extracted both from material on the filter and from a sorbent set up in tandem with the filter. Since the

same air stream goes through these devices, positive correlation would still be expected, but because separate devices are used, the size of the correlation could be reduced.

Since filters are weighed at different times, it makes sense to regard the weighing errors as statistically independent. To indicate this, we could have written $\epsilon_{w,t1,tt1}$ and $\epsilon_{w,t2,tt2}$, times tt1 and tt2. Therefore, their covariances are 0. Thus, for instance,

$\text{Cov}(\epsilon_{w,t1}, \epsilon_{w,t1}-\epsilon_{w,tb}) = \text{Variance}(\epsilon_{w,t1}) - \text{Cov}(\epsilon_{w,t1}, \epsilon_{w,tb}) = \sigma_w^2$.

Total RSDs - Specification of Variables of Interest

In computing the total relative standard deviations for the different mass determinations for total mass at the LOQ, we must take into account any correlations among the different sources of error. The interest here is in the total RSDs for the following determinations, using notation from the section above, "Components of Variability."

i.) total mass collected at approximately the LOQ.

ii.) mass of extractables when the total mass is near the LOQ.

iii.) ratio of mass of extractables to total mass.

iv.) mass of PAH.

v.) ratio of mass of PAH to total mass.

The standard formula for the RSD of a ratio of random quantities is an approximation based on the linearization obtained from a Taylor series expansion of the ratio[3]. This expression is :

$$RSD^2(x/y) = RSD^2(x) + RSD^2(y) - 2Cov(x,y)/[(\text{average of } x)(\text{average of } y)]. \quad (10)$$

Thus, the ratio of iii.), for the case when all extractable mass is weighed, is $(m_{el} - m_{eb})/(m_{tl} - m_{tb})$, which may be written as:

$[\alpha_e + \epsilon_{p,e} + \epsilon_{s,e} + (\epsilon_{w,el} - \epsilon_{w,eb})]$, divided by

$[\alpha_t + \epsilon_{p,t} + \epsilon_{s,t} + (\epsilon_{w,tl} - \epsilon_{w,tb})]$.

The above formula for the $RSD^2(x/y)$ may be applied to the ratio of iii. This RSD is the total RSD, from all sources of variation, computed at the average values of the different sample segments (nonextractable mass and total mass). The total RSD has three sources, pump variation, sampling variation, and weighing variation. Since the squares of these component RSDs sum to the total RSD^2 for both numerator and denominator, and since the covariance of the total error between numerator and denominator is the sum of the covariances of the sources, and the different components are assumed to be independent of each other, it follows that:

$$RSD^2(\text{mass extracted/total mass}) = \tag{11}$$

$$RSD_p^2(\text{mass extracted}) + RSD_p^2(\text{total mass}) - 2Cov_p(\text{ext, total mass})/[(\alpha_e)\alpha_t]$$

$$+RSD_s^2(\text{mass ext}) + RSD_s^2(\text{total mass}) - 2Cov_s(\text{ext, total mass})/[(\alpha_e)\alpha_t]$$

$$+RSD_{wt}^2(\text{mass ext}) + RSD_{wt}^2(\text{total mass}) - 2Cov_{wt}(\text{ext, total mass})/[(\alpha_e)\alpha_t].$$

From this formula it makes sense to treat the total RSD^2 of the ratio as the sum of the three source RSD^2s. Although no assumption of normality is required here for the measurements of interest, it is useful to note that for ratios of normally distributed data, expected values and variances of these ratios are not defined, since the denominator has a nonzero probability of becoming negative. In practice, if the RSDs of the denominator measurements are relatively small, then the probability of having a negative denominator is also small, and this problem does not seem to be important. (See reference [4] for a pertinent discussion.)

Correction Factors for Analysis of a Fraction of a Sample

As was mentioned in the section "Components of Variability" (items c and d), PAH determinations and extractable mass determinations differ from the total mass determinations, since the former determinations are made on only a portion of the total sample. The measured amount of each is inflated by dividing by the fraction of the target total sample solution that was used.

Thus, PAH determinations are made by chromatographic determinations rather than by weighing. A possible model for the PAH injected into the chromatograph is:

$$m'_{pah}=\alpha'_{pah} + \epsilon'_{p,pah} + \epsilon'_{s,pah} + \epsilon'_{a,pah} + \epsilon'_{sol,pah}, \quad (12)$$

where all terms have analogous meanings to those given for m_{pah}, except that $\epsilon'_{sol,pah}$ includes variability associated with using the portion of the total sample, shown as choice (a) in Figure 1. If the entire sample is used, choice (b) in Figure 1, it does not appear.

