TECHNICAL APPENDIX D

COEFFICIENTS OF VARIATION AND ACCURACY REQUIREMENTS FOR INDUSTRIAL HYGIENE SAMPLING AND ANALYTICAL METHODS

The relative variation of a normal distribution (such as the randomly distributed errors occurring in industrial hygiene sampling and analytical procedures) is commonly described by the *coefficient of variation* (*CV*). The *CV* is also known as the *relative standard deviation* (*RSD*). The *CV* is a useful index of dispersion in that limits computed from the true mean of a set of data plus or minus twice the *CV* will contain about 95% of the data measurements. Thus, if an analytical procedure with a *CV* of 10% is used to repeatedly measure some constant physical property (such as the concentration of a chemical in a beaker of solution), then about 95% of the measurements will fall within plus or minus 20% (2 times the *CV*) of the true concentration.

The accuracy required of airborne concentration measurements in the proposed OSHA health standards takes into account (1) random variations in the sampling device (repeatability of the sampling device), (2) random variations in the analytical procedure (repeatability of the replicate analyses of a given sample), (3) systematic errors in the sampling method (determinate errors or bias in the collection technique), and (4) systematic errors in the analytical procedure (determinate error or bias in the analysis).

The term *accuracy* in the proposed OSHA health standards and in this Manual refers to the difference between a measured concentration and the true concentration of the sample. Thus, it includes both the random variation of the method about its own mean (commonly referred to as precision) and the difference between the average result from the method and the true value (commonly referred to as the bias of the method). The term accuracy does not refer to the difference between a measured concentration and the true employee exposure. There are additional considerations that affect the difference between a measured airborne concentration and the true employee exposure. These include sampler location in relation to the breathing zone of the employee and sampling strategy of exposure measurement — both numbers of samples and duration. (Refer to Chapter 3.)

The proposed OSHA health standards state that the accuracy of a method shall have a *confidence level of 95%*. This means that 95% of the measurements must be as accurate as the standard requires. If one assumes the method is unbiased and errors are normally distributed, the *CV* (or relative standard deviation) can be used to judge if the method has the required accuracy. The *CV* in percentage units is defined as the standard deviation of the method, times 100, divided by the true value. The required *total coefficient of variation* (CV_T) of the sampling and analytical method is obtained by dividing the required accuracy by 1.96 (statistical standard normal deviate for 95% two-sided confidence limits, also referred to as *z*-value). Typical required CV_T's would be:

Concentration	*Required accuracy (plus or minus)*	*Required* CV_T
Above permissible exposure	25%	< 12.8%
At or below the permissible exposure and above the action level	35%	< 17.9%
At or below the action level	50%	< 25.5%

The statistical decision techniques in Chapter 4 utilize CV_T. Table D-1 lists some CV_T's for specific NIOSH sampling and analytical procedures. If a specific method is not listed for

