

VC MONITORING - OTHER

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-Has nothing to
do with PVC
or VC
- after 1975

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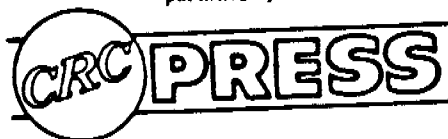


Evaluation of Ambient Air Quality by Personnel Monitoring

*- Has nothing to
do with PVC
or VC
- after 1975*

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manganese, aluminum, iron, titanium, nickel, zinc, silicon, sulfur, sodium, calcium, bromine, chlorine, potassium, and copper. Samples were collected on Millipore membrane filters which were dissolved in acetone in preparation for analysis. Calibration curves were developed using external standards and taking into account the variation in spectral response as the dust layer thickness varies. Background (blank) corrections were included. Standard samples for quantitative emission spectroscopy were prepared by mixing spectroscopically pure oxides of the elements with Ringsdorff graphite and gallium oxide as an internal standard. An aliquot of the centrifuged particulate was also mixed with the graphite-gallium oxide standard. Comparison of the two methods indicated X-ray fluorescence was a valid technique for direct analysis of dusts.^{49c}

Nondispersive X-ray fluorescence analysis has been applied to lead and bromine aerosols collected in downtown Berkeley, California. The technique employed was nondestructive to the filter paper collection medium and required only 2 min/analysis. The equipment was easily rendered portable and could be carried in the field. The ratio of bromine/lead appeared to be significantly different from location to location.^{49d}

3. Neutron Activation

Although rather elaborate equipment for activating and nuclear decay counting is required, the extreme sensitivity and reliability of this direct approach justifies consideration. By means of gamma ray spectrometry and computer techniques, sodium, manganese, chlorine, vanadium, aluminum, bromine, copper, and indium can be determined simultaneously. Polytetrafluoroethylene (PTFE) filters were particularly well suited for sample collection (lowest chlorine content).^{49e} An even greater number of elements that can be detected by this technique were described recently by Gray and his co-workers.^{49f}

2. Cascade Collectors — Respirable Fraction

Probably the best presentation of "respirable" dust sampling and the physiological basis for the selection of appropriate filtration devices was presented by Morton Lippmann⁵⁰ for the interim "Guide for Respirable Mass Sampling" prepared by the AIHA Aerosol Technology Committee⁵² and later included in the ACGIH's *Air Sampling Instruments for Evaluation of Atmospheric Con-*

taminants.¹ Excerpts which follow are presented by permission of the copyright holder.

a. Sampling for Respiratory Hazard Evaluation

Air sampling techniques have been used to obtain information for a variety of purposes. The discussion to follow concerns the specific purpose of sampling for the evaluation of the toxicological insult arising from the inhalation of airborne particles. Air sampling techniques used to obtain information for other purposes, e.g., performance testing of ventilation systems and air cleaners, contamination monitoring in so-called "white" or "clean" room operations, and for basic scientific studies of atmospheric reactions, composition, and capacity for pollutant dispersion may differ, and are beyond the scope of this discussion.

If the objective is to obtain information on the nature and magnitude of the potential health hazard resulting from the inhalation of airborne particles, the techniques must be capable of providing data on the contaminant concentration within the size range which reaches the critical organ for toxic action. In other words, the choice of methods must be based on a recognition of the size-selecting characteristics of the human respiratory tract, in addition to the usual parameters affecting the selection of methods, e.g., the physical limitations of the collection process, and the sensitivity and specificity of the analytical procedures.

There has been an increasing recognition of the importance of the selective sampling of respirable dust in recent years, after decades in which the size-selecting characteristics of the human respiratory tract were largely ignored. The only standard method which provided a means for discriminating against non-respirable particles was the impinger sampling-light field counting technique for pneumoconiosis producing dusts. The Greenburg-Smith impinger, developed in 1922-25 through the cooperative efforts of the U.S. Bureau of Mines, U.S. Public Health Service, and the American Society of Heating and Ventilating Engineers,¹ and the midjet impinger, developed in 1928 by the Bureau of Mines,² efficiently collect particles larger than about $\frac{1}{2}$ micron in a liquid medium. The samples are analyzed by counting the particles which settle to the bottom of a wet counting cell and are visible when viewed through a 10X objective lens. Particles larger than 10μ observed during the count are rejected by many industrial hygienists as "non-respirable." In the alternative approach of gravimetric analysis of the total airborne particulate sample, there is no practical way to discriminate against the oversized particles.

b. Regional Deposition, Clearance, and Dose

The hazard from airborne particles varies with their physical, chemical and/or biological properties. These properties will determine the fate of the particles and their interactions with the host after they are deposited. A basic consideration is that this fate in any given individual varies greatly with the site of deposition within the respiratory tract.