For the PAH suppose that $F'_{e,c}$ denotes the target fraction of the extractable solution that was injected into the chromatograph. In fact, this is another source of error, since the actual injected amount probably differs from the target amount by a random value δ. Thus, the PAH determination is given by:

$$m'_{pah}/(F'_{e,c})=$$

$$\alpha'_{pah}/F'_{e,c} + \epsilon'_{p,pah}/(F'_{e,c}) + \epsilon'_{s,pah}/(F'_{e,c}) + \epsilon'_{a,pah}/(F'_{e,c}) + [\epsilon'_{sol,pah}/(F'_{e,c})]. \quad (13)$$

Perhaps ordinarily the analytical and solution sample variability are included together, and assumed to have a constant RSD. This is convenient for the following reason. Let ϵ' denote any of the variance components. Then

$$Var[\epsilon'/(F'_{e,c})] \sim (1/F'_{e,c})^2 * Var(\epsilon'), \text{ when the error } \delta \text{ of the target is small.}$$

If $Var(\epsilon'_p)=(\alpha'_{pah})^q(LOQ)^{2-q}RSD_p^2$ (see Equation 9), then

$$Var[\epsilon'_p/(F'_{e,c})] \sim (1/F'_{e,c})^{2-q}*\alpha_{pah}^q*LOQ^{2-q}*RSD_p^2, \text{ where } \alpha_{pah}=\alpha'_{pah}/F'_{e,c}, \quad (14)$$

and analogously for sampling variability, where the last RSD is the pump RSD associated with the entire sample at the LOQ. In equation 14 ϵ'_p is the same

as ϵ'_{pah} of equation 12. The assumption of q = 2 is the same as constant RSD, which is ordinarily made for the analytical variability. For analytical and solution variability,

$$\mathrm{Var}[(\epsilon_a + \epsilon_{sol})/F'_{e,c}] = RSD_a^2[(\alpha'_{pah})^2/(F'_{e,c})^2] = RSD_a^2(\alpha'_{pah}/F'_{e,c})^2. \qquad (15)$$

Thus, the analytical variability has no dependence on an unknown q because of the assumption of constant RSD.

For the pump and sampling variability, for q = 2, the variance is identical to that for the component ϵ of the variance of m_{pah}, the measurement for PAH if the entire sample had been used in the chromatograph. For the pump and sampling variability, it was observed above that it makes sense to allow the value q to be between 1 and 2. Thus, the variability of these components for the inflation estimate $m'_{pah}/(F'_{e,c})$ could be much higher than the minimum, achieved when q = 2.

An analogous correction should be done for the extractables. Thus, when a target portion F'_e of the solution containing extractables is used, the following model describes the weight determination for extractables:

$$m'_{el} - m'_{eb} = \alpha'_e + \epsilon'_{p,e} + \epsilon'_{s,e} + (\epsilon'_{w,el} - \epsilon_{w,eb}) + (\epsilon'_{sol,e}), \qquad (16)$$

which can be adjusted by the factor F'_e,

$$(m'_{el}-m'_{eb})/F'_e \sim \alpha'_e/F'_e + \epsilon'_{p,e}/F'_e + \epsilon'_{s,e}/F'_e + (\epsilon'_{w,el}-\epsilon'_{w,eb})/F'_e + (\epsilon'_{sol,e}/F'_e),$$

and, thus,

$$\mathrm{Var}(\epsilon'_{p,e}/F'_e) \sim [1/(F'_e)^{2-q}]\alpha_e^q LOQ^{2-q} RSD_p^2, \qquad (17)$$

assuming that error in F'_e is small, and the minimum variance is achieved when q=2. As with the model for PAH, if the entire sample is used, $\epsilon'_{sol,e}$ does not appear. Note that $\epsilon'_{sol,e}$ and $\epsilon'_{sol,pah}$ should be different variables, since they refer to different aliquots of the same solution.

For the calculations, $\epsilon'_{sol,e}$ will be assumed to be small enough that it can be ignored.

The RSD for weighing is different:

$$RSD^2[(\epsilon'_{w,e1}-\epsilon'_{w,eb})/F'_e] = RSD^2_{wt,cup}/(F'_e F''_e)^2, \text{ (see Equation 6 above)} \qquad (18)$$

where $F'_e=\alpha'_e/\alpha_e$ and $F''_e=\alpha'_e/\alpha_t$.

Total RSDs -- Computational Formulas

The formulas presented in the sections i-v below are summarized in Table I. In the table, the total RSD for each variable is broken down into four pieces, pump, sampling, analytical, and weighing variability. These are, respectively, the variables 3,4,5, and 6 in the table. For each variable of interest, bounds are given in the sections below, for the total RSD of that variable. In all cases, these bounds are obtained by taking q=1 for the maximum and q=2 for the minimum, and $1 \leq q \leq 2$.

I.) $RSD^2(\text{total mass})=RSD^2(m_{t1}-m_{tb})$

See the second column of Table I.

$RSD^2(m_{t1}-m_{tb})=(LOQ/\alpha_t)^{2-qp}RSD_p^2 + (LOQ/\alpha_t)^{2-qs}RSD_s^2 + RSD_{wt}^2$,

where $RSD_{wt}^2=\sigma_{wt}^2/\alpha_t^2$ (Section entitled "Assumptions about Variances and Covariances"), and for qp and qs , $1 \leq q \leq 2$, as described above (Equation 9). The relative variances for pump, sampling, and weighing add because of the assumption of statistical independence. Since the interest here is in total mass near the LOQ, the above expression simplifies to:

$$RSD^2(m_{t1}-m_{tb})=RSD_p^2 + RSD_s^2 + RSD_{wt}^2, \text{ where } RSD_{wt}=0.10 \text{ at the LOQ.} \qquad (19)$$

ii.) $RSD^2(\text{ext. mass})=RSD^2(m_{e1}-m_{eb})$

See the third column of Table I.

$$RSD^2(m_{e1}-m_{eb})$$
$$=Var(\epsilon_{p,e})/(\alpha_e)^2+Var(\epsilon_{s,e})/(\alpha_e)^2$$
$$+Var(\epsilon_{w,e1}-\epsilon_{w,eb})/(\alpha_e)^2$$
$$=Var(\epsilon_{p,e})/(\alpha_e)^2+Var(\epsilon_{s,e})/(\alpha_e)^2+RSD_{wt,cup}^2/F_e^2,$$

(See equation 6.) The components for pump, sampling, and weighing variability add because of the assumption of statistical independence.

