ABSTRACT

LEO MICHAEL BLADE. The efficiency of aqueous sodium bisulfite as a collection medium for formaldehyde, using the midget impinger and varying sampling conditions, and the development of a vapor generation system for use in the study. (Under the direction of AVRAM GOLD, PH.D.)

Currently, the most popular method for the collection of atmospheric samples of formaldehyde, known as the chromotropic acid method (and published by the National Institute for Occupational Safety and Health [NIOSH] as NIOSH Method 3500), includes the use of an impinger containing aqueous sodium bisulfite. A review of the literature indicated that the documentation of the collection efficiency for this method is limited to only a few combinations of air-flow rate, sampling time, and airborne formaldehyde concentration, and the consequent normal sampling time is about 1 hr. This study evaluated the collection efficiency across wide ranges of these factors for the purpose of extending the useful range of the method. A laboratory apparatus was developed that can precisely generate known airborne formaldehyde concentrations ranging from 0.4 to 6.4 ppm, and this generation apparatus was used to conduct the study. Very good collection efficiency, averaging 96%, was found across a wide range of each of the three factors varied in the study. Specifically, flow rates between 0.1 and 1 L/min, sampling times between 1 and 4 hr, and concentrations between 0.4 and 6.4 ppm were determined to provide good collection efficiency. An exception to this statement is that for the combination of long sampling times and high concentrations, a statistically significant trend of declining efficiency was detected; however, it was not determined what physical significance the latter finding held.

TABLE OF CONTENTS

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DEDICATION

To my wife, Leslie

I. INTRODUCTION

Formaldehyde, the simplest member of the family of hydrocarbon compounds known as aldehydes (3), is a colorless, flammable gas with a strong, pungent odor (136). It has a molecular weight of 30.05 (134), its chemical structure is $\begin{matrix} H \\ H \end{matrix}\!\!>\!C = O$ (3), and it is available commercially in an aqueous 37% solution known as Formalin. Formaldehyde (HCHO) is used as a feedstock in the synthetic chemical industry (123) and in the production of synthetic resins (92). It is also used as a disinfectant and tissue preservative (123).

The widespread use of this chemical provides many sources of the vapor in the occupational and general environment. The production and use of HCHO within the chemical industry, the preparation, use, or presence of formaldehyde-based resins during production and handling of many industrial and consumer products, and the use by consumers of resin-containing products which evolve (or "off-gas") free formaldehyde are some sources of environmental levels of HCHO, as is the use of Formalin in various activities such as embalming, disinfecting, and others. Additionally, HCHO is formed during combustion processes and is present in engine exhaust, cigarette smoke, and other combustion-process waste gases (92).

A large number of people are exposed to HCHO, both occupationally (92) and non-occupationally (23), due to the many environmental sources, and this presents a serious industrial and environmental hygiene problem when the health effects of this compound are considered. Its irritant effects on the eyes, respiratory tract, and skin are well recognized (7), and the relatively recent evidence of its animal carcinogenicity (35) has raised concern that this important compound is a potential carcinogen in humans (92). Because of this concern, both the National Institute for Occupational Safety and Health (NIOSH) and the American Conference of Governmental Industrial Hygienists (ACGIH) have revised and tightened their recommendations for acceptable levels of occupational exposure to HCHO (7, 92).

All of this activity has increased the need for accurate, versatile, and practical methods for measuring airborne concentrations of this chemical. Sampling airborne HCHO by drawing the air through an aqueous solution in a midget impinger, and analyzing the solution for HCHO using the chromotropic acid procedure prescribed by NIOSH (45), has remained very popular among industrial hygienists, despite the drawbacks of liquid sampling media for use in the field (especially for breathing-zone measurements). This is because the analytical method has been well characterized in terms of accuracy, offers excellent sensitivity, and has the practical benefits of relatively quick and uncomplicated analysis, low cost, and proven durability (45). These features contrast with those of some of the newer methods which call for solid-sorbent sampling, offering the more convenient sampling

technique but requiring highly sophisticated, costly analytical techniques or having other serious drawbacks (20, 44).

The NIOSH method noted above (impingers/chromotropic acid) does have a further disadvantage, which, unlike its relative inconvenience for breathing-zone sampling, can be corrected. This is a relative paucity of information documenting the collection efficiency of the sampling method under a wide range of conditions. Although the literature search conducted as part of this study (see Part III.B. for a full description) found documentation of the collection efficiency under certain conditions (60, 78, 86, 135), the effects of varying the flow rate (particularly at the very low flow rates) and/or the sampling time (for example, up to 4 or 8 hours) are not well documented. The versatility of the method would be greatly increased if industrial hygienists could confidently collect samples at reduced flow rates over longer portions of a workday (the former keeping total analyte mass to a reasonable level, the latter allowing a simpler sampling strategy for the hygienist). Therefore, this study was undertaken to provide the data required to determine if these modifications are feasible. It is hoped that the results of this study are of value in improving this method, aiding industrial hygienists and other health professionals as they work to better protect the health of industrial workers and of the general public.

II. OVERVIEW OF INDUSTRIAL HYGIENE IMPLICATIONS OF FORMALDEHYDE: A LITERATURE REVIEW

A. Physical and Chemical Properties

Formaldehyde is the simplest member of the family of hydrocarbons known as aldehydes, which are characterized by the carbon-oxygen double bond and at least one hydrogen atom bonded to that same carbon, as shown by the following generic structure: $\begin{matrix} R \\ \diagdown \\ \quad C = O \\ \diagup \\ H \end{matrix}$ (where R is an alkyl group) (3). The chemical and physical properties of formaldehyde (HCHO) are given in Table II-1.

As noted in the Table, this compound is very reactive, combines easily with many substances, and polymerizes easily. The reactivity, and a versatile structure, endow formaldehyde with perhaps its most important characteristic: it can form, in combination with other substances, compounds known as "resin precursors" which can link together to form high-molecular-weight polymeric structures. These polymers, known as "formaldehyde-based resins", include phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde resins, among others (131). These resins, which have great commercial significance, and their chemistry are discussed by Wakeman (130) and others (131).

Table II-1. Chemical and Physical Properties of Formaldehyde

Molecular Weight = 30.05 Molecular Structure $\begin{matrix} H \\ \diagdown \\ C{=}O \\ \diagup \\ H \end{matrix}$

Physical state and description of pure compound (@ 25°C, 760 mmHg):

gaseous, flammable and colorless, with suffocating, pungent odor

Physical properties:

density: of gas (@ 25°C, 760 mmHg) = 1.067 (where air = 1.000)

of liquid (@ -20°C) = 0.815 g/mL

boiling point: (@ 760 mmHg) = -19.5°C; (@ 400 mmHg) = -33.0°C

melting point = -92°C

ignition temperature ≅ 300°C

solubility: very soluble in water (up to 55%);

soluble in ethyl alcohol,ethyl ether

Chemical properties, description:

very reactive, combines readily with many substances, polymerizes easily

Properties of 37% Aqueous Solution known as Formalin:

composition and physical description: 37% formaldehyde by weight,

10-15% methanol (as a stabilizer); colorless aqueous liquid solution

density (@ 25°C) = 1.081 to 1.085 (where water @ 25°C = 1.000) = 9.1 lb/gal

boiling point (@ 760 mm Hg) = 96°C; flash point = 60°C

miscible with water, alcohol, acetone

Sources: The Merck Index, 10th Edition (136); CRC Handbook of Chemistry and Physics, 63rd Edition (134)

B. Uses in Industry and Consumer Products

Formaldehyde (HCHO) is an important industrial chemical used in many processes and in the production of many products (91, 136). It has many pesticide uses: as a germicide, an insecticide, a fungicide (136), a mildew retardant (as vapor from the decomposition of the solid formaldehyde polymer "paraformaldehyde") (25), a general disinfectant and, medically, an antiseptic (7, 123, 136) (including use to disinfect kidney dialysis machines [25]). As a preservative (7, 136), HCHO is used extensively for tissue preservation (123), such as in histology or similar fields (25), and in embalming fluids (7, 92, 123, 136). Other medical (92) and veterinary (136) uses are found. HCHO is also used in photography and tanning (92, 136), fabric finishing (as dye fasteners) and chemical analysis (136), as a corrosion inhibitor (7), and in many other processes (92, 136). The majority of the formaldehyde produced in the United States, however, is used in the production of other chemical substances (14).

Formaldehyde is used as a feedstock for many organic chemicals (7, 123, 131, 136), such as pentaerythritol, hexamethylenetetramine, acetylene derivatives, and various fertilizers (91), and in the production of dyes and explosives (136). Most importantly, however, it is used to produce formaldehyde-based resin systems (14, 131, 136), which are used primarily as binders for wood and paper products (such as particle board, plywood, fiberboard, and various papers) (92), but have many

other uses, such as imparting crease and shrink resistance (92) to fabric used in clothing (25, 123). The production of these versatile resins consumed over 60% of the estimated 5.2 billion lb of (aqueous 37%) HCHO produced in the United States in 1983; almost 40% of the domestic HCHO production was used to produce urea-formaldehyde (UF) resins, while over 20% was used to produce phenolic resins (14). In addition to UF and phenol-formaldehyde resins, melamine-formaldehyde, polyacetal, and other resins are produced (7, 91, 131). The phenolic resins are used to construct plywood, and almost all of the UF resins are used as binders in wood products (14). Other uses for UF resins include production of foams, such as UF foam insulation (UFFI) (23), coatings, and paper (92). Polyacetal resins can be used to mold plastics (92).

C. Sources and Corresponding Concentrations of Airborne Formaldehyde

Innumerable anthropogenic activities are responsible for the introduction of formaldehyde (HCHO) into the air of workplaces, homes and other non-occupational settings, and the ambient outdoor environment. These activities can be divided into the following two broad categories: those involving the combustion of materials, and those which entail the production and/or use of products containing formaldehyde. The former group includes combustion of a wide variety of organic-based materials, which may or may not contain HCHO themselves. The latter group includes: (1) the production of formaldehyde and its aqueous solutions; (2) the use of HCHO and its solutions, either as end products or in the

production of other materials via chemical reactions and/or mixing; and, (3) the use of products and materials containing HCHO.

Table II-2 provides the levels of airborne HCHO associated with many of the combustion processes responsible for its evolution. Table II-3 contains the airborne concentrations associated with the production and/or use of HCHO-containing products. These activities were described in the previous subsection (B.), and include the use of HCHO as a preservative, pesticide, chemical feedstock, and raw material for HCHO-based resins; and the use of these resins in paper, plywood, fabrics and other products.

Table II-2. Combustion Sources of HCHO and Associated Airborne Concentrations

Source	Type of Exposure	Types of Samples	Levels (ppm)*	Notes	References
Scientific glassware-decal application	Occupational	TWA,** personal and area	0.42-0.64		25
Heating of acrylic, polypropylene, polyethylene; thermo-cutting of polyethylene (91)	Occupational	Short-term area	0.37-0.73		25
Welding metals treated with synthetic-resin corrosion inhibitors	Occupational	Short-term	0.05-1.2		99
Solders containing colophony resins	Occupational	Short-term	<0.1		99
Engine exhaust (diesel and gasoline), incinerator effluent, coal-fired power plants (37), incomplete combustion of many organic substances (136)	Environmental	Long-Term	0.04 avg. 0.06 avg. max. 0.16 peak		5
Cigarettes	Non-occupational	Source	<0.1-1.0		107
		TWA Personal	40		92
			0.38 mg/pack	Mainstream	92, 23
Gas-burning stoves	Residential	Source	15-25 mg/hr		23
Cooking	Residential	---	---		65
Kerosene heaters	Residential	Source	0.1-0.4 ug/kJ of heat output		138

*unless noted
** TWA = Time-weighted average

Table II-3. Airborne Concentrations of HCHO Associated with the Production and/or Use of HCHO-Containing Products

Activity/Use	Type of Exposure	Types of Samples	Levels(ppm)	Notes	References
Laboratories: formalin	Occupational	1-hr breathing zone	0.3-2.63 (1/2 between 0.6 and 1.0)	5%-formalin embalming solutions	117
		personal (short- and long-term) and area (long-term)	1.9-2.3		25
		long-term (area and personal)	0.8-2.4		25
		personal TWA*	<0.38-1.04	**	25
		area (short- and long-term)	0.11-0.41	**	
Embalming	Occupational	short-term	0.25-1.39	= range of the mean values for multiple embalming establishments	7
		long-term area	ND***-1.99	embalming fluid was 6 to 52% formalin by weight	47
		personal	ND-2.93		
Hospitals: formalin --and policlinics	Occupational	short-term	0.05-3.5		99
--dialysis unit disinfection	Occupational	personal TWA	0.27-0.63	**	25
		area, long-term	ND-0.90	**	
		area, real-time	0.04-0.50	**	
		peak	0.9-1.6		15
		peak	25		67
--autopsy room	Occupational	---	2.2-7.9		92

* TWA = Time-Weighted Average
** Intermittent use of Formalin
*** ND = none detected

Table II-3. Airborne Concentrations of HCHO Associated with the Production and/or Use of HCHO-Containing Products

Activity/Use	Type of Exposure	Types of Samples	Levels(ppm)	Notes	References
Building materials: resin binders					
---mobile home	Residential	area	<0.1-3.68	complaintant homes	39
---energy-efficient home or building	Residential	area	0.04-0.12		65
--with furnishings	Occupational(office)	area	0.08-0.16		73
		area	0.02-0.12 ND	two locations five locations	25
		long-term	0.041		65
		short-term	0.05-0.77		99
	Residential	short-term	0.01-0.93		99
		area	0.186		65
--also, occupied	Residential	area	0.117-0.218		65
---Urea-formaldehyde foam insulation (UFFI) application	Occupational	---	<0.08-2.4		23
Textiles: resins systems used					
---textile manufacture (durable press et al.)	Occupational	short-term	0.1-0.5		99
		---	<0.1-1.4		92
		---	0.3-2.7		7
		---	up to 4.2		91
		---	0.03-0.15		55
		respirable dust non-respirable dust	0.008-0.01 0.001-0.03	based on range of free-HCHO content, mean dust level	

Table II-3. Airborne Concentrations of HCHO Associated with the Production and/or Use of HCHO-Containing Products

Activity/Use	Type of Exposure	Types of Samples	Levels(ppm)	Notes	References
---durable-press garment manufacturing	Occupational	area, short-term	0.03-0.94		25
		area, peak	0.39-1.12		
		----	0.13-0.45		7
		personal, area	0.1-1.0		123
		----	0-0.8		132
---durable-press garment retailing	Occupational/ Non-occupational	area	0.9-3.3		91
Chemical production: raw material					
---fertilizer	Occupational	----	0.2-1.9		92
---dyestuffs	Occupational	---	<0.1-5.9		92
---unspecified specialty chemicals	Occupational	personal short-term	0.04-1.6		25
		area short-term	0.03-0.43		
Paraformaldehyde packaging	Occupational	personal 8-hr TWA	<0.25-0.85		25
		area real-time	0.28-3.40	area means	
Shoe manufacture: (formalin spraying)	Occupational	short-term	0.9-2.7		99
Adhesives:					
---manufacture	Occupational	short-term	0.8-3.5		99
---use: lamination	Occupational	short-term	0.04-8.		91

Table II-3. Airborne Concentrations of HCHO Associated with the Production and/or Use of HCHO-Containing Products

Activity/Use	Type of Exposure	Types of Samples	Levels (ppm)*	Notes	Ref
Formaldehyde-based resins and glues; their applications					
---manufacture and application	Occupational	---	<0.1-5.5		92
		---	0.4	mean	126
		---	2-30	to treat paper (1961 study)	56
---foundries: mold-core resins	Occupational	short-term	2.7	mean	99
		---	<0.02-18.3		92
		---	0.18-3.9		16
---paper manufacture	Occupational	---	0.14-0.99		92
		personal	0.9-1.6		91
---paper bag manufacture	Occupational	personal	0.14-0.90	wet stock paper, 0.49-1.63 mg/g	106
---particle board manufacture	Occupational	short-term	0.1-4.9		99
		---	0.08-2.7		132
---plywood manufacture	Occupational	short-term	0.1-1.2		99
		---	1.0-2.5		92
		personal,area	0.01-1.1		132
---wood furniture manufacture	Occupational	short-term	0.1-5.4		99
---particle board cabinet manufacture	Occupational	---	0.16-1.69		54
Electrical machinery manufacture: lacquer, treating plastic	Occupational	short-term	0.2-0.5		99
Construction: carbamide lacquer	Occupational	short-term	0.5-7.0		99
Storage of sandpaper: resin glue	Occupational	area	4.5		
		personal	3.16,3.69		129
Carbonless copy forms	Occupational	Source	0.33-0.72	in effluent of air passed by forms	57

D. Known and Suspected Health Effects and Corresponding Air Concentrations

1. Acute Effects

a. animal

Numerous studies of the health effects of formaldehyde have been conducted on various animal species. Although this section is primarily concerned with the inhalation effects, the toxicity studies which have measured the LD_{50} dose level for other routes of exposure provide valuable information which can indicate the relative acute toxicity of formaldehyde compared to other chemicals. Table II-4 provides this information for a variety of species.