TABLE D-1. TOTAL COEFFICIENTS OF VARIATION FOR SOME SPECIFIC NIOSH SAMPLING/ANALYTICAL PROCEDURES

Air contaminant	CV_T	NIOSH method number
Acetic anhydride	0.06	S170
Acetone	0.08	S1
Acetonitrile	0.07	S165
Acetylene tetrabromide	0.10	S117
Acrylonitrile	0.07	S156
Allyl alcohol	0.11	S52
Allyl chloride	0.07	S116
Alpha-methyl styrene	0.05	S26
n-Amyl acetate	0.05	S51
sec-Amyl acetate	0.07	S31
Antimony and compounds (as Sb)	0.09	S2
Arsenic and compounds (as As)	0.06	S309
Arsine	0.06	S229
Asbestos	0.24-0.38	P&CAM239
Barium, soluble compounds	0.05	S198
Benzyl chloride	0.10	S115
Beryllium and beryllium compounds (as Be)	0.06	S339
Butadiene	0.06	S91
2-Butanone	0.07	S3
2-Butoxyethanol	0.06	S76
Butyl acetate	0.07	S47
sec-Butyl acetate	0.05	S46
tert-Butyl acetate	0.09	S32
Butyl alcohol	0.07	S66
sec-Butyl alcohol	0.07	S53
tert-Butyl alcohol	0.08	S63
n-Butyl glycidyl ether	0.07	S81
p-tert-Butyltoluene	0.07	S22
Calcium oxide	0.06	S205
Camphor	0.07	S10
Carbaryl (Sevin)	0.06	S273
Carbon tetrachloride	0.09	S314
Chlorinated camphene	0.08	S67
Chlorobenzene	0.06	S133
Chlorobromomethane	0.06	S113
Chlorodiphenyl (54% chlorine)	0.06	S121
Chloroform	0.06	S351
Chromic acid and chromates	0.08	S317
Chromium, metal, and insoluble compounds	0.08	S352
Chromium, soluble chromic, and chromous salts (as Cr)	0.08•	S323
Copper dusts and mists	0.05	S186
Cresol (all isomers)	0.07	S167
Cumene	0.06	S23
Cyanide (as Cn)	0.10	S250
Cyclohexane	0.07	S28
Cyclohexanol	0.08	S54
Cyclohexanone	0.06	S19
Cyclohexene	0.07	S82
Diacetone alcohol	0.10	S55
Diazomethane	0.08	S137
Dibutyl phthalate	0.05	S33
o-Dichlorobenzene	0.07	S135
p-Dichlorobenzene	0.05	S281
1, 1-Dichloroethane	0.06	S123
1, 2-Dichloroethylene	0.05	S110
1, 1-Dichloro-1-nitroethane	0.05	S213
Diethylamine	0.07	S139
Di-2-ethylhexylphthalate	0.06	S40
Difluorodibromomethane	0.09	S107
Diisobutyl ketone	0.07	S358
Dimethyl acetamide	0.07	S254
Dimethylamine	0.06	S142
Dimethylaniline	0.05	S164
Dimethyl formamide	0.06	S255
Dioxane	0.05	S360
Dipropylene glycol methyl ether	0.06	S69
di-sec-Octyl phthalate (see di-2-ethylhexylphthalate)		
Epichlorohydrin	0.06	S118
2-Ethoxyethylacetate	0.06	S41
Ethyl acetate	0.06	S49
Ethyl acrylate	0.05	S35
Ethyl alcohol	0.06	S56
Ethyl benzene	0.04	S29
Ethyl bromide	0.05	S106
Ethyl butyl ketone	0.09	S16
Ethyl ether	0.05	S80
Ethyl formate	0.08	S36
Ethyl sec-amyl ketone (see 5-methyl-3-heptanone)		
Ethyl silicate	0.06	S264
Ethylamine	0.11	S144
Ethylene chlorohydrin	0.08	S103
Ethylene dichloride (1, 2-dichloroethane)	0.08	S122
Ethylene glycol dinitrate and/or nitroglycerin	0.10	S216
Ethylene oxide	0.10	S286
N-ethylmorpholine	0.10	S146
Glycidol	0.08	S70
Heptane	0.06	S89
Hexachloronaphthalene	0.06	S100
Hexane	0.06	S90
2-Hexanone	0.05	S178
Hexone (methyl isobutyl ketone)	0.06	S18
Hydrazine	0.09	S237
Hydrogen bromide	0.07	S175
Hydrogen chloride	0.06	S246
Hydrogen fluoride (HF)	0.06	S176
Hydrogen sulfide (aqueous)	0.12	S4
Isoamyl acetate	0.06	S45
Isoamyl alcohol	0.08	S58
Isobutyl acetate	0.07	S44
Isobutyl alcohol	0.07	S64
Isophorone	0.06	S367
Isopropyl acetate	0.07	S50
Isopropyl alcohol	0.06	S65
Isopropylamine	0.07	S147
Isopropyl glycidyl ether	0.07	S77
Ketene	0.06	S92
Lead and inorganic lead compounds	0.07	S341
LPG (liquefied petroleum gas)	0.05	S93
Magnesium oxide fume	0.06	S369
Manganese and compounds (as Mn)	0.06	S5
Mesityl oxide	0.07	S12
Methyl acetate	0.06	S42
Methyl acrylate	0.07	S38
Methyl alcohol	0.06	S59
Methyl (n-amyl) ketone	0.07	S1
Methyl "Cellosolve"	0.07	S79
Methyl "Cellosolve" acetate	0.07	S39
Methyl chloroform (1, 1, 1-trichloroethane)	0.05	S328
Methyl cyclohexane	0.05	S94
5-Methyl-3-heptanone	0.10	S13