Also, F_e denotes the fraction of the total mass due to the extractable mass.

$Var(\epsilon_{p,e})=\alpha_e^{qp}\ LOQ^{2-qp}\ RSD_{p,LOQ}^2 = F_e^{qp}\ LOQ^2\ RSD_p^2$

and (See Equation 9)

$RSD_p^2(m_{e1}) = Var(\epsilon_{p,e})/\alpha_e^2=RSD_p^2/F_e^{2-qp}$,

where $1 \leq qp \leq 2$, and its actual value depends upon assumptions about the variances. An analogous equation holds for the sampling error term. Then

$$RSD_p^2/F_e + RSD_s^2/F_e + RSD_{wt,cup}^2/F_e^2 \geq RSD^2(m_{el}-m_{eb}) \geq RSD_p^2 + RSD_s^2 + RSD_{wt,cup}^2/F_e^2. \quad (20)$$

The limits are obtained by replacing qp and qs by either 1 or 2 in the variance expression given above, and F_e is the true fraction of total mass that can be extracted.

These bounds do not take into account analysis of only a portion F_e' of the entire extractable mass. See the fourth column of Table I. To take into account the fraction F_e', we replace F_e above in the RSDs for pump and sampling errors, by $F_e''=F_eF_e'=\alpha_e'/\alpha_t$ (see Equation 17). For the RSD for weighing, we replace F_e by F_eF_e'' (see Equation 18). Thus,

$$(RSD_p^2 + RSD_s^2)/(F_e'') + RSD_{wt,cup}^2/(F_e'F_e'')^2$$
$$\geq RSD^2[(mm_{el}-mm_{eb})/F_e'] \geq RSD_p^2 + RSD_s^2 + RSD_{wt,cup}^2/(F_e'F_e'')^2. \quad (21)$$

iii.) RSD^2(ext. mass/ total mass)$=RSD^2[(m_{el}-m_{eb})/(m_{tl}-m_{tb})]$.

See the fifth column of Table I. The formula given above for the RSD of a ratio is used. Consider RSD_p^2 first, which has the following form, from Equation 10:

RSD_p^2(ext. mass) + RSD_p^2(total mass) - $2Cov_p$(ext. mass, total mass)$/(\alpha_t\alpha_e)$.
The above expression can be written as

$RSD_p^2(m_{e1})+RSD_p^2(m_{t1})-\{2/[\alpha_e(\alpha_t)]*Cov_p(m_{e1},m_{t1})\}$,

in which m_{eb} and m_{tb} do not appear, since there is no pump error associated with these variables. The above expression can be written as

$Var(\epsilon_{p,e})/(\alpha_e)^2 + Var(\epsilon_{p,t})/\alpha_t^2$

$-[2/(\alpha_t\alpha_e)]*[Var(\epsilon_{p,e})+Cov(\epsilon_{p,e},\epsilon_{p,ne})]$,

which can be simplified to

$Var(\epsilon_{p,t})/\alpha_t^2 + (1/\alpha_e)(1/\alpha_e - 2/\alpha_t)Var(\epsilon_{p,e}) - 2Cov(\epsilon_{p,e},\epsilon_{p,ne})/(\alpha_e\alpha_t)$,

$=RSD_p^2+(1-2F_e)(1/F_e)^{2-qp}RSD_p^2 - [RSD_p^2LOQ^{2-qp}/(\alpha_e\alpha_t)](\alpha_t^{qp}-\alpha_e^{qp}-\alpha_{ne}^{qp})$ (See Equations 8&9)

$=RSD_p^2\{1+(1-2F_e)(1/F_e)^{2-qp}-(1/F_e)[1-F_e^{qp}-(1-F_e)^{qp}]\}$ $(\alpha_t=LOQ)$,

which can be shown to be equal to:

$[(1-F_e)/F_e]RSD_p^2\ [(1-F_e)^{qp-1} - (1-F_e^{qp-1})]$, at $\alpha_t=LOQ$ and $1 \leq qp \leq 2$,

which is bounded by $(1-F_e)/F_e\ RSD_p^2$ and 0, when total mass is approximately the LOQ, and F_e is treated as fixed and qp as unknown. An analogous expression holds for the sampling errors.

For RSD_{wt}^2, the weighing errors are taken to be statistically independent.