Table II-4. Acute Health Effects of Formaldehyde, Animal Studies: LD_{50}s (66)

Species	Dose, mg/kg body weight	Route of Administration
Rat	800	oral
Rat	420	subcutaneous
Rat	87	intravenous
Mouse	300	subcutaneous
Rabbit	270	dermal
Guinea pig	260	oral

A common non-lethal effect is skin irritation by direct dermal contact. This irritant effect has been seen in rats and guinea pigs (7); sensitization was noted after repeated application.

The effects on animals of formaldehyde inhalation have been extensively studied. The most important of these effects involve the irritation of the respiratory system; these are summarized in Table II-5.

b. human

As in animals, formaldehyde acts as an acute irritant in humans. Direct contact with formaldehyde solutions affects primarily the site of contact, while the vapor primarily affects the eyes and respiratory tract.

Direct skin contact can cause primary irritation or allergic dermatitis (7). Ingestion has been reported to cause gastrointestinal irritation and damage (including death) (91). Formaldehyde reportedly has caused lasting ocular damage (7), although a 1976 study of a population exposed to an average of 0.4 ppm found no significant effects on visual performance related to exposure level or degree of irritation.

Table II-5. Acute Respiratory Effects of Formaldehyde Inhalation, Animal Studies

Species	Concentration, ppm	Exposure time	Effect	References
Cat	700	8 hr	death	7
Mouse	700	2 hr	death	7
Rat	810	30 min	LC_{50}	91
Guinea Pig	15-16 (aerosol)	10 hr	death	7
Mouse; Rabbit	15-16 (aerosol)	10 hr	approx. LC_{50}	91
Rat (Fischer 344)	15, 6, 2	6 hr/d, 1-9 d	Nasal cavity cell degeneration, necrosis,* inflammation at 15 ppm; increased replication of respiratory epithelial cells at 6 and 15 ppm.	66
Rat (Fischer 344), Mouse (B6C3F1)	0.4-56	10 min	dose-dependent depression of respiratory rate; in rats only, minute-volume compensation.**	34
Guinea Pig	0.31	1 hr	increased airway resistance	91

* Other studies confirm local necrosis, by different route (intrapulmonary injection).

** Therefore, mice receive a lower effective dose.

Formaldehyde induces eye and respiratory tract irritation in most individuals above a vapor concentration in the 0.1 to 5 ppm range (depending upon individual sensitivity) (92); however, it may induce symptoms below 0.1 ppm in individuals with bronchial hyperreactivity (23). Other effects have been documented above 0.25 ppm. Eye irritation only was documented in a population exposed to 0.13 to 0.45 ppm, and among an unacclimatized group whose exposure was only stated to be much less than 5 ppm (7); eye irritation was also documented in a study group exposed to an average of 0.4 ppm (132). However, another study population exposed to 0.25 to 1.39 ppm suffered skin irritation and headaches in addition to eye irritation. Similarly, a study documented eye and upper respiratory irritation, headaches, and cough among a group whose exposure was only stated to be much less than 3 ppm. Two occupational study groups, one exposed to 0.9 to 1.6 ppm and the other to 0.3 to 2.7 ppm (average 0.68 ppm), were found to experience irritation (to the eyes and skin in the former group and to the mucous membranes in the latter) and disturbed sleep; the former group also experienced unusual thirst. Other instances of eye and upper respiratory irritation and general complaints of irritation have been reported to occur in this range of concentrations. Most reports agree that a tolerance to a given level of formaldehyde will develop in time in most individuals. Some suggest that sensitization will occur, but not many reports confirm this (7).

Above 10 ppm, formaldehyde will induce in humans more severe irritation and other symptoms. Between 10 and 20 ppm, coughing, tightening in the chest, a sense of pressure in the head, and palpitation of the heart may occur. Between 50 and 100 ppm, severe respiratory irritation will occur; single acute exposures to these levels have produced pulmonary edema (fluid in the lungs) and even death (92).

2. Chronic Effects

a. animal

The chronic effects of formaldehyde on non-human organisms and tissues include carcinogenic, mutagenic, and other effects. These "other effects," mainly irritant in nature, include low body weight and nasal cavity lesions among groups of monkeys and rats exposed to airborne concentrations of formaldehyde of 1 and 3 ppm almost continuously (22 hr/d) for 26 wk, as well as groups of Fisher 344 rats and B6C3F1 mice exposed to 2, 6, and 15 ppm for 6 hr/d, 5d/wk, for up to 24 mo (66). The Fisher 344 rats and the mice also developed tracheal lesions. In other studies, rats exposed by inhalation to 0.8 and 2.5 ppm for 3 months experienced respiratory system and other histologic changes, while several species exposed to 3.7 ppm, 24 hr/d for 90 d, experienced interstitial inflammation of the lungs; some of these species exhibited

focal inflammatory changes of the heart and kidney, and among rats 1 death was noted (91).

Formaldehyde has tested positive for mutagenicity in bacterial systems. In mammalian-cell assays, it has exhibited mutagenic properties in some species and tissues, but not others; likewise for arthropods in vivo, for which positive results were found for some species and routes of administration but not others, and even vegetables, for which some species but not others tested positive (66).

In an early carcinogenicity study (1963), groups of 42 to 60 C3H mice exposed to 41, 81, and 163 ppm of formaldehyde for 1 hr/d, 3 d/wk, for 35 wk (except for the high exposure group, due to severe intoxication after the 11th day), experienced no pulmonary tumors, but the nasal epithelia were not examined; basal-cell hyperplasia, squamous metaplasia, and atypical metaplasia were seen in most of the exposed animals, and in no controls (66). Two more recent studies, from 1979 and 1980, have demonstrated that formaldehyde is carcinogenic in laboratory animals (92). In one, rats (Fischer 344) and mice (B6C3F1), 240 of each, were exposed 6 hr/d, 5 d/wk for up to 24 months to formaldehyde vapor. Squamous-cell carcinomas of the nasal turbinates developed in 93 rats and 2 mice exposed to 15 ppm, 2 rats and no mice exposed to 6 ppm, no animals exposed to 2 ppm, and no control animals. This type of malignancy is extremely rare in these strains of animal.

In the other study, 100 Sprague-Dawley rats were exposed to 14.6 ppm only (the exposure pattern was otherwise similar to the preceding study), but in conjunction with 10.6 ppm hydrochloric acid (HCl), as a test of their reaction product bis(chloromethyl)ether (BCME). Squamous-cell carcinomas of the nasal turbinates (which are not characteristic of BCME exposure) developed in 25 rats, although they had never been seen in unexposed animals of this strain. Further work was conducted to clarify these results (66). Groups of 100 rats were similarly exposed to formaldehyde only, mixtures of it and HCl mixed before (at high concentrations; presumably, more BCME would form) and during the exposure testing, and HCl only. Nasal carcinomas, almost all squamous-cell, were found in 10, 12, 6, and none, respectively, of the rats in these groups, and in no control animals.

The International Agency for Research on Cancer (IARC) (66) reviewed other studies which reported the induction of local tumors after subcutaneous injection in hamsters and rats and direct application to the oral mucosa in rabbits. These studies suffered from problems like poor reporting, small numbers of animals, and the absence of controls.

b. human

Regarding the chronic effects of formaldehyde on humans, the greatest concern focuses on the issue of carcinogenicity, and numerous studies have now been completed in this regard. However, some other chronic effects have been noted; most of these are related to the irritant properties of this substance. Respiratory effects include airway obstruction and reduced lung function (formaldehyde concentration uncertain due to sampling problems; the range of possible concentrations was 0.4 to 12 ppm) (92), as well as pnuemonitis (7) (inflammation) after 50 to 100 ppm acute exposures (92). Dermatitis has occurred due to dermal exposures (66). Also, menstrual disorders and secondary sterility in women have been reported (66) (exposure levels unknown).

Numerous epidemiologic studies of human populations have now been completed which address the issue of formaldehyde as a carcinogen. These are summarized in Table II-6. No one study provides sufficient evidence to conclude that formaldehyde is carcinogenic in human populations, and some studies cited found no excesses of cancers (although often these studies have suffered from low statistical power to detect significant excesses). Most of the studies have found some elevated risk of cancers associated with formaldehyde exposures, although the results often have not

Table II-b. Epidemiologic Studies on Formaldehyde Exposure and Cancer in Human Populations

Population at Risk	Study Design	Exposure Levels and Duration	Latency	Confounders	Cancer Outcomes	Limitations and Comments	Investigators	Source (reference number)
(1) Pathologists and lab technicians	SMR*	Unknown Levels	"short"(104)	---	Suicide (significant excess); lymphatic and hematopoietic neoplasms among pathologists, but these excesses disappeared in later followup when significant excess of brain cancer (astrocytoma and glioma) was found		Harrington and Shannon Harrington and Oakes	66 101, 104
(2) Physicians involved with laboratory work	SMR	Unknown levels	not specified	---	deficits of lung, esophagus, oral cancers		Doll and Peto	66
(3) Morticians	PMR**	Unknown levels; short average duration	"short"	other embalming-fluid components	significant excess of skin (apparent dose-response relationship), kidney, and brain cancer; no excess respiratory or nasal cancer	low statistical power to detect nasal cancer excess	Walrath and Fraumeni	66
(4) Formaldehyde manufacturing workers	SMR, PMR	Unknown levels; short average duration	some over 20 yr; average was "short"	other chemicals	SMR: non-significant excess of brain and prostate cancer and Hodgkins' disease, with prostate significant in the "over 20-yr latency" group; PMR: significant excess of "all" and prostate cancer	low statistical power to detect various cancer excesses	Wong	66
(5) Formaldehyde and resin manufacturing workers	PMR	Unknown levels; short average duration	"short"	other chemicals	excess of digestive system cancers, but was seen among the youngest (at death) and shortest duration/longest latency groups only	low statistical power to detect various cancer excesses	Marsh	66
			added 4 yrs followup		additional followup: significant excesses of colon, and buccal and pharyngeal cancer	only analyzed for the 4 years of additional followup, rather than combining with previous results; therefore, small numbers of deaths in analysis.	Liebling et al.	101, 104

Table II-6. Epidemiologic Studies on Formaldehyde Exposure and Cancer in Human Populations -- Continued

Population at Risk	Study Design	Exposure Levels and Duration	Latency	Confounders	Cancer Outcomes	Limitations and Comments	Investigators	Source (reference number)
(6) Woodworkers	Case-control	1-ppm-TWA median, 10-yr mean duration; grouped by both parameters	"over 10 years" highest group	wood dust, and other substances, but study controlled for these	non-significant excess of "exposed" among respiratory and related cancer cases, inverse does-response	low statistical power to detect an excess; 10 yr is short latency	Partanen et al.	104
(7) Chemical and plastics workers	SMR	Grouped into levels from <0.1 ppm to >2.0ppm (subjectively estimated)	a "long" group included	other chemicals	significant deficits of leukemia and brain cancer. In one (of six) plants: significant excess of lung cancer (high exposure group) and borderline-significant trend of incidence and exposure level increase, but no relation to duration. In another plant: significant excess of rectal cancer.	small numbers in high exposure/long duration/long latency group	Acheson et al.	101, 104
(8) Various occupations	Case-control	Unknown levels	"over 10 years" longest	wood dust, but adjusted for that	among nasal cancer cases, significant excess of exposure to wood dust and to both wood dust and HCHO, non-significant excess of exposure to HCHO alone (although relative risk is greater among over-10-year-latency group).		Olsen et al.	101, 104
(9) Garment manufacturing workers	PMR, PCMR***	Essentially continuous exposure, currently 0.1 to 1.0 ppm but higher in the past, over-10-yr-duration group included	over-10-year group included	none	significant excess of buccal cavity, liver and "other lymphatic and hematopoietic tissue" cancers (except liver in PCMR analysis) seemingly related to greater-than-10-yr duration and latency	low power to detect excess nasal cancer	Stayner et al.	123
(10) Physicians (pathology, forensics, anatomy)	Case-control	Unknown levels	not specified	---	no effects related to these specialists		Jensen; Jensen and Andersen	104

Table II-6. Epidemiologic Studies on Formaldehyde Exposure and Cancer in Human Populations -- Continued

Population at Risk	Study Design	Exposure Levels and Duration	Latency	Confounders	Cancer Outcomes	Limitations and Comments	Investigators	Source (reference number)
(11) Morticians	SMR	0.02 ppm 40-hr-wk-TWA average; long duration	"long"	phenol	no cancer excesses; only non-malignant excesses (probably alcoholic in origin)	low exposure levels	Levine et al.	104
(12) Chemical workers	Case-Control	3 TWA exposure groups from <0.1 to >2.0 ppm (some assigned by recall of odor), or 2 peak exposure groups (>2 ppm, or not)	"adequate"	other chemicals	non-significant excess of "exposed" among bladder and prostate cancer cases	possible over-matching (104)	Fayerweather et al.	49
(13) Various occupations	Case-control	Unknown levels	unknown	unknown; presumed other chemicals	among nasal cancer cases, significant association with working in textile industry (RR=1.72) (women only), deficit of exposure to HCHO	exposures based on report of subjects	Brinton et al.	32
(14) Anatomists	SMR	3 groups, by specialty; typically 1 to 3 ppm, higher intermittently, estimated exposures	not specified	other chemicals	significant excess of brain cancer (glial cell) and chronic myeloid leukemia, non-significant excess of "all" leukemia, deficit of lung and "all" cancers		Stroup	101
(15) Various occupations	Case-control	Subjective ranking (high, low) by occupation	not specified	---	among lung cancer cases, highly significant excess (RR = 1.5) of those in HCHO-exposed occupations (but no relation to exposure group); among bladder cancer cases, no association.		Coggon et al.	101
(16) Various occupations	Case-control	Subjective rank of exposures; levels unknown	not specified	wood dust and smoking, but study controlled for these	among squamous-cell carcinoma cases, excess of those in "exposed" occupations, but unclear if confounded by wood dust	two independent exposure assessments	Hayes et al.	64

Table 11-6. Epidemiologic Studies on Formaldehyde Exposure and Cancer in Human Populations -- Continued

Population at Risk	Study Design	Exposure Levels and Duration	Latency	Confounders	Cancer Outcomes	Limitations and Comments	Investigators	Source (reference number)
(17) Chemical and manufacturing workers	SMR	Average level 0.25ppm (5 groups from <0.1 ppm to >2.0 ppm plus "trace") by reconstructive indus. hygiene using data (past and present) and subjective estimates; peak values estimated also	over-20-year group included	other chemicals (identities were recorded)	excess Hodgkin's disease (significant rising trend with exposure intensity), lung cancer (significant for wage employees with over-20-yr latency, SMR = 132), and prostate cancer, but no relationship to average, cumulative, or peak exposure; also, excess cancer of the nasopharynx (significant) and oropharynx, but not related to dose		Stewart et al. and Blair et al.	125 26
(18) Garment manufacturing workers	SMR	Essentially continuous exposure, currently 0.15 ppm overall geometric mean (0.08 to 0.20 for departments, by plant) but greater in the past, over-10-yr-duration group included	over-20-year group included	none	significant excess of buccal-cavity cancer (plausible based on duration, latency, and year of first exposure) and connective-tissue cancer, and non-significant excess of bladder cancer, and leukemia and other lymphopoietic neoplasms	buccal cavity cancer is biologically plausible site. No nasal cancer deaths in cohort	Stayner et al.	124

* Standardized Mortality Ratio

** Proportionate Mortality Ratio

*** Proportionate Cancer Mortality Ratio

been consistent between studies, some biologically unlikely sites have been implicated, and confounding variables have been reported. Nevertheless, some researchers now believe that the studies, viewed together, seem to provide sufficient evidence to conclude that formaldehyde plays a role in carcinogenesis. The National Institute for Occupational Safety and Health (NIOSH) has recently stated, "We concur with OSHA that the weight of available evidence...does suggest that formaldehyde exposure may be associated with increased risk of lung cancer, brain cancer, and leukemia, although a plausible carcinogenic mechanism for the latter two findings is not clear...The results of the animal bioassays plus the consistency of evidence from the epidemiologic data indicate that formaldehyde should be regarded as a human carcinogen." (89)

E. Maximum Exposure Level Recommendations and Legal Standards

Recommendations and legal standards for the maximum level of exposure to airborne formaldehyde vapor to protect human health are published by several organizations in the United States. Both the occupational and non-occupational environments are addressed by these compilations. The occupational limits include the Threshold Limit Values recommended by the American Conference of Industrial Hygienists (ACGIH TLVs) (8), the NIOSH Recommended Exposure Limits (NIOSH RELs) (89), and the Permissible Exposure Limits promulgated and legally enforcable by the Occupational Safety and Health Administration (OSHA PELs) (100, 101). A non-occupational limit for all indoor spaces has been recommended by the American Society of Heating, Refrigerating, and Air-conditioning Engineers (ASHRAE) (12). Table II-7 provides these recommendations and standards. Occupational standards of varying magnitude have also been adopted in many foriegn countries (7).