TABLE D-1. TOTAL COEFFICIENTS OF VARIATION FOR SOME SPECIFIC NIOSH SAMPLING/ANALYTICAL PROCEDURES (cont.)

Air contaminant	CV_T	NIOSH method number
Methyl iodide	0.07	S98
Methyl isoamyl acetate	0.06	S37
Methyl isobutyl carbinol	0.08	S60
Methyl isobutyl ketone (see Hexone)		
Methyl methacrylate	0.13	S43
Methylal (dimethoxymethane)	0.06	S71
alpha-Methylstyrene	0.05	S26
Molybdenum, soluble compounds	0.09	S193
Monomethyl aniline (N-methylaniline)	0.09	S153
Morpholine	0.06	S150
Naphtha, coal tar	0.05	S86
Naphthalene	0.05	S292
Nickel, metal and soluble compounds (as Ni)	0.06	S206
Nicotine	0.07	S293
Nitrobenzene	0.06	S217
p-Nitrochlorobenzene	0.10	S218
Nitrotoluene	0.06	S223
Octachloronaphthalene	0.07	S97
Octane	0.06	S378
Ozone (alkaline MI)	0.08	S8
Parathion	0.08	S295
Pentane	0.05	S379
2-Pentanone	0.06	S20
Petroleum distillate (naptha)	0.05	S380
2-Pentyl acetate (see sec-amyl acetate)		
Phenol	0.07	S330
Phenyl ether	0.07	S72
Phenyl ether-biphenyl mixture	0.09	S73
Phenylglycidyl ether	0.06	S74
Phenylhydrazine	0.06	S160
Phosphoric acid	0.06	S333
Phthalic anhydride	0.09	S179
Platinum, soluble salts	0.06	S191
Propane	0.05	S87
n-Propyl acetate	0.06	S48
Propyl alcohol	0.08	S62
Propylene dichloride	0.06	S95
Propylene oxide	0.08	S75
n-Propyl nitrate	0.05	S227
Pyridine	0.06	S161
Rhodium, metal fume and dust	0.08	S188
Rhodium, soluble salts	0.07	S189
Selenium compounds	0.09	S190
Stoddard solvent	0.05	S382
Styrene	0.06	S30
Sulfuric acid	0.08	S174
Tellurium	0.06	S204
Tellurium hexafluoride	0.05	S187
Terphenyls	0.10	S27
1, 1, 1, 2-Tetrachloro-2, 2-difluoroethane	0.07	S131
1, 1, 2, 2-Tetrachloro-1, 2-difluoroethane	0.05	S132
1, 1, 2, 2-Tetrachloroethane	0.06	S124
Tetrahydrofuran	0.06	S78
Tetranitromethane	0.08	S224
Tetryl	0.06	S225
Thallium, soluble compounds (as Tl)	0.06	S306
Tin, inorganic compounds except oxides	0.06	S185
Titanium dioxide dust	0.11	S385
o-Toluidine	0.06	S168
Tributyl Phosphate	0.08	S208
1, 1, 2-Trichloroethane	0.06	S134
Trichloroethylene	0.08	S336
1, 2, 3-Trichloropropane	0.07	S126
1, 1, 2-Trichloro-1, 2, 2-trifluoroethane	0.07	S129
Trifluoromonobromethane	0.06	S125
Triorthocresyl phosphate	0.07	S209
Triphenyl phosphate	0.07	S210
Turpentine	0.05	S88
Vinyl chloride	0.08	—
Vinyl toluene	0.06	S25
Xylidine	0.06	S162
Yttrium	0.05	S200
Zirconium compounds (as Zr)	0.05	S185