Thus,

RSD_{wt}^2(ext. mass/total mass)

$=RSD_{wt}^2$(ext. mass)$+RSD_{wt}^2$(total mass)$-[2/(\alpha_t*(\alpha_e)]Cov(\epsilon_{w,t1}-\epsilon_{w,tb},\epsilon_{w,e1}-\epsilon_{w,eb})$

$=RSD_{wt}^2 + RSD_{wt,cup}^2/F_e^2$, (See equation 6 and discussion preceeding it.)

Since all weighing errors are statistically independent, the covariance in the equation above equals 0.

Thus, the bounds for the RSD of the ratio are:

$$[(1-F_e)/F_e]\ (RSD_p^2+RSD_s^2)+(RSD_{wt,cup}^2/F_e^2 + RSD_{wt}^2) \qquad (22)$$

$$\geq RSD^2(\text{ext. mass/total mass}) = RSD^2(\text{Estimated } F_e)$$

$$\geq RSD_{wt,cup}^2/F_e^2+RSD_{wt}^2,$$

for sampling total mass at approximately the LOQ, where $RSD_{wt}=0.10$. The above bounds depend on the unknown value of F_e, and the limits for the pump and sampling errors are obtained by replacing q by 1 for the maxima and by 2 for the minima.

The bounds above do not take into account the analysis of a portion of the extractable mass. See column six of Table I. To take into account analysis of a fraction, replace F_e above, by $F_e''=F_eF_e'$ for the pump and sampling error, and replace F_e for the weighing errors by F_eF_e''. Doing so, we obtain

$$[1-(F_e'')]/F_e''\ (RSD_p^2+RSD_s^2)+[RSD_{wt,cup}^2/(F_eF_e'')^2 + RSD_{wt}^2]$$

$$\geq RSD^2(\text{ext. mass/total mass}) \qquad (23)$$

$$\geq RSD_{wt,cup}^2/(F_eF_e'')^2+RSD_{wt}^2.$$

iv.) $RSD^2(PAH)=RSD^2(m_{pah}'/F_{e,c}')$

See column seven of Table I. From equations 14 and 15,

$$RSD^2(m_{pah}'/F_{e,c}')=[LOQ/(F_{e,c}'*\alpha_{pah})]^{2-q}(RSD_p^2 + RSD_s^2) + RSD_a^2,$$

where the last component is the RSD^2 for the analytical variability, and the pump and sampling components refer to the RSDs for the total mass at the LOQ. It is assumed that the analytical component has constant RSD. This simplifies to the following bounds when the total mass is approximately equal to the LOQ and when $F'_{e,c}=F'_{pah}$:

$$(1/F''_{pah})*(RSD_p^2 + RSD_s^2) + RSD_a^2 \geq RSD^2(m'_{pah}/F'_{e,c}) \geq RSD_p^2 + RSD_s^2 + RSD_a^2. \quad (24)$$

F''_{pah} is the fraction of the total mass at the LOQ which is actually analyzed in the chromatograph, corresponding to the true amount α'_{pah}.

v.) $RSD^2(\text{PAH/ total mass})=RSD^2[(m'_{pah}/F'_{e,c})/(m_{t1}-m_{tb})]$.

See column eight of Table I. Just as for the ratio RSD_p^2(ext. mass/ total mass), this RSD^2 can be written as

$$RSD_p^2(m'_{pah}/F'_{e,c}) + RSD_p^2(m_{t1}-m_{tb}) - 2Cov_p(m'_{pah}/F'_{e,c}, m_{t1}-m_{tb})$$

$$=Var(\epsilon'_{p,pah}/F'_{e,c})/(\alpha_{pah})^2 + Var(\epsilon_{p,t1})/\alpha_t^2 - 2Cov(\epsilon'_{p,pah}/F'_{e,c}, \epsilon_{p,t1})/(\alpha_{pah}\alpha_t),$$

$$=RSD_p^2+(1-2F'_{e,c}F_{pah})RSD_p^2(LOQ/\alpha'_{pah})^{2-qp}-RSD_p^2[LOQ^{2-qp}/(F'_{e,c}\alpha_{pah}\alpha_t)][\alpha_t^{qp}-(\alpha'_{pah})^{qp}-(1-\alpha'_{pah})^{qp}],$$

$$=RSD_p^2\{1+(1-2F'_{e,c}F_{pah})[1/(F'_{e,c}F_{pah})^{2-qp}]-[1/(F'_{e,c}F_{pah})][1-(F'_{e,c}F_{pah})^{qp}-(1-F'_{e,c}F_{pah})^{qp}]\},$$

which can be simplified to

$$RSD_p^2 \{((1-F''_{pah})/F''_{pah}) [(1-F''_{pah})^{qp-1} - (1-(F''_{pah})^{qp-1}]\},$$

where F''_{pah} is that fraction of total mass actually analyzed in the chromatograph which is PAH. The above expression assumes that the remaining part of the total mass may be described by a model similar to the models describing the other components. This expression has a minimum when q=2 and a maximum when q=1, and for total mass approximately equal to the LOQ, the bounds for the RSD^2 of the estimated fraction PAH are:

$$(1-F''_{pah})/F''_{pah}\ (RSD_p^2 + RSD_s^2) + RSD_a^2 + RSD_{wt}^2$$

$$\leq RSD^2[(m'_{pah}/F'_{e,c})/(m_{t1}-m_{tb})] = RSD^2(\text{Estimated } F_{pah}) \qquad (25)$$

$$\leq RSD_a^2 + RSD_{wt}^2,$$

where the bounds depend upon the unknown value of F''_{pah}, $0 \leq F''_{pah} \leq 1$, and $RSD_{wt}=0.10$. Also, it is assumed that the error in $F'_{e,c}$ is very small compared to other sources of error.