F. Air Sampling and Analysis Methods

A large number of methods have been proposed for the determination of airborne formaldehyde concentrations, utilizing a variety of collection and analytical procedures. This subpart summarizes the important features of many of those which have been published. A number of the methods denoted in the literature as methods for formaldehyde are actually non-specific total aldehyde methods; these are summarized first, in Section 1.

Table II-7. Maximum Airborne Exposure Concentration Recommendations and Legal Standards, ppm

Organization (Area)	Occupational				Non-occupational
	8-hr TWA*	Ceiling**	Maximum Peak***	STEL@	Indoor Maximum
ACGIH	1.0	---	---	2.0	---
NIOSH	---	---	---	0.1@@	---
OSHA, Current	3.0	5.0	10	---	---
Proposed	1.0 or 1.5	---	---	---	---
ASHRAE	---	---	---	---	0.1

* TWA = Time Weighted Average
** Generally, maximum allowed above the 8-hr TWA
*** Maximum peak excursion above the ceiling, allowed for no more than 30 min during an 8-hr shift
@ STEL = Short Term Exposure Limit, a 15-min TWA
@@ Designated as "lowest feasible concentration that can be reasonably or actually measured"

1. Methods for Total Aldehydes (Non-specific for Formaldehyde)

a. Early Methods

The bisulfite method is the classic method of aldehyde determination, and was proposed for use in airborne sampling in 1943 (60). Air samples are collected at flow rates of 1 to 3 Lpm in midget impingers containing 10 mL of aqueous 1% sodium bisulfite ($NaHSO_3$) (sodium hydrogen sulfite) (the collection efficiency is discussed in Part III.B., below), or at 28 Lpm in large impingers with 100 mL of this solution. Formaldehyde reacts with $NaHSO_3$ to form the stable complex sodium formaldehyde bisulfite. For analysis, unreacted bisulfite is destroyed with iodine under neutral conditions, then the solution is made alkaline to decompose the complex. The liberated sulfite is then titrated with standardized iodine solution for an indirect measure of the aldehyde originally collected. The method is sensitive to aldehydes and ketones, and the sensitivity is not the best (60). Slight modifications, including the use of two midget impingers "with fritted disks" in series in an ice bath, and a minor change in the titration procedure, were proposed in 1958 (135).

In 1940, Kersey et al. reported Schryver's method, or the phenylhydrazine method, calling for collection in dilute aqueous phenylhydrazine HCl. Upon subsequent addition of

hexacyanoferrate (III) in acid solution, a reaction occurs to form a purple chromogen, for a colorimetric determination (109). This method was determined to respond to acetaldehyde and acrolein (91). Modifications in the collection procedure have subsequently been reported, including collection in 1.5% potassium hydroxide (91) and in distilled water (22), as well as the impregnation of silica gel with phenylhydrazine to make indicator tubes proposed by Fedotov (91).

b. Newer Methods

The newer (1961) 3-methyl-2-benzothiazolone hydrazone (MBTH) method, although still sensitive to a variety of aliphatic aldehydes, is most sensitive to HCHO. MBTH reacts with HCHO in the presence of iron (III) chloride to form a blue cationic dye in acidic solution, for a spectrophotometric determination (113). Collection in aqueous 0.2% MBTH-HCl (113) or in aqueous 0.05% MBTH in bubblers has been reported, the latter with air flow rates from 0.47 to 1 Lpm (11, 63). The latter is a modification to increase the sensitivity to the parts per billion (ppb) range (63). Collection efficiencies of 95-98% (113) and 84% (63) were reported.

Some other methods for total aldehydes are summarized in Table II-8. Still other methods have been reported,

Table II-8. Some Other Methods for Total Aldehydes

Reagent	Analytical Technique	Reference
2-hydrazinobenzothiazole-p-nitrobenzenediazonium tetrafluoroborate	colorimetric	(112)
5,5-dimethyl-1,3-cyclohexanedione (also called dimedone, methone, dimethyldihydroresorcinol)*	fluorimetric	(110)
resorcinol with NaOH	colorimetric	(140)
o-aminobenzaldehyde	spectrophotometric	(2)

* Reacts to form a crystal; then, collect the particulate (128).

including ones based on alkaline peroxide (71), sodium sulfite (for very high concentrations) (29), and 1,3-cyclohexanedione (or dihydroresorcinol [136]) (110) reagents, and the Envirotech Services, Inc., passive dosimeter, which features collection on a polycarbonate sponge impregnated with 0.1 N NaOH, and analysis by the Purpald method (58). Also, infrared (IR) analysis has been employed, after freeze-trap or evacuated-bulb collection (139) or direct collection into the cell of a continuous monitor such as the MIRAN^{R} Gas Analyzer (19). Good review articles covering many of these methods are available (48, 109, 110).

2. Formaldehyde-specific Methods with Collection in Aqueous Media, Except for the Chromotropic Acid Method

The chromotropic acid method, which is a formaldehyde-specific method with collection in aqueous media, and is the method used in the present study, is reviewed in Section 3, below. Other such formaldehyde-specific methods are discussed in the present Section.

a. Pararosaniline (Schiff's Reagent) Method

One of the most important of these is the pararosaniline method, which utilizes Schiff's reagent (also called Schiff-Elvove reagent [140]): pararosaniline (fuchsin) and

sulfite. It was first reported as a reagent for the determination of formaldehyde by Schiff in 1866 (91), and its reaction with formaldehyde (HCHO) produces a rose-violet chromogen for a colorimetric analysis. Zhitkova (140) was one of the earliest, in 1936, to report the use of this method for the analysis of air samples, and numerous versions have been subsequently published (91). These include collection in 0.005N hydrochloric acid (HCl) (107), modified Schiff's reagent (see a description of this in the next paragraph) (1), and distilled water in midget impingers at high flow rates for short times (<20 min) (43, 83) or in large bubblers (43).

Modified Schiff's reagent is a mixture of dichlorosulfitomercurate (II) complex and acid-bleached pararosaniline hydrochloride; it is more selective than the version described above (83). The modified reagent is currently used in commercially available automatic analyzers (88); according to Godish (58), the only continuous formaldehyde monitor available in 1985 was the TGM 555^{R} by CEA Instruments, Inc., which utilizes this method. (This monitor has a significant "lag" or delay between sampling and display, and should not be considered an "instantaneous instrument" in the same sense as the one discussed in Section 6, below.) A more recent (1981) modified pararosaniline method incorporates bubblers with distilled water ($NaHSO_3$ cannot be used because it is an

interference for this method) in a refrigerated container, a 0.8 Lpm air flow rate for 12 to 24 hr, and color development by the addition of pararosaniline hydrochloride, then sodium sulfite; sulfur dioxide and cyanide are interferences (88).

b. Girard-T Reagent Method

In 1978, the Girard-T Reagent method was published by NIOSH as Method S327 (95); NIOSH currently designates it as Method 3501 (46). This method is based on the reaction of formaldehyde and Girard T reagent, (trimethylaminoacetohydrazide chloride, or [carboxymethyl]trimethylammonium chloride hydrazide [136]). Collection occurs in aqueous buffered Girard T reagent in a midget bubbler at 50 to 200 cc/min. Formaldehyde-Girard T derivative forms from the reaction, and the solution is analyzed polarographically for this derivative after a small amount of mercury is added.

c. 2,4-Dinitrophenylhydrazine (2,4-DNPH) Method

This method utilizes 2,4-DNPH as a reagent, and employs HPLC for analysis. Collection of airborne samples has been reported using aqueous 2,4-DNPH in a high-flow washer packed with Raschig rings, with good collection efficiency up to 50 Lpm of air flow (81), as well as 2,4-DNPH in 2N

HCl solution in 2 midget bubblers in series at 0.5 to 1.5 Lpm (76). This method has been adapted to solid-sorbent collection (see Section 4, below)

d. Other Formaldehyde-specific Methods with Collection in Aqueous Media

Some other formaldehyde-specific methods with collection in aqueous media are summarized in Table II-9. Still other methods have been reported, including ones based on reagents such as 2-hydroxycarbazole (for spot tests; not proposed as an air sampling method) (114), paraphenylenediamine (18), and an equilibrium mixture of potassium tetracyanonickelate and dimethylglyoxime (a test-paper, not air sampling, method) (133), as well as ones utilizing polarographic analysis following simple collection in dilute KOH (91) or in water in a gas scrub tower immersed in an ice bath (85).

3. Method Used in the Present Study: Chromotropic Acid (CTA) Method

Chomotropic acid (CTA), 1,8-dihydroxynaphthalene-3,6-disulfonic acid, in sulfuric acid (H_2SO_4), forms a violet-pink color when warmed with formaldehyde (50). The intensity of the color is essentially proportional to the quantity of formaldehyde present throughout a useful range (93). CTA was first proposed

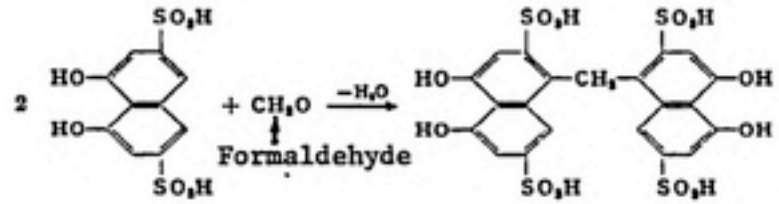
Table II-9. Some Other Formaldehyde-specific Methods with Collection in Aqueous Media

Name of Method	Collection	Analysis		Other Information	Reference Number
		Reagent	Determination		
hydrazine polarographic	aqueous 10% methanol in midget bubblers	hydrazine	polarographic	intended for peak measurements under 10-ppm peak OSHA standard (higher than the currently useful range); good specificity	116
	extra-purified distilled water in midget bubblers (36)	"	"	"	36, 116
2-hydrazinobenzothiazole	aqueous 0.25% 2-hydrazinobenzothiazole in impingers	2-hydrazino-benzothiazole	colorimetric	little interference from other aldehydes; detector tube variation discussed in Section 4, below	112
J-acid	(air sampling method not specified)	0.2% J-acid(6-amino-1-naphthol-3-sulfonic acic [112], or 7-amino-4-hydroxy-2-naphthalenesulfonic acid [136]) in concentrated H_2SO_4	spectrophotometric	more sensitive than CTA method; adapted to solid-sorbent collection in air (discussed in Section 4, below)	112
			spectrofluorimetric (115)	"	112, 115
phenyl J-acid	(air sampling method not specified)	0.1% phenyl J-acid (6-anilino-1-naphthol-3-sulfonic acic) in concentrated H_2SO_4	spectrophotometric	more sensitive than CTA or J-acid (spectrophotometric) methods	112
Hantzsch's reagent (or acetyl acetone [40])	water in jet bubblers (not fritted) (52)	Hantzsch's reagent (acetyl acetone and ammonium salt [90]; mix ammonium acetate, acetic acid, acetyl acetone [71])	colorimetric (90)		52, 90
			spectrofluorimetric (21)		21, 52, 90

as a specific reagent for formaldehyde by Eegriwe in 1937 (41). The chemistry of the color reaction is not known with certainty, but Feigl (50) has proposed the reactions shown in Figure II. He states that, "Since aromatic hydroxy compounds condense with formaldehyde to yield colorless hydroxydiphenylamines, it is probable that the initial step consists of a condensation of the phenolic chromotropic acid with formaldehyde as shown in [equation] (1) [in Figure II] followed by oxidation to a para-quinoidal compound as shown in (2)...Concentrated sulfuric acid participates in both (1) and (2). In the former it functions as a dehydrant to bring about the condensation; in (2) it is an oxidant and is reduced to sulfurous acid."

The air sampling and analysis procedure based on this reagent was proposed in 1954 by McDonald (84) essentially in the form used today, as recommended by the National Institute for Occupational Safety and Health (NIOSH) in NIOSH Method 3500 (45), except that collection in aqueous 1% sodium bisulfite ($NaHSO_3$) (sodium hydrogen sulfite) is now exclusively recommended. (The method was formerly designated P&CAM 125 by NIOSH (93); at that time, collection in distilled water was still recommended.) Procedures sucessfully utilizing collection in aqueous $NaHSO_3$ have been widely reported [33, 78, 79, 86); this collection medium was first proposed as a way to avoid interference by oxides of nitrogen in pollution samples (33), and later to improve collection (86).

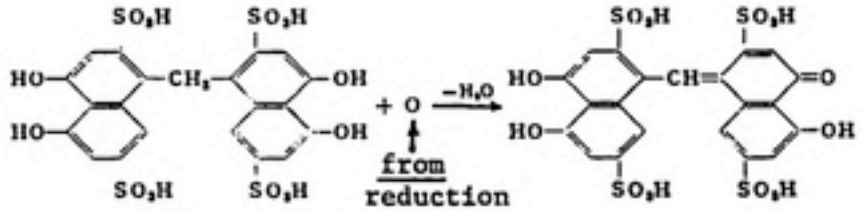
Figure II. Proposed reactions for the formation of pink-violet chromagen from formaldehyde and chromotropic acid (50)



(1)

Chromotropic Acid

Intermediate (colorless hydroxydiphenylmethane compound)



(2)

Intermediate

Chromagen (pink-violet para-quinoidal compound)

Also, samples collected in $NaHSO_3$ are stable in storage (at room temperature) for at least 10 days (69), much longer than samples collected in distilled water (even if refrigerated) (38, 86), as discussed below. The formation of the formaldehyde-bisulfite adduct probably accounts for the enhanced performance of the method when collection in bisulfite is incorporated. A discussion of this is included in Part III.B. The chromotropic acid method is the most commonly used method for airborne formaldehyde determination (116).

The basic procedure of NIOSH 3500 (45) is as follows: Air samples are collected in midget impingers at 0.2 to 1.0 Lpm, although collection efficiency below about 1 Lpm has not been evaluated. This is the method under study; a complete discussion of the collection procedures that have been evaluated is in Part III.B. When sampling in atmospheres with significant particulate concentrations, it is recommended by NIOSH researchers that consideration be given to the possibility that formaldehyde and/or interfering compounds may be released into the stored impinger solutions by desorption from or degradation of the particulates, and that pre-filters be employed when appropriate to eliminate such problems (69). An aliquot of the sample is treated with chromotropic acid (CTA) and sulfuric acid (H_2SO_4), and a purple color develops (45) with no external heating required, as the reaction is exothermic (4). The absorbance of this solution is measured spectrophotometrically at 580 nm, and compared with a

standard analytical curve generated by measuring the absorbance of a series of color-developed solutions of known formaldehyde concentrations. A more complete description of the analytical procedure may be found in Part VI, METHODS; also, a copy of the NIOSH method is provided in Appendix E.

The intensity of the color developed in the reaction has been stated to be proportional to the concentration of formaldehyde in the solution (93); thus, the spectrophotometrically-measured absorbance response is essentially linear with respect to concentration throughout a wide concentration range (4, 84). The analytical precision of the method as listed is ±5% (93), while the overall precision (s_r), including sampling, sample workup, and analysis, is 0.09. The lower detection limit in air is about 0.02 ppm for an 80-L sample, or 0.1 ppm for a 15-L sample (the latter is specified as the lowest reliably quantifiable [short term] concentration in the most recent NIOSH policy statement on formaldehyde [89]); the working range has listed upper limits of 0.4 ppm, or 2 ppm, respectively, although these can be increased by dilution of the aliquot of sample to be analyzed.

Some interferences to this method have been documented, the most serious of which is from phenols. This interference has generally been accepted as a negative bias of 10 to 20% at an 8-fold excess of phenol over formaldehyde (93), but a recent studies indicate that it may be much more serious: a sharp

decline in formaldehyde recoveries, to 50% at a 2-fold excess and 0% at a 20-fold excess of phenol over formaldehyde, was seen in one study (116); in another, at phenol-formaldehyde ratios as low as 3:1, almost total inhibition of the color development in water, and a strong HCHO-concentration-independent inhibition in aqueous 1% $NaHSO_3$, were seen (72). However, phenol can be selectively absorbed from collected samples prior to analysis, using washed XAD-7 polymeric resin, thereby avoiding the interference (62). Acrolein is a slight positive interference; other aldehydes are not (4, 45, 93). Methanol is not an interference, but ethanol and higher alcohols, if present in rather high concentrations (such as tenfold excesses [4, 93] over formaldehyde), are negative interferences (4, 45, 93), as are olefins (alkenes) (45, 93), such as ethylene, propylene, and 2-methyl-1,3-butadiene (93). Pre-trapping with Tenax-GC, a porous-polymer sorbent, has been used to remove ethanol from an air stream being sampled (77). Aromatic hydrocarbons are not serious interferences when collected in water or aqueous bisulfite (4, 118) unless, presumably, they are present in relatively high concentrations, since the reduced interference is due to low collection efficiency of these compounds in the aqueous media (as is also the case for the olefins) (118). This is true for xylene, but if necessary it can be removed with Tenax-GC as described above for ethanol (77). Ketones are generally not an interference (4), although cyclohexanone causes a bleaching of the final color (93), nor is

chloroform (77). Nitrogen dioxide (4) is not generally an interference, although in pollution samples with great excesses of nitrogen oxides concentrations over formaldehyde concentrations, the nitrate and/or nitrite ions formed in the solution are interferences. Sampling in aqueous 10% $NaHSO_3$ has been found to eliminate the interferences from these two ions (33). Dimethoxymethane (methylal) is a positive interference if present in great excess over formaldehyde, but can be pre-scrubbed from an air sample using "Porapak Q" solid sorbent (a styrene-divinylbenzene adsorbent which does not retain significant quantities of formaldehyde) (51). Interferences caused by organic compounds, such as higher alcohols, have been controlled by evaporating the solution to be analyzed to dryness; the formaldehyde has been found to be retained by the CTA so that upon addition of H_2SO_4 the correct amount of purple chromagen is produced (31). An unusual interference problem is caused by aluminum cap liners on sample storage vials (the $NaHSO_3$ in the absorbing solution attacks the aluminum and forms a fine precipitate which interferes with the analysis) (86). Also, of course, any other compound that will release formaldehyde when hydrolyzed with sulfuric acid is a positive interference (30); additional examples include formic acid and dextrose (118).