a chemical, then the general coefficients of variation in Table D-2 may be used with care. Tables D-1 and D-2 apply only to laboratories with adequate maintenance and calibration facilities for sampling equipment (such as pumps) and a quality control program for the analytical laboratory.

The CV_T's in Table D-1 were reported by the NIOSH Measurement Research Branch and obtained from NIOSH Contract CDC-99-74-45, Laboratory Validation of Air Sampling Methods Used to Determine Environmental Concentrations in Work Places, June 26, 1974 to July 30, 1976. Additional work in this area was performed by Reckner and Sachdev (D-1) under NIOSH Contract HSM 99-72-98.

TABLE D-2. GENERAL COEFFICIENTS OF VARIATION FOR SOME SAMPLING/ANALYTICAL PROCEDURES

Sampling/analytical procedure	CV	Data sources*
Colorimetric detector tubes	0.14	A
Rotameter on personal pumps (sampling only)	0.05	B
Charcoal tubes (sampling/analytical)	0.10	C
Asbestos (sampling/counting)	0.24-0.38	D
Respirable dust, except coal mine dust (sampling/weighing)	0.09	E
Gross dust (sampling/analytical)	0.05	E

*Data source references

A. Leidel, N. A., and K. A. Busch: Statistical Methods for the Determination of Noncompliance with Occupational Health Standards, NIOSH Technical Information, HEW Pub. No. (NIOSH) 75-159, Cincinnati, Ohio 45226, 1975.

B. NIOSH Engineering Branch estimate of typical calibrated pumps capable of the range 1.5 to 3.0 lpm.

C. Conservative estimate by the authors. Recent work under NIOSH Contract CDC-99-74-45 have shown typical CV_T's (precision only) of 0.05 to 0.09 for charcoal tubes.

D. Leidel, N. A., S. G. Bayer, R. D. Zumwalde, and K. A. Busch: USPHS/NIOSH Membrane Filter Method for Evaluating Airborne Asbestos Fibers, NIOSH Technical Information Report, Cincinnati, Ohio 45226 (to be published, 1977).

E. NIOSH Engineering Branch estimate based on the use of pumps in the flow range 1.5 to 3.0 lpm and a collected mass of at least 1.0 milligram.

If an analytical coefficient of variation different from that given in Tables D-1 and D-2 is available from a laboratory, it is better to use a computed total coefficient of variation. It is important to realize that CV's are not directly additive, but that the CV_T increases as the square root of the sum of the squares of component CV's. In general there are only two component CV's: the CV_P for the sampling pump and the CV_A for the analytical method. Thus, the CV_T would be calculated from

$$CV_T = \sqrt{(CV_P)^2 + (CV_A)^2}$$

where

CV_P = pump CV, generally taken as 0.05
CV_A = analytical CV

Example:

Charcoal tubes were used to sample for acetone and were taken to a local laboratory for analysis. The laboratory reported that its CV_A for acetone on charcoal tubes was 0.09. The CV_T is calculated as

$$CV_T = \sqrt{(0.05)^2 + (0.09)^2} = 0.10$$

Another example dealing with coal mine dust samples was given by Leidel and Busch (D-2).

REFERENCES

D-1. Reckner, L. R., and J. Sachdev: Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents. NIOSH Technical Information, HEW Pub. No. (NIOSH) 75-184, Cincinnati, Ohio 45226, 1975.

D-2. Leidel, N. A., and K. A. Busch: Comments — Statistical Methods for Determination of Noncompliance. American Industrial Hygiene Association Journal, 36:839-840, 1975.