The analytical component is contributed only by the PAH determination, and the weighing component only by the total mass component. It is assumed that the analytical component has constant RSD. Also, $RSD_{wt}^2=\sigma_{wt}^2/\alpha_t^2=\sigma_{wt}^2/LOQ^2$.

Application to a Real-World Problem -- Metal Working Fluids (MWF).

Estimation of total method bias for MWF:

Biases are defined relative to sampling conventions concerning ideal sampler operation. Aerosol sampling bias, which should be similar to that in metal working fluids, has been addressed by Bartley et al [5], who report that sampling bias is highly affected by the aerodynamic diameter of the aerosol being monitored. Biases range from +5% to -30% for the 2-mm cyclone filter, for aerosols ranging in aerodynamic particle size from less than 5 to 25 um. Biases are defined relative to sampling conventions concerning ideal sampler operation. Baron et al. [6] have demonstrated a significant bias depending on the orientation of the sampler to the wind. Preliminary reports of ongoing work at Health Safety Executive (London) indicate that sampling efficiencies of most conventionally used aerosol samplers are biased (especially for larger diameter particles) and very dependent upon wind speed [7]. Further research must be completed and published before a firm estimate of aerosol method bias can be obtained.

Determination of Limit of Quantitation(LOQ)

The LOQ can be determined from an estimate of σ_{bb}, the standard deviation of a blank determination, which can be obtained from repetitive weighings of blank filters or filter cassette assemblies. Such values have been reported by several laboratories [8], [9], [10] and are listed in Table II along with the computed values of the LOQ.

The information from sets 1, 3, 6A and 6B were obtained with 6-place (micro) balances. Under certain conditions, the quantitation limits for each of these datasets would support a standard of 0.1 mg/m^3.; however, datasets 1 and 3 were obtained for filters only and may not reflect problems encountered during storage of an entire sampling assembly. For example, datasets 6A and 6B are components of a large dataset provided to NIOSH by MSHA. Both sets were obtained by MSHA using an environmentally-controlled, robotized weighing operation in a dust sample laboratory. The data in set 6A were obtained with the backup pad in place; those in set 6B were obtained with the pad removed. Our evaluation of the two datasets indicate a significant trend (increasing weight) in dataset 6A but no comparable trend in dataset 6B. Thus, under the most optimal weighing conditions (environmental control and complete automation), the backup pad was apparently collecting moisture during storage at room temperature. Any method employed for sampling MWF which includes use of a backup pad (e.g. NMAM method 0500) could be subject to the same storage bias. Thus, bias associated with changes in the weight of blank filters must be adjusted for, before computing the estimated LOQ. Additional problems may be encountered during storage of MWF aerosol on the filters as volatile components of the aerosol evaporate or migrate e.g. to a backup solid sorbent, although this phenomenon may be mitigated by storage at reduced temperatures. Dataset 7 is apparently under consideration for establishment of the lower quantitation limit for the MSHA dust method [11]. However, this dataset overstates the imprecision expected because it compares weights of 300 tamper-proof cassettes obtained with a 5-place balance by the cassete manufacturer to those obtained with a 6-place balance by MSHA. If all MWF aerosol weight determinations were done with the same balance (or balance type) before and after sampling, a lower LOQ would be viable.

Estimation of Total Method Precision:

There are three sampling and analytical contingencies of major concern for sampling MWF. These include sampling aerosol only, determining solvent extractables, and analyzing PAH. It is useful to estimate the maximum imprecision associated with sampling and analysis at the LOQ for each error source. The aim here is the determination of whether measurements made at the LOQ can meet the NIOSH accuracy criterion [1]. This determination can be made by computation of the minimum values of RSDs of interest, according to formulas given in the section above, "Total RSDs -- Computational Formulas."

Potential sources of error for the measurements of interest are pump error, sampling error, weighing error, and chromatographic error. The magnitudes of these sources of imprecision are generally unknown; assumptions must be made to allow for them in establishment of a standard. Generally, the pump precision is assumed to be 0.05. Intersampler variability may be quite large, depending on the orientation of the sampler to the airstream, particle size, static particle charge, and wind velocity [3,4, 5, 6,]. For example, Bartley et al.[3] have demonstrated an intersampler variabilty ranging from 2 to 10 % for the 2-mm cyclone filter. In addition, a 10% intersampler variabilty because of charge effects in the 10-mm cyclone filter has been reported [8]. Other sources of variability have also been discussed [9]. Although the issue of intersampler variability remains to be settled, an upper limit for this parameter of approximately 0.10 appears to be reasonable.

For aerosol sampling only, the analytical imprecision at the LOQ is assumed to be entirely due to the gravimetric analysis and is established to be less than

or equal to 0.10 at the LOQ. Pooling all sources of analytical and sampling variability enables computation of a maximum RSD_T of 0.15 for aerosol sampling only at the LOQ. (See row 2 of Table III, which uses Formula (19): $(0.05^2 + 0.10^2 + 0.10^2)^{.5} = 0.15$.)