Samples collected in $NaHSO_3$ are stable in storage (at room temperature) for at least 4 weeks, according to one study, far longer than the 2 days for those collected in distilled

water (86). A recent investigation by Daggett and Stock of the stability of stored environmental samples collected in 1% $NaHSO_3$ also indicates excellent stability, at least 8 days for refrigerated and un-refrigerated samples (38). Also, a NIOSH study found good stability for at least 10 days for similar un-refrigerated samples stored in Nalgene^R cross-linked polyethylene (CPE) bottles, with declines in recoveries noted by the 30th day (69). (A previous study found some deterioration of field samples refrigerated overnight, despite collection in bisulfite, while laboratory-generated samples were not affected [75]. However, the Daggett and Stock study found a similar decline in recovery to be temporary, possibly due to some unknown slow equilibrium process, and it reversed itself [38]. Furthermore, the deteriorating field samples were collected in a textile plant [75], where a pre-filter should have been incorporated to keep potentially interfering particulate-borne compounds out of the samples [69].)

Numerous variations in the sampling technique have been employed, although few have been evaluated for their effects on collection. Some of those used are: flow rates from 0.1 to 1.1 Lpm (5, 73, 78); sampling times of 90 min to 24 hr (19, 58, 73, 75, 120); use of Greenburg-Smith impingers (78, 79); use of fritted bubblers (84, 120); and, aqueous NaOH as the collection medium (84). Collection of diesel exhaust samples in ethanol has also been utilized, but dry-ice temperatures were needed

for collection and NO_2 was an interference (80). Another variation, the purpose of which is to account for particulate containing HCHO (or compounds with the potential to degrade to HCHO) in an air sample, calls for the use of a pre-filter and, if appropriate, the extraction of HCHO from the filter with aqueous 1% $NaHSO_3$ for a separate CTA analysis (69). Also, minor variations in the procedure for sample work-up and analysis have been reported. For example, the addition of a step to concentrate the sample if its concentration is below the detection limit has been reported (84).

A major modification of the procedure for certain "source" samples (5, 80, 118), as well as environmental samples for total aldehydes (6), calls for collection of the air sample in a solution of CTA and H_2SO_4, which simplifies the procedure, and raises the collection efficiency and sensitivity (4). However, this may increase the collection of certain contaminants to the point of their becoming interferences. For example, olefins can be a negative interference with the analysis if collection is conducted this way (although their collection efficiency appears to be sufficiently reduced at flow rates equal to or exceeeding 1 Lpm to essentially eliminate the interference) (4). Aromatic hydrocarbons can also become interferences using this modification (4). A similar, but slightly different, modification calling for addition of a solution of H_2SO_4 containing CTA to the aliquot of sample (collected in the standard way) was rejected

due to declining recovery as the HCHO concentration increased (86).

Modifications to the basic procedure to allow easier simultaneous determination of HCHO and related compounds have been published. One of these, for combining HCHO and total aldehyde samples, calls for sampling with bubblers containing aqueous 0.05% 3-methyl-2-benzothiazolone hydrazone (MBTH) so that an aliquot of solution can be analyzed for total aldehydes by the MBTH method (described in Section 1.b, above) (87). Another such modification, for simultaneous determination of HCHO, acrolein, and low-molecular-weight (MW) aldehydes (C_2 to C_5) calls for sampling with impingers containing aqueous 1% $NaHSO_3$, in an ice bath, so that aliquots can be analyzed for acrolein by a modified mercuric-chloride-hexylresorcinol method and for the C_2 to C_5 aldehydes by gas chromatography (GC) (79); this procedure can be expanded to include low-MW ketones, and the ice-bath collection can be deleted if acrolein is not present (78). These two modifications have also been combined, with sampling in MBTH for the analysis of total aldehydes, and subsequent analysis for acrolein using the 4-hexylresorcinol method (6).

4. Formaldehyde-specific Methods with Collection on Solid Sorbents

One of the earlier methods for sampling airborne formaldehyde with collection on a solid sorbent, first reported in

1975 (137), utilizes collection on alumina at an air flow rate of 200 cc/min for up to 30 min, followed by immediate elution with aqueous 1% methanol for at least 16 hr. The solution obtained is then analyzed by the chromotropic acid method (described in Section 3, above). A significant loss of analyte from the sorbent occurs after 1 hr, which is why the sampling time is limited and the elution must be done immediately; the methanol in the eluting solution stabilizes the desorbed formaldehyde. This method was published by the National Institute for Occupational Safety and Health (NIOSH) in 1977 as P&CAM 235 (94). The air concentration range is 0.3 to 42 ppm; NIOSH indicates that only 1 hr of elution is required. Other methods with collection on solid sorbents that are based on analytical techniques discussed in Sections 2 and 3, above, have been reported; these are summarized in Table II-10.

In 1980, NIOSH published P&CAM 318 (96). This method utilized a specially-prepared charcoal sorbent, impregnated with a proprietary chemical (by SKC, Inc., Eighty Four, Pennsylvania). The formaldehyde was desorbed from the charcoal with hydrogen peroxide for analysis by ion exchange chromatography. This method is no longer recommended due to instability of the samples in storage, believed to be related to the length of storage time and the storage temperature, which can result in loss of analyte (119).

Table II-10. Some Other Methods with Collection on Solid Sorbents and Analytical Techniques Discussed in Sections 2 and 3, above

Name (Reagent/Method of Section 2 or 3, above)	Sorbent	Impregnated (I) or Coated (C) with Reagent	Sampling Conditions		Desorb with	Lower Limit of Detection, ppm	Reference Number
			Flow Rate, L/min	Volume, L			
2,4-DNPH*	Silica gel	I	0.1-0.2	20	Acetonitrile	0.10	20
J-acid	Chromosorb W	C	0.2	3	H_2SO_4	0.2	24
Pararosaniline	Molecular sieve	(no)	2	30	Water	0.03	68
CTA	Silica gel	(no)	0.03-0.5	15	Aqueous 1% $NaHSO_3$	0.17	19
2-hydrazinobenzothiazole	Silica gel	I	(Detector tube)		Unspecified	Unspecified	111

* An alternate method utilizing 2,4-DNPH coated on XAD-2 resin and analysis by GC has been reported (13).

For long term and personal sampling, NIOSH currently recommends NIOSH Method 2502 (44) (formerly P&CAM 354 [97]). This method incorporates XAD-2^{R} resin coated with 2-(benzylamino)ethanol for collection. Airborne formaldehyde reacts with the latter to form 3-benzyloxazolidine, which is stable on the sorbent. The oxazolidine is analyzed by gas chromatography (GC) with flame ionization detection (FID) to quantify the formaldehyde equivalent originally collected. The method was formally evaluated using a flow rate of 10 to 50 cc/min, over an air concentration range of 0.46 to 3.92 ppm, for sample volumes of 1 (@ 3 ppm) to 15 L; however, further work indicates a range of 0.1 to 23 ppm should be obtainable at 80 cc/min for 8-hr samples. The reported detection limit indicates that the method is not as sensitive as the chromotropic acid method, but no interferences are known except acid mists (which may inactivate the sorbent).

5. Diffusional (Passive) Monitors

Commercially produced samplers for airborne formaldehyde are available which are based on collection by diffusion of formaldehyde into a sampling media, followed by analysis of the media by the producer's laboratory, or by the user. These products include: the duPont Pro-Tek^{R} C-60 Series II Formaldehyde badge; the 3M Formaldehyde Monitor; and, the Passive Formaldehyde Kit by Air Quality Research, Inc. Each of these utilizes diffusion in the collection of analyte, and

incorporates aqueous 1% $NaHSO_3$ as the absorbing solution as well as analysis by some version of the chromotropic acid (CTA) method discussed in Section 3, above. The differences between them mainly involve the design of the collection device: The duPont product has a multicavity diffuser element containing the absorbing solution, the 3M version uses a fiber filter pad impregnated with the absorbing solution, and the Air Quality Research product contains a pad similar to that in the 3M Monitor but at the end of a Palmes diffusion tube (58, 74). Evaluations of these monitors have been published (19, 58, 74) and should be consulted prior to the use of them.

Each of the above diffusional monitors may provide the benefit of selectively sampling for formaldehyde in comparison to any interfering compounds present, since the diffusion coefficient for formaldehyde is larger than that of most compounds interfering with the CTA method (68).

6. Instantaneous Instruments

The Lion Formaldemeter Model 681^R by MDA Scientific, Inc., is, according to Balmat and Meadows, the only instrument available in 1985 for the instantaneous determination of formaldehyde levels in air. The determination is made from an electrochemical reaction in a fuel-cell-type detector. An accurate measure of formaldehyde concentrations ranging from 0.3 to 5 ppm is obtainable within 20 sec, but many other

compounds, such as methanol, ethanol, formic acid, phenol, resorcinol, and furfuryl alcohol, will also oxidize in the fuel cell and thus act as positive interferences (19). This instrument is not a "continuous monitor" like the TGM 555[R] discussed in Section 2.a, above.

7. Other Methods (Formaldehyde-specific)

a. Gas and Gas-liquid Chromatography (GC and GLC) Methods (Direct Analysis)

GLC methods are apparently not suitable for the direct determination of low concentrations of formaldehyde in air due to interference and sensitivity problems (137). A GC method for formaldehyde utilizing direct injection of air has been evaluated and found to have poor sensitivity (71).

b. Collection in Non-aqueous Liquid Media

An air sampling and analysis method for formaldehyde utilizing collection in a non-aqueous solution in a midget impinger (at a moderate air flow rate) was reported to have excellent collection efficiency. The sampling solution was the reagent 2-diphenylacetyl-1,3-indandione-1-hydrazone, plus a catalyst (HCl), in acetonitrile. A reaction occurs in the sampling solution to form an azine derivative, which is analyzed by high-performance liquid chromatography (HPLC) with fluorescence detection (127).

8. Additional Notes on Sampling and Analysis of Airborne Formaldehyde

With the wide variety of methods available for the sampling and analysis of airborne formaldehyde, it may be difficult to select the best one for a given situation. A good comparison of the Schiff's reagent, phenylhydrazine, 2-hydrazinobenzothiazole, 2-hydrazinobenzothiazole-p-nitrobenzenediazonium tetrafluoroborate, MBTH, CTA, J-acid, and phenyl J-acid methods for formaldehyde and other aldehydes, all of which were discussed in the above Sections, is provided by Sawicki, Hauser, and McPherson (112); this review may give additional assistance when selection of any of these methods is contemplated.

Regardless of the sampling and analytical method chosen for formaldehyde quantitation, special care should be taken at all stages in the handling of the reagents, glassware, samples, etc., and in the selection of materials and equipment. Formaldehyde is very reactive, as noted in Section II.A, and can be bound by certain materials; conversely, it can be evolved by the decomposition of many organic chemicals (as discussed in Section II.C), such as contaminants in the environment or the equipment, or materials of construction of the equipment. An example of these types of problems is the contamination of stored samples by the materials used in sample

vial caps (86). Air samples for formaldehyde collected in aqueous solutions are contaminated by Bakelite^{R} caps, even when lined with polythene liners (Teflon^{R} liners are needed to solve the problem), because the Bakelite^{R} is a source of formaldehyde.

Additionally, some research concerning sample storage is applicable to all of the aqueous collection methods. Although loss of analyte over time has often been attributed to polymerization, evidence that biological action is in great part responsible for such losses has been provided by this research (82).

Finally, it should be noted that various investigators have proposed numerous general methods of selectively removing some of the interfering compounds from formaldehyde samples. For example, as noted in the discussion of the CTA method, Frankel et al. proposed a pre-scrub of airborne organics using "Porapak Q" solid sorbent (a styrene-divinylbenzene adsorbent which does not retain significant quantities of formaldehyde) (51).

III. COLLECTION EFFICIENCY OF GASES IN LIQUID MEDIA -- GENERAL CONSIDERATIONS AND SPECIFICS RELATING TO FORMALDEHYDE

A. General Considerations of Gas Absorber Performance

1. Absorption by Solution

The absortion theory of gases and vapors from air, as developed by Elkins et al. (42) in 1937, assumes that gases and vapors behave like perfect gases (102) and dissolve to give a perfect solution (42, 102). Another condition of the theory is that diffusion of a contaminant gas or vapor reaches equilibrium between the liquid and gaseous phases for each air bubble or incremental volume of air, before the contact of the air with the absorbing solution ends (17, 53).

Elkins et al. began their theoretical treatment of this topic by defining the rate of absorption (42). Specifically, the rate of change in the concentration (mole fraction) (x) of gas dissolved in liquid with respect to the change in the ratio (v) of moles of air sampled to moles of liquid is expressed as:

$$\frac{dx}{dv} = p - kx \qquad (1)$$

The partial pressure of the contaminant gas (p) in the incoming air is expressed as a mole fraction of the atmospheric pressure, as is the vapor pressure of the gas (k) over its pure liquid phase at the ambient temperature. The expression "kx" refers to the vapor pressure of the gas from the solution of concentration (mole fraction) "x." This expression is based on the assumption of a perfect solution: that the vapor pressure of the gas above a solution of that fractional concentration is simply the product of that fraction (x) multiplied by the vapor pressure from the pure substance (contaminant, in the liquid phase) (k). The above equation, then, indicates that the rate of absorption is proportional to the difference between the incoming gas' partial pressure and the vapor pressure of the gas from the solution (at its instantaneous concentration of dissolved gas). The assumption of a perfect solution is may be incorrect, with solutions deviating from the predicted behavior in both directions; however, simple vapor pressure data is available for many chemical compounds (while experimental data on liquid-vapor equilibria is available for few solvent-solute systems) making this assumption very important if predictions are to be made about absorber performance. In cases where substantial deviation from ideal behavior is suspected, a simple experimental procedure for the determination of the value of the volatility constant (k), proposed in 1950 by Elkins (43), may be used. This is described later in this Section.

Upon integrating the equation (1) of the previous paragraph between the limits $x = 0$, $v = 0$, and $x = x_1$, $v = v_1$, simplifying, and rearranging, the following equation may be derived:

$$x_1 = p(1 - e^{[-kv_1]}) / k \qquad (2)$$

Dividing by pv_1 gives:

$$x_1 / pv_1 = (1 - e^{[-kv_1]}) / kv_1 \qquad (3)$$

The efficiency is equivalent to the term x_1 / pv_1 because of the following: $v_1 = M_{[a][1]} / M_1$, so $pv_1 = pM_{[a][1]} / M_1$, where M_a = moles of air and M_1 = moles of liquid. Calling the total moles of contaminant gas introduced into the sampler (in M_a) "M_g", $pv_1 = M_{[g][1]} / M_1$; x_1 can be stated as $M_{[g][a][1]} / M_1$, where $M_{[g][a]}$ is moles of gas absorbed into the liquid, so the M_1 terms cancel leaving $x_1 / pv_1 = M_{[g][a][1]} / M_{[g][1]}$. The last term represents the number of moles of gas absorbed by the liquid divided by the total number of moles of gas (brought into the sampler), which is the definition of efficiency of absorption. Substituting efficiency (E) for the term x_1 / pv_1, the equation for efficiency may be arrived at. It is:

$$E = (1 - e^{[-kv_1]}) / kv_1 \qquad (4)$$

Based on the above equation (4), Elkins et al. state that efficiency depends only on: the number of moles of air sampled; the number of moles of the absorbing liquid; and, the volatility of the contaminant being collected (42, 102).