There are a number of major subdivisions within the

and documentation for the "Interim Guide on 'Respirable' Mass Sampling"¹ of the AIHA Aerosol Technology Committee.

i. Measurement of Mass Concentrations within Size Graded Aerosol Fractions

Since the dose from inhaled toxicants is dependent on the regional deposition, which is dependent on particle size, the best dose estimates for a material whose toxicity is proportional to absorbed mass can be derived from a knowledge of the mass concentrations within various size ranges. Such information can be obtained in several ways: (1) by separating the aerosol into size fractions corresponding to anticipated regional deposition during the process of collection; (2) by making a size distribution analysis of the airborne aerosol, e.g., with a confuge, cascade impactor, light scattering aerosol spectrometer, etc.; and (3) by making a size distribution analysis of a collected sample.

The most reliable information can be obtained using methods in which the aerosol is fractionated on the basis of aerodynamic diameters in much the same manner as it is fractionated within the respiratory tract. Thus, differences in particle shape and density are automatically compensated for.

Light scattering instruments which sort the pulses resulting from the scattered light from individual particles can provide information on the distribution of airborne particle diameters. In converting this information to a size-mass distribution, an average particle density must be assumed. Furthermore, the accuracy of the diameter distribution is dependent on the particle shape, index of refraction and surface roughness. For example, Whitby and Vomela report that for India Ink particles, which absorb light and have a rough surface, the indicated size was 1/2 to 1/5 of the true size for the three different instrument designs tested.

Further opportunities for error arise when the size distribution analysis is performed on collected samples. It is almost impossible to examine the sample in the original state of dispersion. Thus, particles which were unitary in the air may be analyzed as aggregates and vice versa.

% Deposition -	10	20	30	40	50	60	70	80	90	100
Diam. (μ) -	2.2	3.2	3.9	4.5	5.0	5.5	5.9	6.3	6.9	7.1
(for spheres of unit density)										

U.S. Atomic Energy Commission (AEC) - A second standard, established in January 1961 at a meeting sponsored by the AEC Office of Health and Safety,² defined "Respirable Dust" as that portion of the inhaled dust which penetrates to the non-ciliated portions of the lung. This application of the concepts of respirable dust and concomitant selective sampling was intended only for

Furthermore, particles analyzed by microscopy will be graded by a linear dimension or by projected area diameter, and these are normally larger than the true average diameter.

j. Standards and Criteria for Respirable Dust Samples

British Medical Research Council (BMRC) - In 1952, the British Medical Research Council adopted a definition of "respirable dust" applicable to pneumoconiosis producing dusts. It defined respirable dust as that reaching the alveoli. The BMRC selected the horizontal elutriator as a practical size selector, defined respirable dust as that passing an ideal horizontal elutriator, and selected the elutriator cut-off to provide the best match to experimental lung deposition data. The same standard was adopted by the Johannesburg International Conference on Pneumoconiosis in 1959.

In order to implement these recommendations, it was specified that:

1. For purposes of estimating airborne dust in its relation to pneumoconiosis, samples for compositional analysis, or for assessment of concentration by a bulk measurement such as that of mass or surface area, should represent only the 'respirable' fraction of the cloud.
2. The 'respirable' sample should be separated from the cloud while the particles are airborne and in their original state of dispersion.
3. The 'respirable fraction' is to be defined in terms of the free falling speed of the particles, by the equation $C/C_0 = 1 - f/f_c$, where C and C_0 are the concentrations of particles of falling speed f in the 'respirable' fraction and in the whole cloud, respectively, and f_c is a constant equal to twice the falling speed in air of a sphere of unit density 5μ in diameter.