It may be appropriate to determine the solvent-extractable mass, especially if the filter contains both nuisance dust as well as MWF. Extractables are removed by washing the filter in an appropriate solvent; an aliquot of this extract is then delivered to a tared container. The solvent is then evaporated to dryness and the mass difference determined. As is shown in equation 20, the percent extracted, F_e, affects the precision. For the calculations shown in Table III, it is assumed that $RSD_{wt,cup}=RSD_{wt}$. (See discussion preceeding equation 6.) We have considered the effect on the overall RSD for three situations, where the fraction extracted corresponds to 10, 50 and 90% of the total mass sampled. The total RSDs for these three possibilities are shown in row 3 of Table III. For instance, for $F_e=0.9$, the calculated total RSD for all extractables is $(0.05^2 + 0.10^2 + 0.11^2)^{.5}=0.158$, according to the minimum value given by equation (20). For the estimated fraction of mass extracted relative to total mass, the total RSD is no lower than 0.15, even for $F_e=0.90$. This is shown in row 4 of Table III, where $RSD_T=RSD_w=(0.10^2+0.10^2/.9^2)^{.5}$, according to the minimum value provided by equation (22). For this minimum value all contributions from the sampling and pump errors disappear in the computation of the minimum total RSD, a consequence of the assumption of constant RSD for pump and sampling variability.

For analysis of PAHs, the precision of the overall analytical procedure will also be affected by the precision of recovery of the PAHs from the collection media and the precision of analysis of the PAHs of interest. Method 5506 [10] reports RSDs for analysis of 15 individual PAHs ranging from 0.02- 0.13. In order to estimate an analytical precision for a "group" PAH method, these estimates have been pooled to yield an overall precision estimate of 0.063. This means that the overall analytical method error (RSD_T) of the group PAH method alone could be as high as 0.13, i.e. if neither of the weighing procedures affects the method precision. (In row 5 of Table III, the minimum value from equation (24) is used to obtain the total RSD equal to $(0.05^2+0.10^2+0.063^2)^{0.5}$, or 0.128.) If the PAH content is expressed as mass PAH/total mass sampled, then the weighing precision will enter into the estimate of the overall precision. Even for high recovery, e.g. 90%, method imprecision could be no lower than 0.12. (In row 6 of Table III, the minimum value from equation (25) is applied to yield $0.118=(0.10^2 + 0.063^2)^{0.5}$.)

NIOSH requirements for an acceptable sampling and analytical method are that 95% of all samples collected must fall within +/- 25% of the true mean or standard value, accounting for both bias and imprecision within the sampling method [1]. For a method having zero bias, the maximum tolerated RSD is 0.128. The NIOSH precision criteria would marginally be met for sampling and analysis of the group PAHs only relative to the total aerosol. For all other sampling and analytical method scenarios, these criteria would not be met. It is important to remember that for all of the measurements that require weighings, there is a minimum value of 0.10 associated with weights at the LOQ.

Summary

These calculations indicate that RSD estimates depend upon the assumptions made for the different components of the total variance. Lower confidence limits on the total RSDs are useful, since they are generally relatively large compared to the RSDs required to meet the NIOSH 25% accuracy criterion. A fuller discussion would provide the upper bounds on the total RSDs. Application is provided here to a real-world gravimetric-analysis situation in order to demonstrate the utility of this approach.

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Table I:Summary of Formulas,True Total Mass at LOQ (Section "Total RSDs,Computational Formulas," Parts i-v)