In the equations above, the implicit assumption is made that the process described by the rate equation (1) proceeds to completion (as defined by v_1), i.e, that diffusion of the gas reaches equilibrium between the liquid and gaseous phases for each air bubble (53). In equation (2), x_1 is dependent upon v_1 (as well as k and p). In other words, this equation is predicting that, for a given volatility (vapor pressure "k"), incoming concentration "p," and mole ratio "v_1" of air to liquid, a concentration "x_1" in the liquid will be formed by absorption proceeding to the maximum extent possible. This treatment simply does not consider the rate of absorption with respect to time. If insufficient time is available, absorption will be incomplete, x_1 will not be reached, and the collection efficiency will be thus reduced. Therefore, the final equation for collection efficiency (4) actually describes the maximum efficiency that can occur (53), if sufficient time is given for the absorption to occur.

As can be seen in equations (2), (3) and (4), the incoming air concentration (p) affects the final concentration in the liquid (x_1) in equation (2) but cancels out of the efficiency equation (4) because it appears in the definition of efficiency

(which is proportional to the ratio of x_1 and p). As noted above, however, there is a time-dependent absorption rate; it will be dependent upon the concentration "p" because the actual mechanism of absorption is diffusion through and between the air and liquid, and diffusion flux (time rate of transfer of material) is dependent on concentration differences (based on Fick's First Law [102]). As absorption proceeds, increasing the value of x, and of the term kx, kx (which is also the minimum concentration in the exiting air even if the maximum predicted absorption occurs) may approach p, in which case the diffusion may be too slow and collection efficiency will suffer.

The following is a qualitative description of the mechanism of absorption by solution: Before sampling begins, there is no gas dissolved in the solution, so at the instant sampling begins, the vapor pressure of the gas from the liquid solvent is zero. However, gas is immediately absorbed into the solution and as soon as this occurs, there is a finite vapor pressure which is always dependent upon the concentration of gas dissolved in the solvent. Therefore, for practical purposes, absorption is never complete (102); it can only proceed to a portion of completion, and the portion is governed by the relationship between the vapor pressure of the dissolved gas and the partial pressure of the gas in the incoming air. As noted above, it is assumed that diffusion reaches equilibrium for each gas bubble or incremental volume of gas before its contact with absorbing solution ends (17). Put

another way, an air bubble entering the sampler contains a certain (assumed to be relatively high) concentration, and the gas diffuses into the liquid until the airborne concentration is equal to the vapor pressure from the dissolved gas. The exiting air contains this concentration. Therefore, the portion of the gas in the bubble that is absorbed reflects the difference between these concentrations. During sampling, some vapor will escape but it is replaced (102); this is because the net quantity of contaminant absorbed from a bubble is determined as stated above, so no additional net loss will occur.

As sampling proceeds and more gas is dissolved, the dissolved gas concentration rises, and thus does its vapor pressure, until the latter reaches (or, more accurately, approaches) the airborne partial pressure (defined as the product of total pressure and molar concentration for a perfect gas). If this occurs, then the incoming air concentration will already be at the equilibrium concentration (which is determined by the vapor pressure and thus the liquid concentration) for the current, high liquid concentration. At this point, there is no net diffusion required to reach equilibrium (since it is already achieved) so no further absorption occurs; therefore, continued sampling will not increase the concentration of gas in solution once this situation, which is in effect an overall equilibrium, is established (102). Mathematically, this occurs when the air volume (molar quantity) becomes large enough that the

exponential term in the equation (4) above tends to disappear leaving efficiency inversely proportional to the air volume sampled (53). In fact, if the incoming air concentration were to be reduced when this situation existed, or to such an extent at any other time to where the vapor pressure were to exceed the partial pressure in the incoming air, then desorption from the liquid will occur instead of further absorption. This will lower the concentration of the dissolved gas.

The discussion of the previous paragraph does not actually contradict the assertion by Elkins et al., based upon their formulae, that the concentration of vapor in the air is not a determinant of collection efficiency (102). It merely reflects the fact that the concentration of the contaminant must be sufficiently high that "v" remains below specified values (17) (since efficiency is inversely proportional to "v" [17]). If the concentration (p) is too low, a large sample volume (and thus large "v" value) may be needed to obtain an analytically detectable concentration "x," causing the situation described in the previous paragraph to occur.

Since efficiency is also inversely proportional to "k," this sampling procedure is limited to materials with acceptably low vapor pressures (17). Elkins et al. (42) state that efficiency of collection can be increased by cooling the solution (reducing contaminant volatility [k]) (17, 42, 102), increasing the solution volume by adding more bubblers (17, 42, 102), or altering sampling device design (102).

Both Elkins et al. (42) and Gage (53) state that sampling rate is not a determining factor for collection efficiency (102). However, this is based on the equations derived above, with the assumption of complete absorption up to the theoretical maximum. This is not necessarily going to occur, and sampling rate could in practice have an effect on it. For example, if the sampling rate is too high, not enough time will be allowed for maximum transfer. If it is too low, with certain sampler designs it could be possible for insufficient turbulence to be created to allow thorough mixing, with no compensating increase in residence time or decrease in bubble size.

In the above treatment by Elkins et al. (42) of absorber performance, only a single absorber is considered. The theoretical collection efficiency of a series of absorbers will exceed that of a single one because each successive unit can achieve the same efficiency (fraction removed) as the previous one, but starts with a reduced incoming concentration. Therefore, at the end of the series, the exiting concentration will be much lower than that exiting the first absorber, meaning the efficiency of removal is better. The mathematical treatment which they used to consider multiple absorbers produces additional terms in an equation similar to equation (2) above. For two absorbers in series, the following equation can be derived in a similar fashion to that shown for equation (2):

$$y_1 = p(-e^{-[kv_1]} - kv_1 e^{-[kv_1]}) / k \qquad (5) \ ,$$

where "y" is the concentration (mole fraction) of gas dissolved in the liquid in the second absorber. It should be noted that the denominator of the term "v" is the number of moles of liquid in each absorber, not the total amount from both of them. The average concentration in the absorbing solution when the contents of both absorbers are combined is:

$$(x_1 + y_1)/2 = p(2 - 2e^{-[kv_1]} - kv_1 e^{-[kv_1]}) / 2k \qquad (6).$$

The addition of further absorbers adds similar new terms.

Elkins et al. also considered the effects of deviation from an ideal solution. They made refractive index curves and measured the volume change on mixing for the systems which they were considering, and used these characteristics to predict the deviation from ideal solution behavior. In almost every case, these predictions accurately predicted the degree and direction of deviation from the absorber system performance predicted by the mathematical models; the mathematical models otherwise successfully predicted absorber performance (42). The investigators did not propose reasons why one system considered, tetrachloroethylene in amyl acetate, did not as closely follow the predicted behavior as other tested systems did (42); perhaps the possibility of insufficient mixing and/or absorption time leading to incomplete absorption played a role in this.

In 1950, Elkins (43) again proposed the equations (1), (2), and (3), above, as well as the discussion of the effects of multiple absorbers. Additionally, however, he proposed a simple experimental procedure for the determination of the value of the volatility constant (k) if substantial non-ideality of solution is suspected, rendering the use of vapor pressure data invalid. This procedure calls for pure air to be aerated through a dilute solution of the gas in the solvent of interest, followed by determination of the concentration of the final solution. The molar quantities of air and solution must be determined by measurement, and the following equation may then be employed:

$$\ln(x_0 / x) = kv \qquad (7),$$

where "x_0" and "x" are the initial and final concentrations of the solution, respectively, and "k" and "v" are as before. Of course, poor mixing and/or insufficient residence time could lead to inefficient desorption, making the volatility appear artificially low, so care should be taken to avoid those problems.

As discussed above, the assumption made by Elkins et al. in the mathematical treatment of absorber performance (that diffusion of a gas or vapor reaches equilibrium in each air bubble) is not always valid in "real world" situations, and because of this, the efficiency calculated from their equation must be

considered the maximum theoretically achievable efficiency, and must be verified by testing. Many factors (beyond the three that they propose as influencing collection efficiency) will influence the extent to which this assumption is met in a given situation. These, in turn, will influence the collection efficiency. In practice, then, collection efficiency will be influenced by a wide variety of factors (17) of both theoretical and practical importance, including: (1) The degree of contact between the gas and the absorbent (determined by the size of bubble [17, 43]) (17); (2) The duration of contact (determined by the length of the path through the absorbent which the bubbles must move across, and the rate of gas flow) (17, 43); (3) The rates of diffusion in and between the gas and liquid phases (transfer coefficients) (17, 103); (4) The degree of solubility of the contaminant in the absorbent (17, 103); (5) The volatility of the contaminant (17, 103) (numbers [4] and [5] are related because the solvent effect of the liquid, when the solubility is high, causes depression of the vapor pressure [103]); (6) The volume of air sampled (17); (7) The volume of the liquid absorbent (102); (8) The concentration of the gas in the air; and, (9) The deviation of the solution from ideality (42, 43).

In 1960, Gage (53) used water as an absorbent for airborne ethylene oxide to test the relative importance of some of the above factors on collection efficiency. His results reflected the effect of increasing air sample volume on the efficiency

predicted by the equations developed by Elkins et al., above. He found that gas flow rate had some effect when its value was rather high. For this system, he found no effect when varying the absorber design among three types.

Neale and Perry (98), in 1959, also performed experiments to test the effect of some of the above factors on collection efficiency. Their results also reflected the effect of increasing air sample volume on the efficiency predicted by the equations above, but recoveries averaged 4% below the theoretical maximum. They attributed this fact to the mechanical efficiency of the absorber. They also tested various sizes of solvent containers and delivery tubes for simple gas washing bottles (such as impingers; the types of absorbers are discussed below). Container size had no effect but delivery tubes with narrow jet openings, like impinger stems or capillary tubes, gave performance superior to those that did not (with the latter being the best). This finding is perhaps associated with bubble size and/or delivery velocity. Finally, these investigators tested the effects of changing temperatures on collection efficiency. Although the equations presented above would predict a loss of efficiency with higher temperatures due to increased volatility (k) of the gas being collected, these investigators suspected that the decrease in solution viscosity with higher temperatures could tend to increase the mechanical efficiency and thus the collection efficiency. These effects would then, to some extent, offset one another. Their results tended to confirm this.

Neale and Perry (98) developed equations effectively similar to those of Elkins et al. (42) (equations [1] through [4]) except that sampling rate and sampling time were used in place of total sample "volume" (actually molar quantity of air). Therefore, a time term (t) appears in their equations. However, this does not reflect a consideration of the time rate of diffusion discussed above, and should not be mistaken for such; complete absorption to the theoretical maximum is still assumed in the investigators' mathematical treatment of the subject.

2. Absorption by Chemical Reaction

Unlike the case of absorption by solution, with absorption by chemical reaction complete retention is possible as long as sufficient time is allowed for complete reaction and a sufficient excess of reagent solution is maintained (53, 102). It does depend upon the volume of air bubbles produced by the bubbler and the interaction of contaminant with reagent molecules (102). This is a recognition that the contaminant must migrate through the air bubbles to the solution before the reaction can occur, and insufficiently intimate contact will cause poor collection efficiency. If essentially complete reaction does occur, then complete retention is possible because, unlike the case of absorption by solution, the concentration of contaminant in the solution will remain essentially zero as the reaction consumes the contaminant.

Therefore, the volatility of the contaminant itself becomes irrelevant as a source of incomplete collection.

In the case of absorption by chemical reaction, then, collection efficiency will be influenced by the following factors: (1) The degree of contact between the gas and the absorbent (determined by the size of bubble, which may be affected by rate of gas flow [53]); (2) The duration of contact (determined by the length of the path through the absorbent which the bubbles must move across as well as the rate [53] of rise through the liquid, and the rate of gas flow); (3) The rates of diffusion in and between the gas and liquid phases (transfer coefficients); (4) To a slight degree, the degree of solubility of the contaminant in the absorbent (if the gas is totally insoluble it may never interact with the reagent); (5) The rate of chemical reaction (17); (6) The molar quantity of contaminant to be collected and reacted (determined by the volume of air sampled (17) and the concentration of the gas in the air); (7) The molar quantity of reagent in the liquid absorbent (determined by the volume of the liquid (102) and the concentration of the reagent [17]); (8) The nature of the reaction product (i.e., it should be non-volatile and chemically stable, and, for most types of analyses [except, for example, when a precipitate is desired], easily soluble in the absorbing solution; otherwise, the effectiveness of collection will suffer); and, (9) The volume of liquid solvent (to ensure that the reaction product will remain dissolved, when desired).

The above factors are similar to those for absorption by solution, except that the volatility and loss of solute (contaminant of interest) are no longer a consideration, while certain aspects of the reaction, such as its rate (point [5] above) and the need to maintain sufficient reagent (points [6] and [7] above), become added considerations.

In 1960, Gage (53) used formaldehyde in sulfuric acid as a reagent/absorbing solution for airborne chlorobenzene to test the relative importance of some of the above factors on collection efficiency. For this system, he found that fritted bubblers and special narrow-flask impingers increased efficiency of collection over ordinary impingers and impingers filled with glass beads. Gage also used a cathode-ray oscilloscope to determine bubble size at various gas flow rates, and then determined collection efficiencies at various flow rates. The bubble diameter increased with increasing flow, while the collection efficiency decreased with increasing flow.

3. Final Comments, Both Types of Absorption

Both types of absorption may be negatively affected by excessive volatility of the solvent liquid (absorbing solution) itself, as it may evaporate sufficiently during sampling to significantly reduce the volume available for absorption of the solute, thus reducing the collection capacity. Collection at

lower temperature may be employed to reduce solvent volatility and control this problem (103).

4. Types of Absorbers

There are four basic types of absorbers (102). These are: simple gas washing bottles (including impingers); spiral and helical absorbers; fritted bubblers; and, glass-bead columns (102). The first includes simple designs which provide streams of individual bubbles moving through the absorbing solution, while the latter three are more complex to provide for more intimate contact between the air and the solution, increasing the efficiency over the simpler type (122). The latter may be less practical to use, for reasons such as being subject to clogging and/or difficult to clean due to the complexity of the physical shapes (122), so the gas-washing bottles are preferred whenever they are sufficiently effective. The length of travel through the collecting medium in a simple washing bottle is approximately equivalent to the height of the liquid (103, 122), whereas in spiral and helical absorbers the path may be five to ten times longer (103, 122). In impingers, the constricted tips of the inlet tubes may increase the efficiency by decreasing the bubble size, compared to other types of simple washing bottles (43). In fritted glass bubblers, air bubble size depends upon the diameter of the orifices from which they emerge and on the the liquid (103, 122); some liquids tend to allow a heavy froth to

form, increasing the contact time (103, 122). Packed glass-bead columns are especially useful for viscous liquids (103, 122), and provide a large surface area for collection when wetted with absorbing solution (103, 122). A fifth type of absorber, the spray tower, may be useful in specific instances (17).

The performance of none of the absorbers has been systematically evaluated, but many specific applications have been shown through testing to have acceptable performance characteristics (90% or better collection efficiency has been considered a satisfactory minimum as a rule) (17).

5. Testing of efficiency

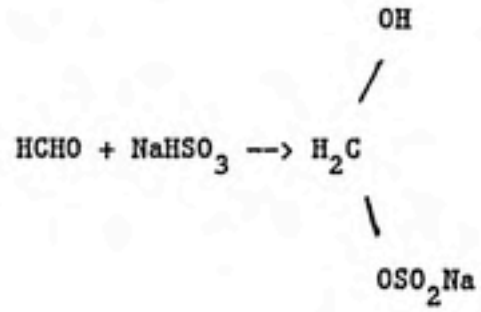
Frequently, in the past, the performance of a single absorber has been checked by comparing the relative performance of two in series. The presence of relatively large quantities of contaminant in the second would reveal poor performance in the first (17). However, lack of significant amounts in the second does not necessarily indicate high efficiency in the first (17, 103), since it may be that the contaminant is not trapped effectively by either absorber (103).

B. The Collection Efficiency of Aqueous Sodium Bisulfite for Airborne Formaldehyde

The collection of airborne formaldehyde with aqueous sodium bisulfite is the system under study. The collection efficiency of water and other aqueous solutions for formaldehyde was reviewed where appropriate in Part II.F, above, as part of the literature review of sampling and analytical methods for formaldehyde, but the discussion of the theoretical and experimental aspects for the bisulfite system was not included in II.F.3, which reviewed the chromotropic acic method (which is used to analyze samples collected with this system) so that it could be discussed in depth here.

1. Absorption by Solution or by Chemical Reaction

Formaldehyde will react rapidly with sodium bisulfite in aqueous solution to form the non-volatile sodium formaldehyde-bisulfite compound (60) (also known as oxymethyl sodium sulfonate [1]):



This compound is stable and will decompose only if the solution is made distinctly alkaline (60); the dissociation constant (K_a) for the formaldehyde-bisulfite ion ($H_2C[OH]OSO_2^-$) has been determined to be $10^{-11.7}$ (121). Therefore, it can be concluded that absorption by chemical reaction will account for most of the absorption which occurs.