A sampling device which meets these requirements would have a sampling efficiency vs. size curve suggested by Davies.³ It is illustrated in Figure II.5 and defined as follows:

"insoluble" particles which exhibit prolonged retention in the lung. It was not intended to include dusts which have an appreciable solubility in body fluids and those which are primarily chemical intoxicants. Within these restrictions, "respirable dust" was defined as follows (Figure II.7):

Particle Size vs. Respirability

Size* (μ)	10	5	3.5	2.5	2
% Respirable -	0	25	50	75	100

*Sizes referred to are equivalent to an aerodynamic diameter having the properties of a unit density sphere.

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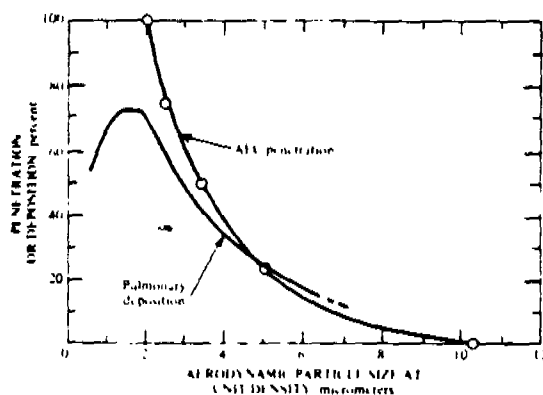


FIGURE II.7. Aerodynamic particle size at unit density - respirable mass deposition curve. (From Lippmann, M., *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*, 4th ed., ACGIH, Cincinnati, O., 1972. With permission.)

American Conference of Governmental Industrial Hygienists (ACGIH) - The application of respirable dust

"1. for respirable dust in mg/M^3 :

$$\frac{10 \text{ mg}/\text{M}^3}{\% \text{ Respirable Quartz} + 2}$$

Note: Both concentration and % Quartz for the application of this limit are to be determined from the fraction passing a size-selector with the following characteristics:

Aerodynamic Diameter (μ) (unit density sphere)	2.0	2.5	3.5	5.0	10
% Passing Selector	90	75	50	25	0

"2. for 'total dust' respirable and nonrespirable:"

$$\frac{30 \text{ mg}/\text{M}^3}{\% \text{ Quartz} + 3}$$

For both cristobalite and tridymite: Use one-half the value calculated from the count or mass formulae for quartz."

It can be seen that the size-selector characteristic specified in the ACGIH standard is almost identical to that of the AEC, differing only at 2μ , where it allows for 90% passing the first stage collector instead of 100%. The difference appears to be a recognition of characteristics of real particle separators. For practical purposes, the two standards may be considered equivalent.

The proposed mass concentration limits were obtained by a comparison of simultaneous impinger and size-selective samples collected in the Vermont granite sheds.¹⁰ Since the original impinger sampling and microscopic particle counting standards were based on epidemiological investigations which had been performed 3 to 4 decades earlier in some of the same granite cutting sheds, it was possible to make a valid comparison of "respirable" mass and particle count.

sampling concepts to other toxic dusts and the relations between respirable dust concentrations and accepted standards such as the ACGIH Threshold Limit Values (TLV's) are more complicated. Unlike the MPC's for radioisotopes, which are based on calculation, most TLV's are based on animal and human exposure experience. Thus, even if the data on which these standards were based could be related to the particle size of the dust involved, which unfortunately is unlikely, there would probably be a different correction factor for each TLV, rather than a uniform factor such as 0.25.

Despite the enormity of the task of establishing alternative or revised TLV's based on "respirable" dust concentrations, ACGIH has made a start. At the annual meeting in St. Louis, Missouri on May 13, 1968, ACGIH announced¹¹ in their "Notice of Intended Changes" alternate mass concentration TLV's for quartz, cristobalite and tridymite (three forms of crystalline free silica) to supplement the TLV's based on particle count concentrations. For quartz, the alternative mass values proposed are

The U.S. Department of Labor has adopted the ACGIH size-selector criteria for respirable dust and extended its application to coal dust and inert or nuisance dust. In their revised Safety and Health Standards for Federal Supply Contracts published in the Federal Register,¹² the ACGIH quartz, tridymite, and cristobalite were adopted along with the following respirable dust limits:

Coal Dust (Respirable fraction less than 5% SiO_2)	$2.4 \text{ mg}/\text{M}^3$ or $\frac{10 \text{ mg}/\text{M}^3}{\% \text{ SiO}_2 + 2}$
Inert or Nuisance Dust Respirable Fraction	15 MPPCF or $5 \text{ mg}/\text{M}^3$ (30 MPPCF or $10 \text{ mg}/\text{M}^3$) ¹³

Discussion of standards for respirability - Basically, there are two sampler acceptance curves described in the preceding discussion, and they have similar, but not identical characteristics. This is illustrated in Figure 11.5. The shapes of the curves differ because they are based on different types of collectors. The BMRC curve was chosen to give the best fit between the calculated characteristics of an ideal horizontal elutriator and lung deposition data, while the AEC curve was patterned more directly after the Brown, et al.⁶⁰ upper respiratory tract deposition data and is simulated by the separation characteristics of cyclone type collectors. In most field situations, where the geometric standard deviation (σ_g) of the particle size distribution is greater than two, samples collected with instruments meeting either criterion will be comparable. For example, Mercer calculated the predicted pulmonary (alveolar) deposition according to the ICRP Task Group deposition model⁶¹ for a tidal volume of 1450 cm³ and aerosols with $1.5 < \sigma_g < 4$. He found that a sampler meeting the BMRC acceptance curve would have about 10% more penetration than a sampler meeting the AEC curve.⁶²

The goal of obtaining air concentration data related to health hazard can be approached in several ways. For "insoluble" dusts, two-stage samplers consisting of a pre-collector, with a cut-off characteristic like that of the upper respiratory tract, and an efficient second stage can provide the desired information with minimal sampling and analytical effort. For other toxic materials, or for aerosols where the contaminant of interest is a minor mass constituent, it may be necessary to obtain the overall size-mass distribution in order to determine the mass concentration in different size ranges appropriate to the sites of toxic action.

Since the "respirable" dust standards outlined in the preceding section were intended for "insoluble" dusts, most of the samplers developed to satisfy their criteria have been relatively simple two-stage devices. In recent years, multi-stage samplers designed to simulate deposition within more restricted subdivisions of the respiratory tract have been developed. These and other multi-stage samplers will be discussed in the sections to follow.

k. Two-Stage "Respirable" Dust Samplers

A two-stage respirable dust sampler consists of a first stage whose collection efficiency falls from very high to very low as the aerodynamic particle size decreases from 10 to 2 μ , and a second stage with high collection efficiency for all particle sizes. Horizontal elutriators and cyclones have been most widely used as first stage collectors, while filters have been used as the second stage in most two-stage samplers.

Cyclones... can be operated in any orientation without significant change in their collection characteristics.⁶³ The only precaution necessary is to avoid turning them upside down during or after sampling, which could cause dust from the cyclone to fall onto the filter or out through the inlet. This independence of orientation, combined with their smaller physical size at comparable flowrates, are [sic] among the reasons that most of the recent two-stage personal sampler designs have been built around miniature cyclones as the pre-collectors. These

samplers, combined with filter collectors as the second stage and newly developed miniature battery powered air pumps are small and light enough to be worn throughout a work shift.

Most of the miniature battery powered pumps are diaphragm or piston type air movers and therefore produce a pulsating flow. This would appear to render them unsuitable for pulling air through pre-collectors whose collection characteristics are flowrate dependent. The BCIRA cyclone of Higgins and Dewell⁶⁴ is equipped with a pulsation damper in order to overcome this problem. However, the problem may not be as severe as it appears at first glance, at least for those applications when the parameter of interest is the "respirable" mass measured on the second stage. Knight and Lichti⁶⁵ have demonstrated that variations in airflow are corrected to some extent by changes in cyclone collection efficiency. For non-fibrous test aerosols, including mica and silica, there was essentially no change in the mass collected on the filter for flowrates between 1.3 and 2.65 lpm. As the flowrate increases, the aerosol mass entering the cyclone increases proportionally, but so apparently does the collection efficiency. In an elutriator, the effect would be the opposite; an increase in sampling rate would result in an increase in penetration to the filter.

Many of the cyclone pre-collectors were initially calibrated using polydisperse test aerosols of irregularly shaped particles. The curves of collection efficiency vs. size, published by Lippmann and Harris⁶⁶ and Hyatt, et al.,⁶⁷ were determined from the comparison of the particle size distribution analyses of up and downstream samples made by optical microscopic measurements. More recent calibrations using spherical test aerosols or irregular particles with measured terminal settling velocities have indicated that the diameters were overestimated in the original calibrations.