Variable	Total Mass (Part i)	Extracted Mass, All Extracted (Part ii)	Extracted Mass, Portion Extracted (Part ii)	Ratio: Extracted/ Total, All extracted (Part iii)	Ratio: Extracted/ Total, Portion extracted (Part iii)	PAH (Part iv)	PAH, as Fraction of Total (Part v)
1.Measurement	$m_{t1}-m_{tb}$	$m_{e1}-m_{eb}$	$(m'_{e1}-m'_{eb})/F'_e$	$(m_{e1}-m_{eb})$ $/(m_{t1}-m_{tb})$	$(m'_{e1}-m'_{eb})$ $/[F'_e(m_{t1}-m_{tb})]$	$m'_{pah}/F'_{e,c}$	$(m'_{pah}/F'_{e,c})$ $/(m_{t1}-m_{tb})$
2.True Mean	α_t=LOQ	α_e	$\alpha_e=\alpha'_e/F'_e$	$\alpha'_e/\alpha_t=F_e$	$\alpha_e/\alpha_t=F_e$	α_{pah}	$\alpha_{pah}/\alpha_t=F_{pah}$
3.RSD_p^2: Pump RSD_p^2 for Total Mass at LOQ.	RSD_p^2	RSD_p^2	$(1/F''_e)^{2-qp}$ $*RSD_p^2$	$[(1-F_e)/F_e]RSD_p^2*$ $[(1-F_e)^{qp-1}-1$ $+F_e^{qp-1})]$	$(1/F''_e-1)*RSD_p^2$ $*[(1-F''_e)^{qp-1}$ $-1+(F''_e)^{qp-1}]$	$(F''_{pah})^{qp-2}$ RSD_p^2, $F''_{pah}=\alpha''_{pah}/\alpha_t$	$(1/F''_{pah}-1)*RSD_p^2$ $*[(1-F''_{pah})^{qp-1}$ $-1+(F''_{pah})^{qp-1}]$
4.RSD_s^2: Sampling RSD^2 for Total Mass at LOQ.	RSD_s^2	RSD_s^2	$(1/F''_e)^{2-qs}$ $*RSD_s^2$	$[(1-F_e)/F_e]RSD_s^2$ $*[(1-F_e)^{qs-1}-1$ $+F_e^{qs-1})]$	$(1/F''_e-1)*RSD_s^2$ $[(1-F''_e)^{qs-1}$ $-1+(F''_e)^{qs-1}]$	$(F''_{pah})^{qs-2}$ RSD_s^2	$(1/F''_{pah}-1)*$ RSD_s^2 $*[(1-F''_{pah})^{qs-1}$ $-1+(F''_{pah})^{qs-1}]$
5.RSD_a^2: Analytical RSD^2						RSD_a^2	RSD_a^2
6.$RSD_{\alpha t}^2$: RSD^2 for Weighing for Total Mass at LOQ	$RSD_{\alpha t}^2=\sigma_{\alpha t}^2/\alpha_t^2$	$RSD_{\alpha t,cup}^2/F_e^2$	$RSD_{\alpha t,cup}^2$ $/(F_eF''_e)^2$, $F''_e=\alpha'_e/\alpha_t$	$RSD_{\alpha t,cup}^2/F_e^2$ $+RSD_{\alpha t}^2$	$RSD_{\alpha t,cup}^2$ $/(F'_eF''_e)^2$ $+RSD_{\alpha t}^2$		$RSD_{\alpha t}^2$
7.Covariance of pump or samp. errors in m_{c1} &m_{c2}, for $m_{t1}=m_{c1}+m_{c2}$.		$Cov(e_{p,e},e_{p,ne})$ $=.5LOQ^{2-qp}RSD_p^2$ $*(\alpha_t^{qp}-\alpha_e^{qp}-\alpha_{ne}^{qp})$. Likewise for sampling errors.	Cov $(e'_{p,e}/F'_e,e_{p,nee})=$ $.5LOQ^{2-qp}RSD_p^2/F'_e$ $*[\alpha_t^{qp}-(\alpha'_e)^{qp}-(1-\alpha'_e)^{qp}]$. Likewise for sampling errors.			Cov $(e'_{pah}/F'_{e,c},e_{npp})=$ $LOQ^{2-qp}\ RSD_p^2/F'_{e,c}$ $*.5[\alpha_t^{qp}-$ $(\alpha'_{pah})^{qp}-$ $(1-\alpha'_{pah})^{qp}]$. Likewise for samp.	

Remarks:

a.) Formulas above assume α_t=LOQ.
b.) For a ratio (x/y), $RSD^2(x/y) \sim RSD^2(x) + RSD^2 - 2Cov(x,y)/((\text{mean } x)(\text{mean } y))$
c.) Exponents qp and qs used in RSD_p^2 and RSD_s^2 satisfy $1 \leq q \leq 2$.
d.) The terms F_e', $F_{e,c}'$, F_e'', F_{pah}'', used when a portion of a component is extracted, are functions of either the actual mass of extractables or of PAHs analyzed.
e.) $e_{p,nee}$ denotes pump errors for the nonextractable plus extractables not weighed. e_{npp} denotes pump error for the non-PAH plus PAH not injected into the chromatograph.

TABLE II

				Mean STD Dev $\bar{S}D$ -µg-			Minimum Supportable Standard mg/m³ @ 2L/min, 8-hr shift
SET	FILTER TYPE	n	Ref	Balance 6-pl	5-pl	LOQ est[3] ug	2
1	DM-800(PVC-ACRN)	20	(8)	4.8	--	68	0.07
2	DM-800(PVC-ACRN)	20		--	20.9	296	0.31
3	GFF/A	20		5.7	--	80.6	0.08
4	GFF/A	20		--	21.2	300	0.31
5	Al Cassette	4		--	26.4	373	0.39
6	MSHA dust[1] cassette weighings	65/46d	(9)				
	a. combined within and between day			5.5	--	77.8	0.08
	b. subset combined within and between day	10/31d		4.2	--	59.4	0.06
7	MSHA dust[2] cassette weighings (between laboratory)	300/2mo	(10)	20.5		290	0.30

DM 800 = Gelman polyvinylchloride acrylonitrile filter-
GFF = glass fiber filter type A.