Absorption by solution must be considered as possibly acting as a mechanism that is partially responsible for the absorption of the formaldehyde. This mechanism would become important in the case where large sample volumes and/or high sampled concentrations caused all of the available $NaHSO_3$ in the absorbing solution to be consumed, so that no further absorption by reaction could occur. Also, the small portion of the formaldehyde which is not reacted with NaHSO3 due to the reaction equilibrium will remain in solution, and will exhibit the characteristics of absorption by solution. (The reaction is rapid, so this effect is unlikely to be caused by the speed of the reaction). Gage (53) discussed cases in which retention of a gas was found to be partially due to reaction and partially due to absorption. Whenever absorption of formaldehyde into aqueous solution does occur, the theoretical efficiency should be high since the water-air "partition coefficient" has been stated to have a value of 500 (71) (this apparently refers to the inverse of the vapor pressure constant [k]).

2. Experimental Investigations of this System

Some investigations of the collection efficiency of aqueous sodium bisulfite for airborne formaldehyde have been documented. These are summarized in Table III. As can be seen in the Table, generally high efficiencies have been documented under the conditions which have been tested.

Table III. Studies of the Collection Efficiency of 1% Aqueous Sodium Bisulfite in Midget Impingers for Formaldehyde

Investigator(s), Date, Reference Number	Air Sampling Rate, L/min	Sampling Time, min	Air Sample Volume, L	Airborne Formaldehyde Concentrations, ppm	Collection Efficiency, % Collected 1st Impinger	2nd Impinger	3rd Impinger	Notes
Meadows & Rusch 1983 (86)	ns[1]	ns	60	5	98	---	---	
Levaggi & Feldstein 1969 (78)	0.7	ns[2]	ns	1.4	96	4	nil	
	1.1	ns[2]	ns	5.9	92	7	0.5	
Goldman & Yagoda 1943 (60)	1	ns	ns	7	100	---	---	Results based on % carryover to the 2nd impinger.
				21	97	---	---	
				101	98	---	---	
	3	ns	ns	7	96	---	---	
				20	97	---	---	
				78	98	---	---	
Wilson 1958 (135)	1	~60	ns	0.48	93	0	---	
	2	~60	ns	0.48	90	0	---	
	1	~60	ns	0.48	100	0	---	Impingers in ice bath
	2	~60	ns	0.48	100	0	---	
Balmat & Meadows 1985 (19)	0.2	480	96	1.08	93.5-123.1 (N=4)	---	---	Referred to impinger results from 15-30 min, 0.5 L/min samples
	0.5	480	240	1.08	75.0-123.1 (N=4)	---	---	
	0.5	480	240	0.05	94-99+ (avg ≅ 99) (N=10)	---	---	

1 ns = not specified

2 implied to be 15 to 30 min

IV. STUDY OBJECTIVES

The basic objective of this study is to determine if an acceptable collection efficiency for airborne formaldehyde vapor occurs, throughout a useful concentration range* when collecting atmospheric samples with midget impingers containing 20 mL of aqueous 1% sodium bisulfite (as specified in the chromotropic acid method for formaldehyde as currently prescribed in Method 3500** (45) of the National Institute for Occupational Safety and Health [NIOSH]), if volumetric flow rates below those which have been previously evaluated,*** and/or total sampling times exceeding those previously evaluated,*** are utilized.

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* As defined in Part V, "Study Design", based upon the concentration levels discussed throughout Part II.

** This method is discussed in Part II, Section F; also, a photocopy is provided in Appendix E.

*** Part III reviews the previously documented collection efficiency and the sampling conditions to which it applies. Generally, collection efficiencies of 93 to 100% have been achieved but flow rates less than 1 L/min and sampling times exceeding 60 min have not been tested.

More specifically, the study compares the actual concentration of formaldehyde in the sampled atmosphere with the measured formaldehyde concentration under the sampling conditions being tested, and determines if the collection efficiency is significantly reduced (statistically) from the rate previously documented*** under different sampling conditions.

The broader objective is to increase the versatility of this sampling method by documenting the collection performance at reduced flow rates over longer portions of the workday (the former keeping total analyte mass to a reasonable level while the latter allows a simpler sampling strategy for the industrial hygienist).

V. STUDY DESIGN

A. Overview

This study is a laboratory, rather than field, study. The reason for this choice is that a laboratory study provides superior control over the possible variables, and an air-sampling method intended for field use should be laboratory evaluated prior to field testing. In order to evaluate the collection efficiency of the sampling method of interest with a laboratory study, it is necessary to repeatedly generate test atmospheres with known concentrations of formaldehyde, sample the atmospheres with the sampling method, and analyze the samples and calculate the sampled concentrations. The sampled concentrations are then compared with the "known" concentrations of the test atmospheres to determine the efficiency of collection (defined as the former divided by the latter, and usually expressed as a percentage). Prior to conducting this evaluation, the concentration range to be used and the ranges of the sampling parameters to be measured (volumetric air-flow rate and sampling time) must be determined, as must the number of levels of each of these parameters and the number of replicate samples at each level needed to ensure valid results. The determination of these specifics of the design is described below, in Subpart B of this part.

Two types of vapor generating systems, static and dynamic, were considered for this study. A static generating system generally consists of a large chamber of known volume, containing clean air, into which a known quantity of the contaminant of interest is introduced; this provides a known initial concentration. As the sampling is conducted, the contaminant-laden air is drawn into the sampler and clean air must be introduced to the chamber to take its place. This causes the concentration to decay during the test, which is undesirable since a fairly constant concentration is needed to investigate the relationship between sampling performance and vapor concentration. A dynamic generating system generally consists of an apparatus into which clean air and contaminant are each introduced at a known, constant rate throughout the test period, providing a constant vapor concentration.

A special consideration with formaldehyde vapor is the need to establish an equilibrium in terms of "wall effects" - absorption of a portion of the generated vapor onto the walls of the generating system - and other efects (this is discussed later, in Section 2.a of Part VI.B), which would presumably be difficult in a situation in which the concentration is changing. A static generating system, with its large chamber, generally has a relatively large internal surface area compared to a dynamic system, further enhancing the wall effects problem. Furthermore, a dynamic system can be operated for a time period prior to the collection of samples from its output, during which an

equilibrium between the vapor and the absorbed vapor can be approached (59). The characteristics of a dynamic generating system are much more suitable for this study with respect to each of the considerations above. This is particularly true considering the excellent generation system reproducibility required to use the calculated concentration based on the feed rates to the system as the "known" concentration in the generating system, as discussed in the next paragraph. Therefore, the dynamic generation principle was chosen for this study.

Using a design as thus far described, it is necessary to establish an accurate means for determining the "known" concentration in the generating system. Either an independent sampling method of known accuracy must be employed at all times, or a calculated concentration based on the feed rates to the system must be used. The former creates practical problems related to large numbers of samples and analyses required simultaneously, while the latter may not be accurate due to metering problems or losses of vapor in the system. In order to employ solely the calculated concentration based on feed rates, there would be a need to first evaluate or "calibrate" the generating system to establish that its precision and accuracy were within acceptable bounds. It was decided to attempt such an evaluation so that the experimental portion of the study could be conducted without an independent sampling method. In general, the method used to evaluate the generation system is similar to

that described above for conducting the main experiment (collection efficiency evaluation), except it is reversed: a sampling and analytical method of well-documented accuracy and precision is used to sample the generation system output, and the generation efficiency is represented by the calculated concentration from the latter divided by the sampled concentration of the former (usually expressed as a percentage).

For this study, NIOSH Method 3500 (45) (the same one under study for changes in collection efficiency) was suitable for use in the evaluation of the generation system, as long as only the well-documented sampling procedures were used (1 L/min flowrate, 60 min sampling time). Using this method also simplified the overall study design because during each of the two phases (generation system evaluation and collection efficiency study) a combined measure of generation and collection efficiency can be documented and compared, without a need to separate the two; changes in the combined efficiency can be attributed to the sampling conditions under study since the generation system parameters can be held constant throughout.

The generation system was designed considering the temperature and pressure of the atmosphere provided to the samplers, by conscious attempts to keep the mixture at near-ambient conditions and by providing for measurement devices to ensure that such conditions were indeed provided. However, the relative humidity was neither controlled nor monitored. This is because an

impinger containing an aqueous media was used in the method under study, and the air in the bubbles entering the impinger should very quickly approach saturation (100% relative humidity) regardless of the water vapor level in the incoming atmosphere; effectively, then, humidity was not a variable.

B. Specifics of the Design

This Subpart will discuss the selection of the numerical values of the parameters which are varied in the study, first considering the numerical ranges needed to meet the study objectives, and then the statistically required numbers of values; it will also discuss the statistical requirements on other design considerations, such as replicate data needed, to assure statistical validity of the study. This discussion generally pertains to the actual experimental phase of the study (as opposed to the evaluation of the formaldehyde vapor generating system, which is discussed briefly in Part VI.B.4 and fully in Appendix B; however, the generating system does need to be able to provide formaldehyde vapor in the concentrations and quantities needed to study the sampling system as specified by this design). Of course, the final design is necessarily affected by practical considerations, and by the performance of the generating system as documented in Appendix B. The actual values used in the course of the study to meet the specifications of the design presented in this Part are presented in Part VI.B.

1. Determination of Desired Ranges of Variation for Parameters Varied in Study

a. Concentration Range

For occupational health and environmental health purposes, it would be desirable to evaluate the sampling method across a range of roughly 0.1 to 10 ppm of airborne formaldehyde simply because this is the range of the maximum airborne exposure concentration recommendations and legal standards published by various relevant organizations (see Table II-7 in Part II.E), and thus presumably the range in which the method will be called upon to perform. For practical purposes, however, the 10 ppm level (OSHA Maximum Peak) is unnecessarily high because excessive irritation at concentrations even well below this have been documented (see Part II.D.1.b), so that workers probably cannot tolerate this level. Therefore, it would not be expected to be encountered frequently. The exposure data in Part II.C confirm that, today, exposure levels rarely exceed 5 ppm. Therefore, a convenient number between 5 and 10 ppm may be chosen as the upper limit of the range. Health effects have rarely been documented at levels below 0.1 ppm (see Part II.D), so the use of the 0.1-ppm level seems reasonable as the lower limit if stable generation of this concentration can be achieved. (The generation of

formaldehyde-containing atmospheres is considered difficult (78), with the problem being greater as the levels are reduced toward 0.1 ppm (59); the wall effects (59) requiring the achievement of equilibrium (59, 135), or other problems, may be the cause).

b. Volumetric Air-flow Rate Range

Considering the study objective (see Part IV) of evaluating the collection efficiency of the sodium bisulfite solution/impinger sampling system for formaldehyde at volumetric air-flow rates below those previously evaluated, the contents of Table III in Part III.B.2, which contains data from previously published studies of this system, were reviewed to help determine what range of flowrates should be studied. (An exception to this is that the 1985 study of Balmat and Meadows (19) was published after this review and decision process was completed.) Generally, flowrates of 1 to 3 L/min have been previously studied, so 1 L/min was chosen as the upper limit of the desired range. One main purpose of decreasing the flowrate is to allow for longer sampling times (for example, up to a full 8-hr shift in industrial-hygiene sampling, instead of only 1 hr as traditionally recommended [93]) while keeping the total volume collected in the same range as when 1 L/min is used, so that the mass of formaldehyde collected remains

in the same range for similar airborne concentrations. A lower limit for the flowrate of 0.1 L/min was selected since it is a convenient value that meets the above criterion. To ensure that such a low flowrate was practical, a personal sampling pump was used to draw 0.1 L/min of air through an impinger containing 20 mL of water; it was found by visual observation and several flowrate measurements that this flowrate could be consistently maintained.

c. Sampling Time Range

As noted above, it is desirable to be able to use the sodium bisulfite solution/impinger sampling system for formaldehyde for longer sampling times (for example, up to a full 8-hr shift in industrial-hygiene sampling, instead of only 1 hr as traditionally recommended [93]), so evaluating the collection efficiency over longer times than those previously evaluated (see the contents of Table III in Part III.B.2, which contains data from previously published studies of this system) is also desirable. Generally, sampling times were not specified in the studies but were implied to be rather short (<1 hr); a 1-hr sampling time was specified in one study (135). (As noted in Subsection b, above, the 1965 study of Balmat and Meadows [19] was published after the previously published studies of this system were already

reviewed and used to help determine the range of sampling times to be studied.) The lower limit of the times studied was thus chosen to be 1 hr. Both 4-hr (half-shift) and 8-hr samples can be convenient for industrial hygienists to collect, so these were considered the desirable values for the intermediate and upper levels of sample time to be studied. Section 2, on the statistical design, provides more information on the selection of the upper limit of the range which was actually selected.

2. Statistical Design

The following criterion was used to formulate the statistical design of the experimental study: an 80% power of detecting, for one or more airborne formaldehyde concentration levels, sampling time levels, or volumetric air-sampling flowrate levels, a difference of 16 percentage points in collection efficiency from a collection efficiency of 96% (i.e., detecting a collection efficiency of less than 80%). The collection efficiency of the method under study has been documented under sampling conditions of approximately 1 L/min flowrate and 1 hr sampling time, and averages 96% (as determined for the evaluation of the generation system in Section 4 of Part VI.B); this is why detecting a significant difference from 96% when the sampling times and flowrates were varied was desired. As determined by the evaluation of

the generation system (Section 4 of Part VI.B), the generation efficiency averages 91%. It is convenient to measure the combined generation and collection efficiency (which is proportional to the collection efficiency, since the generation efficiency has been determined to be constant) when actually operating the experimental system. From the generation system evaluation, the combined efficiency under the previously documented sampling conditions was determined to be 87.3%; at the criterion level of 80% collection efficiency, the combined efficiency will be the product of that and the generation efficiency (80% x 91%), which is 72%. Thus the design was actually formulated to detect a difference of 15 percentage points (between 87.3% and 72%) in combined (generation and collection) efficiency. Also used to formulate the statistical design of the experimental study was the coefficient of variation (C.V.) of 3.7% from the generation system evaluation experiment, which is associated with the error term in the ANOVA for that data; this error term includes sampling and analytical imprecision and any other unknown variables.

The design was based upon varying the following parameters: the number of airborne formaldehyde concentration levels; the number of sampling time levels; the number of volumetric air-sampling flowrate levels; the number of replicate generations ("runs") per combination of the above three parameters; and, the number of replicate samples collected per "run."

A family of proposed study designs was developed. Each design, consisting of a proposed numerical value for each of the five parameters noted above, was subjected to a power calculation of the Analysis of Variance (ANOVA) type; if it was found to have sufficient power for this analysis, it was then subjected to a power calculation for an analysis by response-surface determination. The reason for this was the intention to use a two-step analysis, with the ANOVA performed first, possibly followed by the response-surface analysis; therefore, the chosen design needed sufficient power for both types of analyses. The purposes and details of the two analyses that were planned, and the methods used to make the power calculations for each, are described in the following paragraphs.

ANOVA -- The ANOVA around which the proposals were designed was intended to test for significant differences among the mean combined efficiencies for the various levels of each parameter (concentration, flowrate, and sampling time) and each two-way-interaction combining these parameters. Variation due to generation imprecision ("run"-to-"run" variability) would be included in the error term, as would variation due to sampling and analytical imprecision, or any other unknown variables. The power calculations used the number of degrees of freedom available from: the main effects of concentration, sampling flowrate, and sampling time (three of the parameters above); the two-way

interactions of each of these three parameters (flowrate and concentration, time and flowrate, and time and concentration); and, the error term containing the remaining degrees of freedom needed to allow for the total number of samples called for in the specific proposed design.

Replicate generation "runs" were specified (for at least some combinations of the values of the parameters) in the proposed study designs to act as the lowest level in the analysis. Variation associated with the lowest level cannot be specifically investigated, as discussed in the statistical design of the generation system evaluation in Section a of Appendix B; rather, it will appear in the error term along with other untested sources of variability. The component of variation for this source of imprecision ("run"-to-"run" variability) was investigated in the generation system evaluation (Appendix B) and found to be not significant (see also Section 4 of Part VI.B), so it is not necessary to further investigate it in the experimental phase. However, replicates were needed so that imprecision associated with "run"-to-"run" variablity in generation efficency, and other sources of imprecision, would properly be placed in the error term, thereby allowing proper testing of the variability associated with the next highest level in the analysis (the higher-order interactions). They were also needed to help provide the total number of samples needed for the designed number of degrees of freedom.

Because the results of the generation system evaluation experiment (in Section 4 of Part VI.B) indicated that the coefficient of variation (C.V.), associated with the sampling and analytical imprecision, was only 3.7%, little imprecision requiring replicate samples per "run" (to obtain an accurate average sampled-concentration value) was expected. Also, as noted in the previous paragraph, investigation of the component of variation associated with "run"-to-"run" variablity, which would require replicate samples per "run," is not necessary. Therefore, the designs initially proposed specified only one sample (no replicates) per "run" (which by definition contributes no degrees of freedom); if none of these designs had met the criteria, then designs with replicates would have been proposed (but it can be seen below that this was not necessary).