For example, the 10 mm nylon cyclone described by Lippmann and Harris⁶⁶ as having collection characteristics closely matching the AEC acceptance curve at 2.8 lpm, has been recalibrated by Sutton,⁶⁸ and Knuth,⁶⁹ Tomb and Raymond⁷⁰ and Ettinger and Royer.⁷¹ Sutton, using polydisperse lacquer spheres whose terminal settling velocity distributions he measured with a Timbrell⁷² spectrometer before entering and after penetrating the cyclone, reported that the cyclone matched the AEC curve at 2.0 lpm. Knuth used monodisperse polystyrene latex and ferric oxide spheres whose terminal settling velocities were measured with an elutriator tube,⁷³ and reported that to meet the AEC criteria the flowrate should be 1.4 lpm. Tomb and Raymond⁷⁰ used a test aerosol of polydisperse coal dust and analyzed up and downstream samples for particle size distribution with the Coulter Counter. They report that the penetration curve obtained at 2.0 liters most closely approximated the AEC criteria. Ettinger and Royer⁷¹ used a monodisperse aerosol of a 4:1 methylene blue:uranine mixture. They found that the collection characteristics matched the AEC criteria at 1.7 lpm. They also showed that the application of a shape factor correction to the Tomb and Raymond data⁷⁰ made that data consistent with their own. Knight and Lichti⁶⁵ compared the penetration of a variety of test aerosols through elutri-

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Adrian L. Linch has recently retired from E.I. du Pont de Nemours and Company as laboratory supervisor for the industrial hygiene and clinical laboratories of the medical division at Chambers Works in Deepwater, New Jersey.

Mr. Linch holds a bachelor's degree in chemical engineering (1933) and a master's degree in biochemistry (1934) from the University of Denver.

During his 39-year career with du Pont, Mr. Linch conducted research and development in such areas as the manufacture of dyes, dye intermediates, rubber chemicals, organic mercurials, tetraethyl lead, fluorocarbons, stabilization of aromatic amines, and the design of laboratory glassware. In addition to the medical laboratories, his career has included supervision of a Manhattan project laboratory for a plant producing fluorocarbons and uranium derivatives.

In 1952 he entered full-time practice in industrial hygiene. Biological monitoring procedures for the control of exposure to the cyanogenic aromatic nitro and amino compounds were developed under his supervision; personnel monitoring programs for alkyl lead and mercury derivatives, asbestos, radiation, silica-bearing dusts, and carbon monoxide also were established. Additional specialties involved development of air sampling and analysis techniques, design of personnel monitoring equipment, and protective clothing.

Mr. Linch is a member of the American Chemical Society, the American Industrial Hygiene Society, and the American Academy of Industrial Hygiene, and is a Fellow of the American Association for the Advancement of Science and the Franklin Institute.

Mr. Linch's bibliography includes over 70 publications. In addition to *Evaluation of Ambient Air Quality by Personnel Monitoring*, he has also written *Biological Monitoring for Industrial Chemical Exposure Control* for CRC Press.

OCCUPATIONAL SAFETY AND HEALTH

GENERAL INDUSTRY STANDARDS



UNITED STATES DEPARTMENT OF LABOR
W. J. Usery, Jr., Secretary
Occupational Safety and Health Administration

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General Industry



January 1, 1976

OSHA Safety and Health
Standards (29 CFR 1910)

U.S. Department of Labor
Occupational Safety and Health Administration

OSHA 2206
(Revised January 1976)

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- has nothing
to do w/ health
effects
- as to where
this came from
& the date

desorption process. Desorption efficiency should be determined on the same batch of charcoal tubes used in sampling. Results indicate that desorption efficiency varies with loading (total vinyl chloride on the tube) particularly at lower values, i.e., 2.5 ug.

- 8.5-2 Procedure for determining desorption efficiency. Charcoal tubes from the same batch as that used in obtaining samples are used in this determination. A known volume of vinyl chloride gas is injected into a bag containing a known volume of air. The bag is made of Tedlar (or a material which will retain the vinyl chloride and not absorb it) and should have a gas sampling valve and a septum injection port. The concentration of the bag may be calculated at room temperature. The known volume is then sampled through a calibrated sampling pump. At 1 liter, the bag is sampled in this manner. These tubes are used in the same manner as the samples. Samples taken with a gas tight syringe are also injected into the GC. The concentration is compared to the standards.