1. Data provided by MSHA and re-evaluated by NIOSH; includes 75 MSA samplers studied for 40 d; Due to evident weight gain by the backup pad during storage, the backup pad was removed from 10 of these samplers to obtain the information in the subset shown.
2. Data provided by and worked up by MSHA; samples originally weighed on 5-pl balance by cassette supplier and 6-pl balance by MSHA.
3. LOQ = 10* $\sqrt{2}$ * (standard deviation of an individual weighing)

TABLE II CONTINUED

Given the problems that may be encountered during sampling and analysis of MWF (including storage), a conservative lower estimate of the weighing precision is appropriate. Dataset 6A has been selected for establishment of this LOQ since it includes within- and between-day error as well as imprecision associated with weighing of an entire sampling assembly. The weighing precision obtained for this dataset, 9.1 ug, corresponds to an LOQ of 129 ug and agrees reasonably well with the LOQ of 100 ug cited for the NIOSH nuisance dust method 0500 [2]. Given an LOQ of 129 ug, the lowest supportable standard would be 0.09 mg/m^3 ; however, since the methodology must be accurate at 0.5 X the REL, the lowest feasible standard is 0.2 mg/m^3. If it is necessary to sample the vapor phase, where flowrates may be restricted to 1.0 L/min, the lowest feasible standard would be approximately 0.5 mg/m^3. Moreover, these levels may not be realistic, since they do not take into account the many sources of bias and imprecision, e.g., pump error, discussed below.

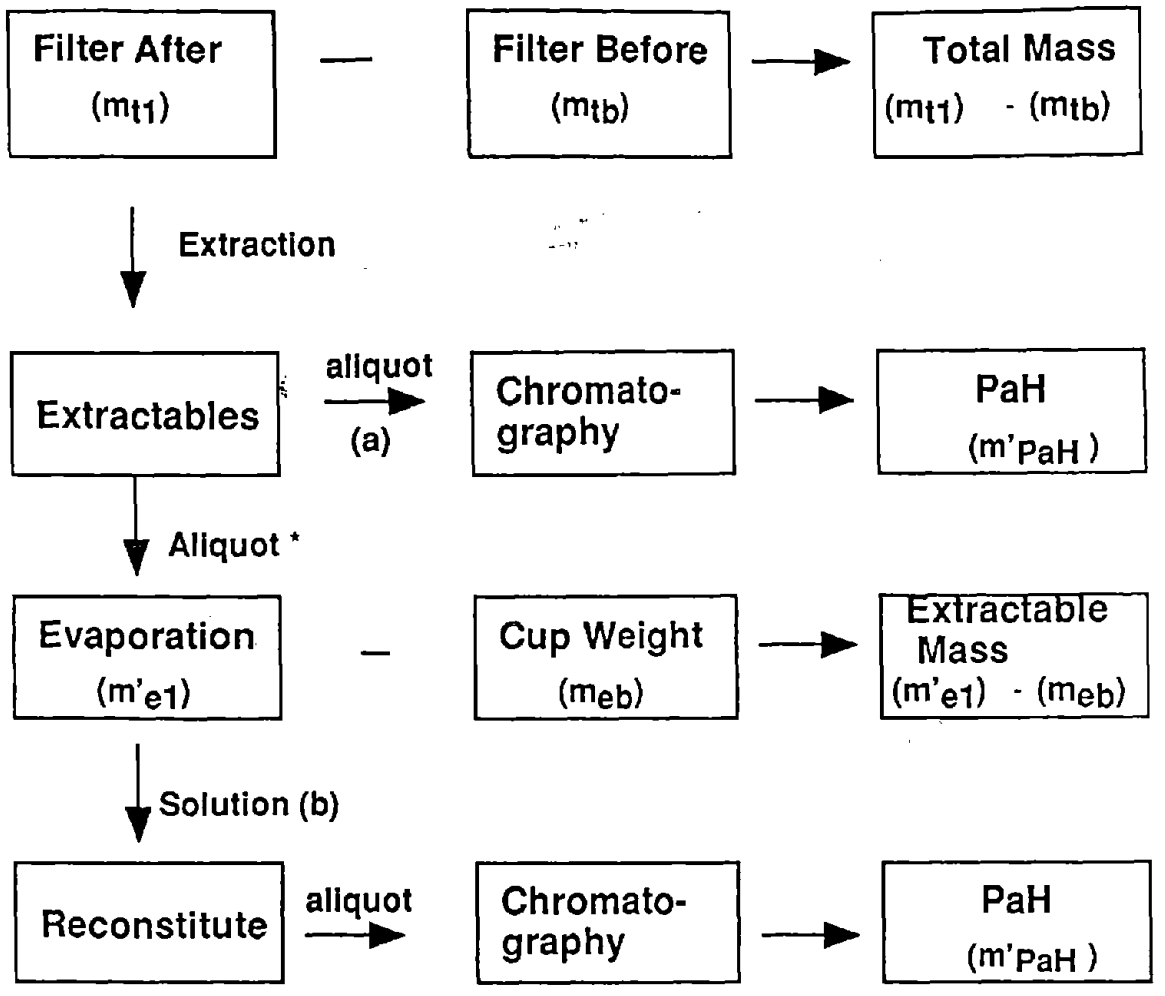

Figure 1. Flowchart Summary of Gravimetric/Analytical Operations Considered. Above, (a) and (b) provide two alternative means of determining the PaH: either (a) based on an aliquot of the the total solution or (b) re-constitution of the entire sample of extractables and subsequent use of an aliquot of the re-constituted sample. The symbol (aliquot) * indicates that either an aliquot of the extractables solution may be used in the evaporation cup or that the entire solution may be used . Thus, two options are indicated for extractables as well.