Analysis by Response-Surface Determination — The proposed ANOVA would indicate whether discreet levels of a parameter vary significantly from the other levels. However, it was recognized that also testing for significant trends in the data, by treating each parameter as a continuum (as each of these parameters are), was likely to be very informative, and could be more appropriate for the final analysis than the discreet treatment of the ANOVA. Therefore, each proposed design was also subjected to a power calculation for an analysis by response-surface determination; this type of analysis, which is based on a regression model and is

normally computer generated, can be very informative regarding trends in the data. It provides two-dimensional contour-map diagrams of the response of a selected parameter at a selected level of significance, with respect to two other parameters selected as the axes.

The power calculations used the number of degrees of freedom available from: the main effects of concentration, sampling flowrate, and sampling time (as for the ANOVA, above); the two-way interactions of each of these three parameters (flowrate and concentration, time and flowrate, and time and concentration); the quadratic terms, each related to the square of one of the three main effects (included to allow testing for significant curvature); and, an error term containing the remaining degrees of freedom needed to allow for the total number of samples called for in the specific proposed design. For the reasons discussed above for the ANOVA, the designs initially proposed specified only one sample (no replicates) per "run," which again contributes no degrees of freedom. (It can be seen below that, as for the ANOVA, above, it was not necessary to later propose designs with replicates.) So, the analysis around which the proposals were designed was intended to test for significant trends in combined (generation and collection) efficiencies between concentration levels, levels of flowrate, and levels of sampling time, between various combinations of values for each of the two-way-interaction combination parameters, and

between levels of the values squared for each of the main effects. As discussed above for the ANOVA, variation due to generation imprecision ("run"-to-"run" variability) would be included in the error term, as would variation due to sampling and analytical imprecision, or any other unknown variables.

It should be noted that the designs were formulated with the intention of performing the analyses with the aid of the General Linear Models Procedure of the Statistical Analysis System (SAS), a mainframe computer package. SAS cannot provide a contour map with more than two dimensions, but there are three main effects under investigation. Therefore, more than one diagram, each representing one discreet level of one of the main effects, were determined to be needed; in other words, one main effect could not be displayed as a continuum, but would rather have only discreet values represented. It was judged to be most important to display concentration and sampling flowrate as continua so that they could be evaluated across selected ranges; sampling times could be evaluated at discreet levels, because, even if the results of the analyses possibly indicated that one sample time should not be used, the sampling method would still be useful at the other time(s). In order to maximize the number of samples on each diagram and minimize the number of diagrams (while still providing an evaluation of more than one sampling time), the designs initially proposed specified

only two sampling-time levels; of course, if none of these designs had met the criteria, then designs with more levels would have been proposed (but it can be seen below that this was not necessary).

The best design meeting the criteria with respect to both types of analyses (ANOVA and response-surface determination) was selected. The following design was selected and used:

2 sampling-time levels

3 concentration levels of airborne formaldehyde and

3 air-sampling flowrate levels per sampling-time level

Following number of generation "runs" per combination of concentration level and flowrate level:

		Air-sampling flowrate level		
		A	B	C
Concentration level of airborne formaldehyde	A	1	1	2
	B	1	2	1
	C	2	1	1

1 air sample collected from each generation "run"

24 air samples, total

VI. METHODS

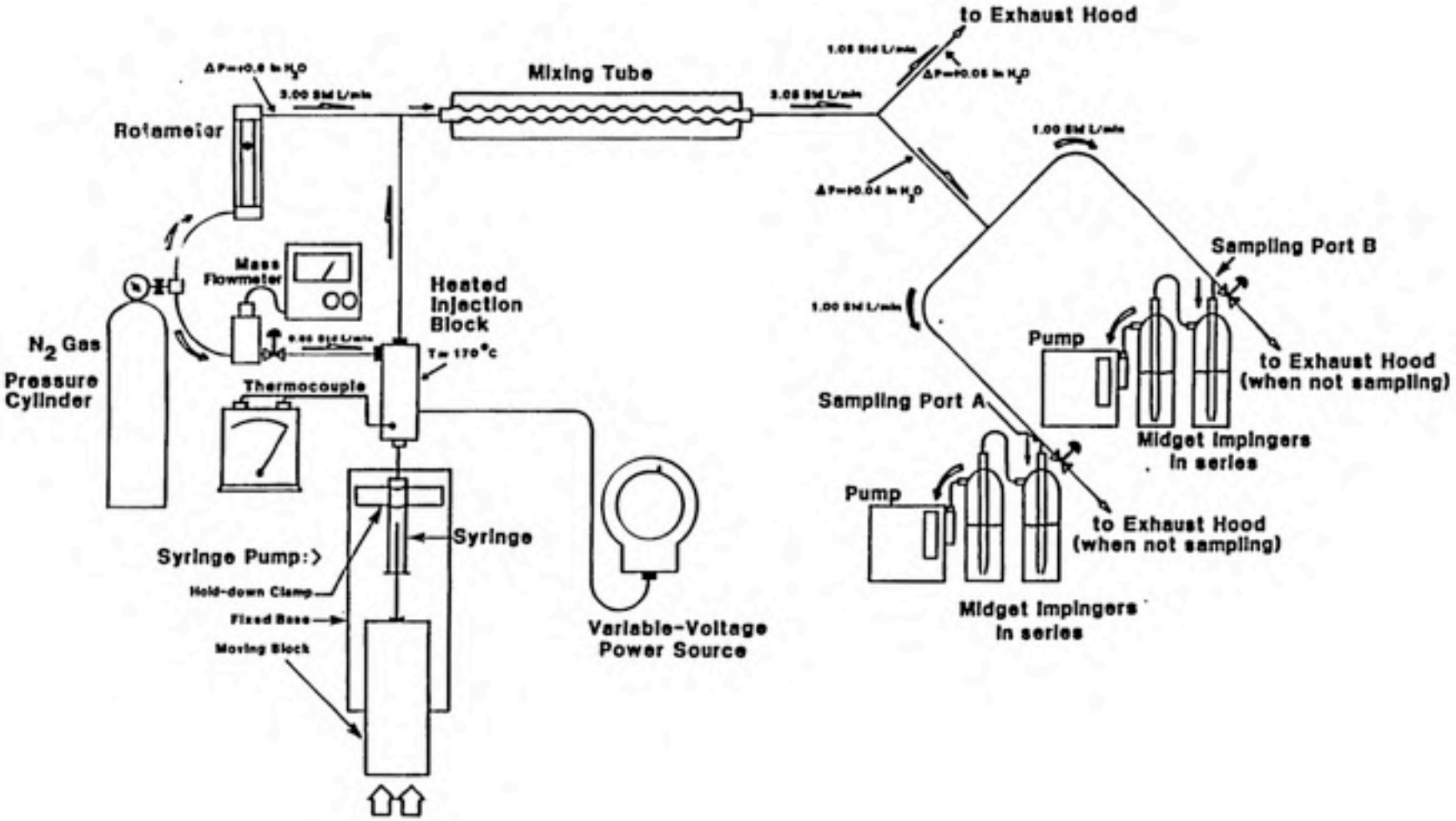
A. Apparatus Used

1. Generation System

A requirement of this study was the development of a system to generate, with good precision and reproducible accuracy, known concentrations of formaldehyde in air. The need for good reproducibility was particularly great due to the study design element, outlined in Part V, Study Design, stipulating that the generation system parameters (material input rates or quantities), rather than an independent sampling and analysis method, would be used to determine the formaldehyde concentrations.

A dynamic generation system design (as opposed to a static system) was chosen because it was considered to better meet the above requirement, along with other reasons. The reasons for this selection are fully discussed in Part V. Figure VI-1 is a schematic diagram of the generation and sampling system used in the study. Specifications for the equipment and materials are provided in Section 4 of this Subpart, "Equipment and Materials Specifications." The following is a description of the generation system and its principles of operation.

Figure VI-1. SCHEMATIC DIAGRAM OF DYNAMIC FORMALDEHYDE VAPOR - GENERATION SYSTEM AND SAMPLING SYSTEM WITH TYPICAL OPERATING PARAMETERS



The essence of the design of the generation system is the continuous direct injection, at a controlled rate, of formalin (aqueous 37% formaldehyde with 10% to 15% methanol as a stabilizer), or formalin diluted with purified water, into a carrier gas stream. The formaldehyde concentration and injected volume of the solution, the gas flow rate, and the elapsed time are all known and are used to calculate the formaldehyde concentration in the gas stream. This design is similar to ones used by Wilson (135) and Levaggi and Feldstein (78); the system hardware is in many ways quite similar to that used by the latter investigators.

The generation and sampling system is constructed almost exclusively from glass and Teflon^{R} (or Teflon^{R}-faced) materials to reduce interaction between the formaldehyde vapor and the system components. In fact, the generated mixture contacts no other material between the point of injection (at the tip of the syringe needle) and the collection media in the impingers, except for a stainless-steel fitting at the outlet of the heated injection block.

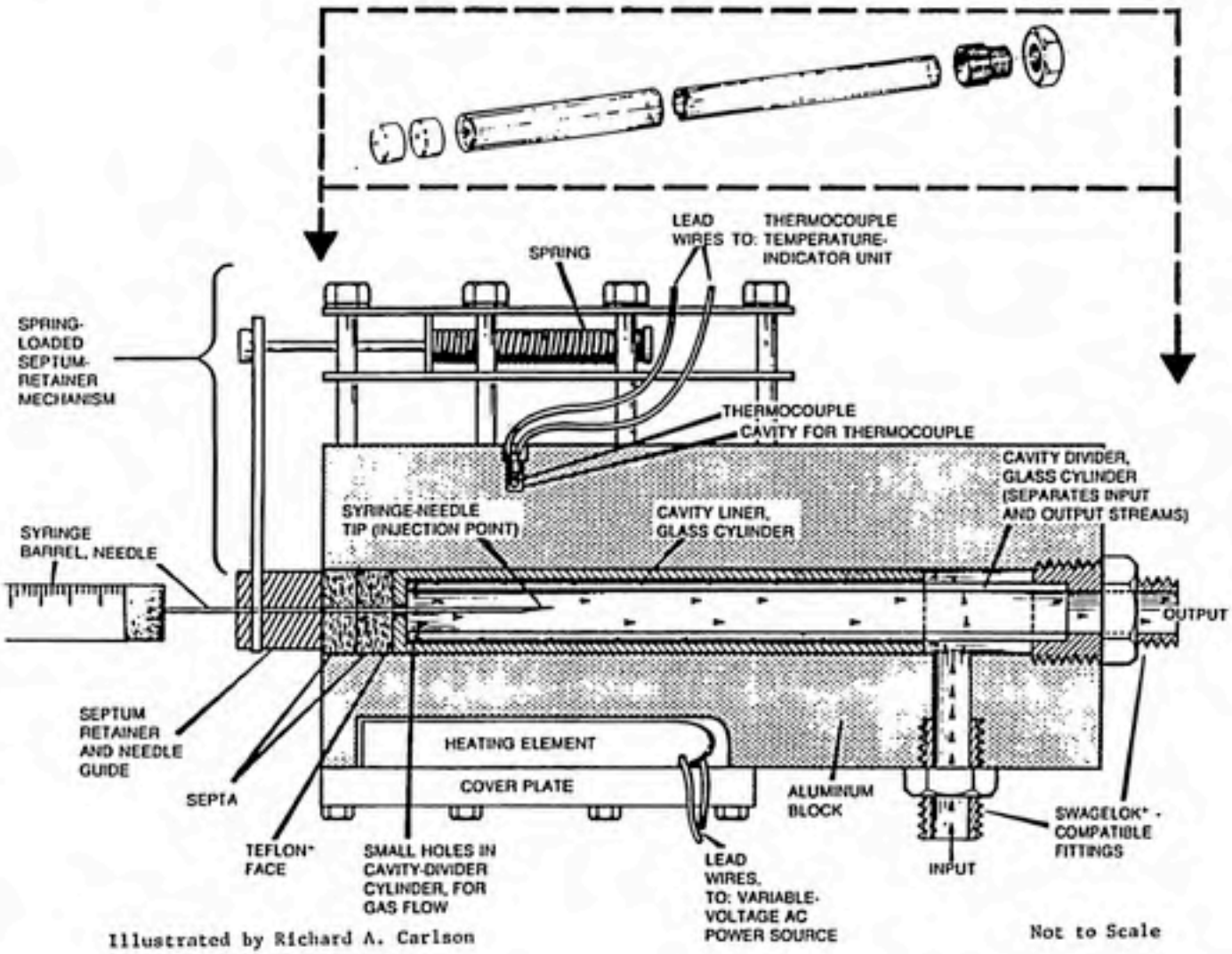
The use of purified nitrogen, rather than air, was recommended (59) as the carrier gas for this study. It is readily available in purities exceeding 99.995% and is a reasonable substitute for air, which is 79% nitrogen itself. The nitrogen is obtained in cylinders at high pressure, and a

regulator is used to control the pressure of the gas as it is discharged from the cylinder into the system. The pressure from this discharge is utilized as the motive force to move the gas through the entire generating system.

The gas, upon leaving the regulator, is piped to a brass Swagelok^{R} "T-fitting," where the flow is split. A portion of the flow is routed via 3/8-in.-I.D. Teflon^{R} tubing, through a needle valve to the transducer of the mass flowmeter, then to the heated injection block. The gas must follow a rather tortuous path through small passages within the injection block (see Figure VI-2), so the flow rate is restricted to less than 100 cc/min (0.100 L/min).

The total gas flow rate through the system is much greater than this (see Subpart B of this Part, "Procedures," for information on the flow rates actually used), and the remaining gas flow, originating at the Swagelok^{R} "T-fitting," bypasses the heated injection block. This stream moves through 1/4-in.-I.D. Teflon^{R} tubing, past the bulb of a mercury thermometer (located in a Nalgene^{R} "T-fitting") to check for temperature decreases due to the expansion to lower pressure, through the rotameter, to a glass "T-fitting." There is rejoins with the output stream from the heated injection block, diluting the formaldehyde concentration that the output stream contains. The combined, formaldehyde-containing gas stream then enters the mixing

Figure VI-2. Drawing of Heated Injection Block with cutaway showing internal passages and gas flow path, and exploded view of internal parts.



Illustrated by Richard A. Carlson

Not to Scale

tube, which is discussed later in this Section. The rotameter has a needle valve, for flow control, upstream from the tapered tube and float ball. A static pressure tap connected to a manometer is located just downstream from the rotameter. It is used to determine the pressure and thus the density at the rotameter float so that corrections to the flow rate can be made.

The heated injection block, shown in Figure VI-2, is a machined aluminum block with threaded openings (for special Swagelok^{R}-compatible fittings) for the gas inlet and outlet, a straight-bore opening for insertion of a septum, and an external cavity in which the heating element is placed. The heating element is held in place by an aluminum cover plate. There is also a septum retainer that also acts as a syringe-needle guide, which is attached to a spring-loaded mechanism that is bolted to the block. Internally, there are two special glass tubes that line the internal cavity and direct the flow, as shown in the Figure. A 9.5-mm-diameter Teflon^{R}-faced septem is used.

The injection block was slightly modified to allow a thermocouple to be attached so that the temperature of the block can be determined. This was done by drilling a small hole in the block, just large enough so that the thermocouple end would snugly fit into it. This was done at a location aligned with the center (with respect to the long dimension)

of the heating element, about halfway between the exterior wall and interior cavity of the block, and was sunk to a depth roughly one-half the thickness of the block. The outer portion of the hole was enlarged to allow the insulation on the lead wires to easily fit into the hole. The wires lead to the temperature indicator unit. The thermocouple end was seated in the hole along with a heat-transfer material (a paste-like substance) to allow good contact between the block and the thermocouple, and the lead wires are retained in the hole by an epoxy-type cement.

Electrical power to the heating element is provided and regulated by a variable-voltage transformer which in turn operates on standard AC power. The voltage to the element is manually adjustable to obtain the desired block temperature.

A Hamilton^{R} 10-ul syringe with Teflon^{R}-tipped plunger, glass barrel, and stainless-steel removable needle is used to deliver the formaldehyde-containing injection solution. The removable needle has a Teflon^{R} ferrule. During injection, the syringe needle is pierced through the septum to a depth that places the needle tip (i.e., injection point) adjacent to the center (with respect to the long dimension) of the heating element and to the thermocouple-end location. This is done so that the injection-point temperature is as close as possible to the measured temperature.

The continuous injection of the syringe contents at a controlled rate over a period of time is accomplished with a syringe pump. This device is composed of: a fixed base, containing a motor, controls, reduction gears, and a holder to fix the position of the syringe barrel; and a movable plastic block which slowly moves against the syringe plunger button, depressing the plunger and ejecting the injection solution. A rack-and-pinion gearset, with the pinion on the output shaft on the base and the rack inside the movable block, transmits the motive force from the motor to the block. Speed is adjustable with a three-range switch and a continuously-adjustable knob.