The desorption efficiency is calculated by dividing the average weight of the blank divided by the weight of the vinyl chloride standard.

Desorption efficiency

The difference between the weight of the blank and the weight of the vinyl chloride standard is the weight of the vinyl chloride standard.

Weight on blank standard gas mixture

- has nothing to do w/ health effects - as to where this came from & the date

9. Calibration and Standard

CAUTION: Laboratory Operations Involving Carcinogens

Vinyl chloride has been identified as a human carcinogen and appropriate precautions must be taken in handling this gas. Specifically, the Occupational Safety and Health Administration has promulgated regulations for the use and handling of vinyl chloride. The regulations currently serve as an emergency standard and may be found in 29 CFR 1910.93q (Section 1910.93q in Title 29 of the Code of Federal Regulations available in the Federal Register, Vol. 39, No. 125, Thursday, June 27, 1974.) Note that the above is an emergency standard (temporary) and will be replaced by a permanent standard in October of 1974.

A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in ug/1.0 ml versus peak area. There are two methods of preparing standards and as long as highly purified vinyl chloride is used, both are comparable.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations of the FID response.

9.1 Standard Preparation

Gravimetric Method - Vinyl chloride is slowly bubbled into a tared 10-ml volumetric flask containing approximately 5 ml of toluene. After 3 minutes, the flask is again weighed. A weight change of 100-300 mg is usually observed. The solution is diluted to exactly 10 ml with carbon disulfide and is used to prepare other standards by removal of aliquots with different sized syringes. Subsequent dilution of these aliquots with carbon disulfide results in a series of points that are linear from the range of 0.2 nanograms per injection, the minimum detectable amount of vinyl chloride, to 1.5 micrograms per injection.

Volumetric Method - A 1-ml gas sample of pure vinyl chloride is drawn into a gas-tight syringe and the tip of the needle is inserted into a 10-ml volumetric flask containing approximately 5 ml of CS₂. The plunger is withdrawn slightly to allow the CS₂ to enter the syringe. The action of the vinyl chloride dissolving in the CS₂ creates a vacuum and the syringe becomes filled with the solvent. An air bubble (~2%) is present and was found to be due to the void volume in the needle of the syringe. The solution is returned to the flask and the syringe is rinsed with clean CS₂ and the washings added to the volumetric. The volumetric is then filled to the mark with CS₂. Other standards are then prepared from this stock solution.

Standards are stored in a freezer at -20°C and are found to be stable at this temperature for three days. Tight-fitting plastic tops on the volumetrics seem to retain the vinyl chloride better than ground glass stoppers.

10. Calculations

10.1 The weight, in μg , corresponding to each peak area is read from the standard curve for vinyl chloride. No volume corrections are needed, because the standard curve is based on $\mu\text{g}/1.0\text{ ml}$ CS₂ and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct } \mu\text{g} = \mu\text{g}_s - \mu\text{g}_b$$

where:

μg_s = μg found in front section of sample tube

μg_b = μg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.
- 10.4 This total weight is divided by the determined desorption efficiency to obtain the total μg per sample.
- 10.5 The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T+273}$$

where:

V = volume of air in liters at 25°C and 760 mm Hg

V_s = volume of air in liters as measured

P = Barometric pressure in mm Hg

T = Temperature of air in degree centigrade

- 10.6 The concentration of the organic solvent in the air sampled can be expressed in mg/m^3 , which is numerically equal to $\mu\text{g}/\text{liter}$ of air

$$\text{mg}/\text{m}^3 = \mu\text{g}/\text{l} = \frac{\text{total } \mu\text{g (Section 10.4)}}{V_s}$$

- 10.7 Another method of expressing concentration is ppm, defined as μl of vinyl chloride/liter of air

$$\text{ppm} = \mu\text{l of vinyl chloride}/V_s$$

$$\text{where: } \text{ppm} = \frac{\mu\text{g of vinyl chloride}}{V_s} \times \frac{24.45}{62.5}$$

24.45 = molar volume at 25°C and 760 mm Hg

62.5 = molecular weight of vinyl chloride

11. References

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