As discussed earlier in this Section, the formaldehyde gas mixture, after injection and dilution, enters the mixing tube. This is provided to ensure that a homogeneous, uniform-concentration mixture reaches the sampling ports downstream. The mixing tube is actually a glass condenser, with the coolant jacket empty and the gas flowing through the center section. The constrictions and expansions in this section create turbulence which ensures complete mixing (62).

Upon leaving the mixing tube, the gas enters the sampling manifold, with the excess routed through the exhaust line to a laboratory hood, as shown in Figure VI-1. Notice that the two sampling ports each receive flow via identical routing; this is done to ensure that pressure drops are the same to

each sampling port. This prevents "starvation" of a sampling port, the creation of low pressure at its inlet so that the flow rate is less than expected. If only one sample must be collected from a given generation "run" (as described in Section 5 of Part VI.B, below), no physical modification is made to the sampling manifold; rather, one port is clamped off, simply diverting a larger portion of the gas flow to the exhaust line. The flow into the sampling port(s) is caused and controlled by the vacuum sampling pump(s) on the sampling train(s), discussed in the next Section. A static pressure tap connected to a manometer is provided at the sampling manifold.

2. Sampling Trains

The schematic diagram of the generation and sampling system, Figure VI-1, shows the location and configuration of the sampling trains. Specifications for the equipment and materials are provided in Section 4 of this Subpart, "Equipment and Materials Specifications."

The sampling equipment is essentially identical to that used in industrial hygiene field measurements. Each sampling train consists of two midget impingers, each containing 20 mL of aqueous 1% sodium bisulfite, connected in series by 1/4-in.-I.D. Teflon^{R} tubing and attached to an SKC^{R} Universal personal sampling pump via Tygon^{R} tubing of the

same I.D. The tubing to the pump contains a static pressure tap connected to a manometer to estimate the pressure drop across the sampling train. The inlet to the first impinger in series is connected to the sampling port of the generating system, a 1/4-in.-I.D. Teflon^{R} tube. The impingers used were each determined to have a nozzle-to-base distance of 5 mm.

The pumps used, SKC^{R} Universal personal sampling pumps, are designed to operate in a constant-volume mode. They automatically compensate for changes in pressure drop at the inlet during use, to maintain the volumetric flow rate determined from a calibration. The pumps, although battery-powered, are connected to an SKC^{R} recharger unit during use to prevent any change in flow rate due to variations in battery voltage.

3. Analytical System

The samples are analyzed with the spectrophotometric procedure described in NIOSH Method 3500 (45) (formerly NIOSH P&CAM 125 [93]), a copy of which is provided in Appendix E, using the equipment and materials named therein. These items include reagents, such as chromotropic acid and sulfuric acid, associated laboratory glassware (which is generally Pyrex^{R} or Kimax^{R}, and is Class A when necessary for volumetric measurements), and a spectrophotometer.

The spectrophotometer is a Beckman[R] Model 25 double-beam instrument, with provision for the use of a vacuum-operated "sipper cell." The sipper cell is a special cuvette with small tubing ends and internal passages which allow the solution ready for analysis in the sample beam to be drawn by vacuum into the cuvette, rather than requiring the operator to open the sample-compartment door and manually remove, fill, and replace the cuvette. The double-beam feature allows a cuvette containing a color-developed reagent blank to be placed and left in the reference beam during analysis; this allows the absorbance of the reagent blank and the sample to be compared, giving an absorbance reading which represents the additional absorbance (over the reference [zero] level) provided by the sample in the sample beam. The use of the instrument is described more fully in the subsequent Subpart B, "Procedures." The specifications for the spectrophotometer as well as for the other equipment and materials used in the analytical system are provided in the next Section of this Subpart, "Equipment and Materials Specifications."

4. Equipment and Materials Specifications

The specifications for the equipment used in the generation, sampling, and analytical systems, and discussed in Sections 1, 2, and 3, are provided in Table VI-1. Also provided in Table VI-1 are specifications for other equipment used in the

Table VI-1. Equipment Specifications

Item	Manufacturer, Model Name and Number	Size or Measurement Range	Serial Number	Specifications
Spectrophotometer	Beckman Instruments, Inc., Model 25/1331 Ultraviolet/Visible Digital Reading and/or Recording Spectrophotometer	0.000 to 2.000 Absorbance Units (AU); 190 to 700 nm (wavelength)	1001365	Double-beam optical principal Wavelength accuracy ± 0.5 nm Photometric accuracy 0.5% of reading, or 0.001 AU, whichever is larger Stability better than 0.004 AU/hr Range: effective lower limit is 0.010 AU*; optimum is 0.3 to 1.2 AU
Rotameter	Union Carbide Corp., Linde Division. Part No. 201-4334 tube.	0 to 150 scale units	---	Approximately 3 L/min (air) at 80 scale units
Mass flowmeter	Teledyne Hastings-Raydist, Hastings Mass Flowmeter Model LF-100	0 to 100 std. mL/min (air) nominal flow rate	3085	The transducer is matched to the receiver unit. It is Hastings Mass Flow Transducer Model F-100, Serial 3988.
Syringe	Hamilton 1701RN Gas-tight Syringe	10 uL	---	Gas tight, Teflon^{R}-tipped plunger, removable needle.
Automatic pipette	Eppendorf 4710	100 to 1000 uL	013723F	Adjustable range (in 1-uL increments) of volumes. Polypropylene disposable tips. Accuracy ± 1.0 to 0.5%. Precision ± 0.7% (<150 uL) ± 0.5 to 0.2% (≥150 uL)
Septum	Supelco, Inc., Microsep^{R} F-174	9.5-mm diameter	---	Teflon^{R}-faced
Mixing tube	(unknown manufacturer), condenser	---	---	Dimensions: Length: 22-1/4 in I.D.s = inlet/outlet: 3/8 in constrictions: ~1/8 in expansions: ~ 1-1/8 in Number of: constrictions: 9 expansions: 8

Table VI-1. Equipment Specifications -- Continued

Item	Manufacturer, Model Name and Number	Size or Measurement Range	Serial Number	Specifications
Heated injection block	Hamilton GC port	---	--	Dimensions of aluminum block: 8 cm x 2.5 cm x 2.5 cm Fittings: stainless steel Liner and internal guide: glass
Pumps	SKC, Inc., Universal Sampler Model Aircheck I	1 to 3500 mL/min airflow rate	---	Constant flow control Pressure range: Flowrate, mL/min: 500 / 1000 / 2000 / 3000 / 3500 Maximum pressure drop, in H_2O: 25 / 30 / 20 / 15 / 8
Syringe pump	Sage Instruments, Model 355	---	---	Block moves approximately 2.6 cm/hr**
Variable-voltage autotransformer	Staco Energy Products Co., Type 3 PN 1010	0 to 140 V	8004	Input 120 V AC, 50 or 60 Hz Output 0 to 140 V AC, 10 ampere maximum
Impingers	Ace Glass, Inc., Midget Impingers	25-mL vial	---	24/40 ground glass joint, 5-mm nozzle-to-base distance
Analytical balance	Metler Instruments Corp., Model #51	0 to 159.99999g	606125	Mechanical-digital display
Thermocouple	Blue M Electric Co., Cat. No. APL-500	-18 to 340'C	---	Scale ranges: 0 to 340'C, and 0 to 630'F

* Based on experience gained during this study.

** This is the rate that the syringe pump provided during the study. The speed control was malfunctioning, and no adjustment was possible.

procedures discussed in Subpart B, "Procedures," but not specifically mentioned in Sections 1, 2, or 3. The specifications for the materials, such as chemicals, discussed in the aforementioned Sections and/or Subpart are given in Table VI-2.

Provided in Appendix D are the specifications for equipment and materials used exclusively in calibration procedures (excluding the development of the standard analytical curve for the spectrophotometer) and/or other measurements of equipment parameters. (These procedures themselves are also described in Appendix D).

B. Procedures

1. Calibrations and Other Measurements of Equipment Parameters

a. All Relevant Equipment Except Spectrophotometer

Descriptions are available in Appendix D of the methods used to calibrate instruments such as the rotameter, mass flowmeter, sampling pumps, and others; also available there are descriptions of the procedures used to determine other equipment parameters such as the nozzle-to-base distances of the impingers.

Table VI-2. Materials Specifications

Item	Specifications
Chromotropic acid (CTA) reagent, aqueous 0.1%	Ingredients: Fisher Scientific Co. C-613 Certified A.C.S. Chromotropic Acid Sodium Salt, Lot 745265; filtered/distilled water
Absorbing solution, aqueous 1% sodium bisulfite ($NaHSO_3$)	Ingredients: Fisher Scientific Co. S-654 Certified A.C.S. Sodium Bisulfite, Lot 736103; filtered/distilled water
Formalin	Fisher Scientific Co. Certified A.C.S. Formaldehyde Solution, 37% w/w: Lot 850007, actual assay 37.0%; "Baker Analyzed" A.C.S. Reagent Grade Formaldehyde Solution, 37% w/w: Lot 233611, actual assay 37.2%. Both contain 10 to 15% methanol.
Formaldehyde Standard Solution "A"	1.00 mg formaldehyde/mL aqueous solution; Ingredients: Formalin, filtered/distilled water
Formaldehyde Standard Solution "B"	10.0 ug formaldehyde/mL solution; Ingredients: Formaldehyde Standard Solution "A", 1% $NaHSO_3$ Absorbing Solution
Injection solutions	Formaldehyde concentrations of 4.99 and 5.17, 20.0 and 20.7, 79.8, 170, and 319 mg/mL solution; Ingredients: Formalin, filtered/distilled water.
Distilled water	Produced using an all-glass-and-Teflon^R distiller by boiling tap water, condensing steam with a tap-water-cooled condenser, collecting condensate.
Filtered/distilled water	Obtained from NIOSH Division of Physical Sciences and Engineering; they filter tap water with a Milli-Q^R water filtration system (by Millipore Corp.), then distill the filtrate as described above for "distilled water".
Carrier gas (purified nitrogen [N_2])	99.995% pure nitrogen

b. Spectrophotometer

Two important operations were required to prepare the Beckman Model 25 Spectrophotometer for use in the analysis of the samples generated in this study. The major one of these was, of course, the preparation of a standard analytical curve, or "calibration curve". This operation will be discussed in subsequent paragraphs. Prior to this work, however, it was important to test the performance of the instrument in three crucial areas against objective standards (105). These areas are wavelength accuracy, absorbance accuracy, and photometric linearity. The methods used to test these areas of performance are specified by the manufacturer, Beckman Instruments, Incorporated (105), and are discussed in Appendix D. It was recommended that the performance tests be repeated quarterly (27). In this way, continued accuracy of the instrument readings is assured.

The preparation of the standard analytical, or "calibration," curve was generally performed in the manner described in NIOSH Method 3500 (45) (see Appendix E for a copy of this method). Briefly, this involves the preparation of "spike" solutions of known formaldehyde concentrations in 4 mL aliquots by diluting formaldehyde standard solution "B," also of known concentration, with absorbing solution. Formaldehyde

standard solution "B" is simply a known dilution (also with absorbing solution) of standard solution "A", which is in turn a known dilution of formalin, the commercially available aqueous 37% formaldehyde solution (see Table VI-2 for the specifications of the formaldehyde-containing solutions as well as the sodium bisulfite absorbing solution). Each "spike" solution contains one of the following quantities of formaldehyde: 0.00, 1.00, 3.00, 5.00, 7.00, 10.0, 12.0, 15.0, and 20.0 ug. The "spike" solutions are reacted with chromotropic acid, followed by sulfuric acid, to develop the characteristic color, and the color-developed solutions are analyzed in the spectrophotometer (with the baseline, or "zero", determined by the absorbance of the non-formaldehyde-containing blank [0.00 ug]). The procedures used to develop the color and to analyze the spikes are similar to those used to analyze "unknown" samples, and are described in Section 2.d, "General Operation of the (Analysis) System," later in this Subpart (a detailed description is available in the NIOSH Method, in Appendix E). The absorbance values read from the instrument are plotted against the formaldehyde mass values to form a standard analytical curve.

Five standard analytical curves were initially generated, with the intention of combining the data to obtain a composite curve. The purpose of this was to obtain a

large amount of data to mask the effect of variations in dilutions and sample preparations. The composite curve then would have greater accuracy than single curves prepared at the time of analysis of each group of "unknown" samples.

Several steps were initially taken, and are taken during system operation, to ensure that the composite calibration curve remains valid over the time period during which it was generated and used. In order to determine that any variation in the calibration curve data was not due to variations in the instrument performance, a brief performance check was conducted prior to use of the instrument on each day that calibration data was generated. This daily performance, or "calibration," check is simply a portion of the instrument performance tests discussed earlier in this Subsection (and described in Appendix D). Specifically, the test for absorbance accuracy is performed, but only at a wavelength of 590 nm. This wavelength was chosen because, of the wavelengths specified for the complete performance test, it is the closest to 580 nm, the wavelength used in the actual analysis. This daily calibration check is also repeated, again daily, prior to the use of the instrument to analyze "unknown" impinger samples from the generating system during subsequent phases of the study. This ensures that no inaccuracy is

introduced to the results of the analyses by variations in instrument performance. Periodically when the instrument is being used to analyze samples, additional "spikes" are prepared and compared to the composite calibration curve. This provides an additional check on the validity of the curve, as other sources of variation besides changes in instrument performance can be detected, such as problems with the chemicals. These last two procedures act as an effective "recalibration" of the standard analytical curve.

The raw calibration-curve data are presented in tabular, as well as graphical, form in Appendix A. These data were handled in such a manner as to produce the most accurate composite calibration curve possible. First, all data from the first calibration curve (Run 1) was deleted, leaving Runs 2 through 5. The reasons for this deletion include visible variation (28) of the plotted data from a reasonably smooth curve (which is especially noteworthy given the fact that the data were generated on the first day of analytical work and the technique used was not refined) and slight problems with "zero drift" in the instrument. Second, data were generated at 12.0 ug formaldehyde in Runs 4 and 5, although this level had not been included in the first three runs, while 20.0 ug, a level generated in the first three runs, was not used in the last two. The reason this was done is that the

results of the earlier runs were plotted, and the response appeared to deviate from linearity rather substantially at the higher concentrations. As noted previously in the documentation of the analytical method (Part II.F.3), previous investigators have noted an essentially linear response for this analysis (4, 84). Therefore, it was determined to be unwise to use the portion of the curve with the more obvious (although not extreme) deviation from linearity (28), and desirable to more clearly define the intermediate area of the curve where it appeared that the deviation from linearity (if true linearity anywhere existed) began. Finally, after all data were collected and the results plotted, it was decided that only the portion of the data between 0.00 ug and 12.0 ug would be utilized for the composite calibration curve. Although the entire curve had a clear, but very slight, curvature, the portion above 12.0 ug had more curvature and much greater variability within the data. Limiting the usable portion of the curve does not create problems with its use in analyzing samples because samples can be diluted by a known factor to decrease the absorbance value of the color-developed solution to a lower value that lies within the usable portion. The data set used to construct the composite calibration curve is also presented in tabular, as well as graphical, form in Appendix A.

The data used to construct the composite calibration curve were analyzed statistically for three reasons: to test for variation from run to run (and investigate other sources of variation), to investigate selected models to determine the line or curve of best fit, and to document the predictive value of the chosen curve. The analyses were performed with the aid of the General Linear Models Procedure of the Statistical Analysis System (SAS), a mainframe computer package. A description of the tests performed, the results of these tests, and the interpretations of the results is included in Appendix A, but a brief description of these items is presented in the following paragraphs, along with the conclusions reached.

The data were subjected to an analysis of variance (ANOVA) to determine if "run" was a significant source of variation. No significant variation was found from run to run ($p = 0.0829$), and this fact allowed the final decision to combine the data from all four runs to create the composite calibration curve. Although the differences from run to run were not statistically significant, the rather low "p" value creates suspicion that, in fact, very slight run-to-run variations exist, and that all the variation is not due to sample-to-sample differences in the "spikes". If this suspicion were true, its implications support the use of a composite

calibration curve, because slight run-to-run variation could be partially caused by slight imprecision when preparing formaldehyde standard solution "B," and the composite curve is more representative of the true situation than any single curve affected by this imprecision. A subjective examination of the data supports this contention, since even two runs chemically analyzed during the same session, but with the use of different "B" standard solutions being the only known difference, appeared to have slightly differing slopes.

The combined data were subjected to regression analyses, both first and second order (linear and quadratic forms, respectively). The quadratic form was considered because it was recommended that, if the data supported the use of a slightly curved model, it was not necessary to impose a linear model upon it (28).

The correlation coefficients for the both the linear and quadratic form were extremely good (0.996 and 0.999), as were subjective evaluations of fit (for the quadratic form, this can be seen using Figure VI-3 discussed below). However, as discussed in Appendix A, the intercept of the quadratic model did not vary significantly from zero (while that of the linear model did), and significant curvature was indicated by the fact that the quadratic-term coefficient (in the quadratic

Figure VI-3. Spectrophotometric Composite Calibration Curve from Quadratic Equation (with "mean-values" estimated curve). (a) Full View.

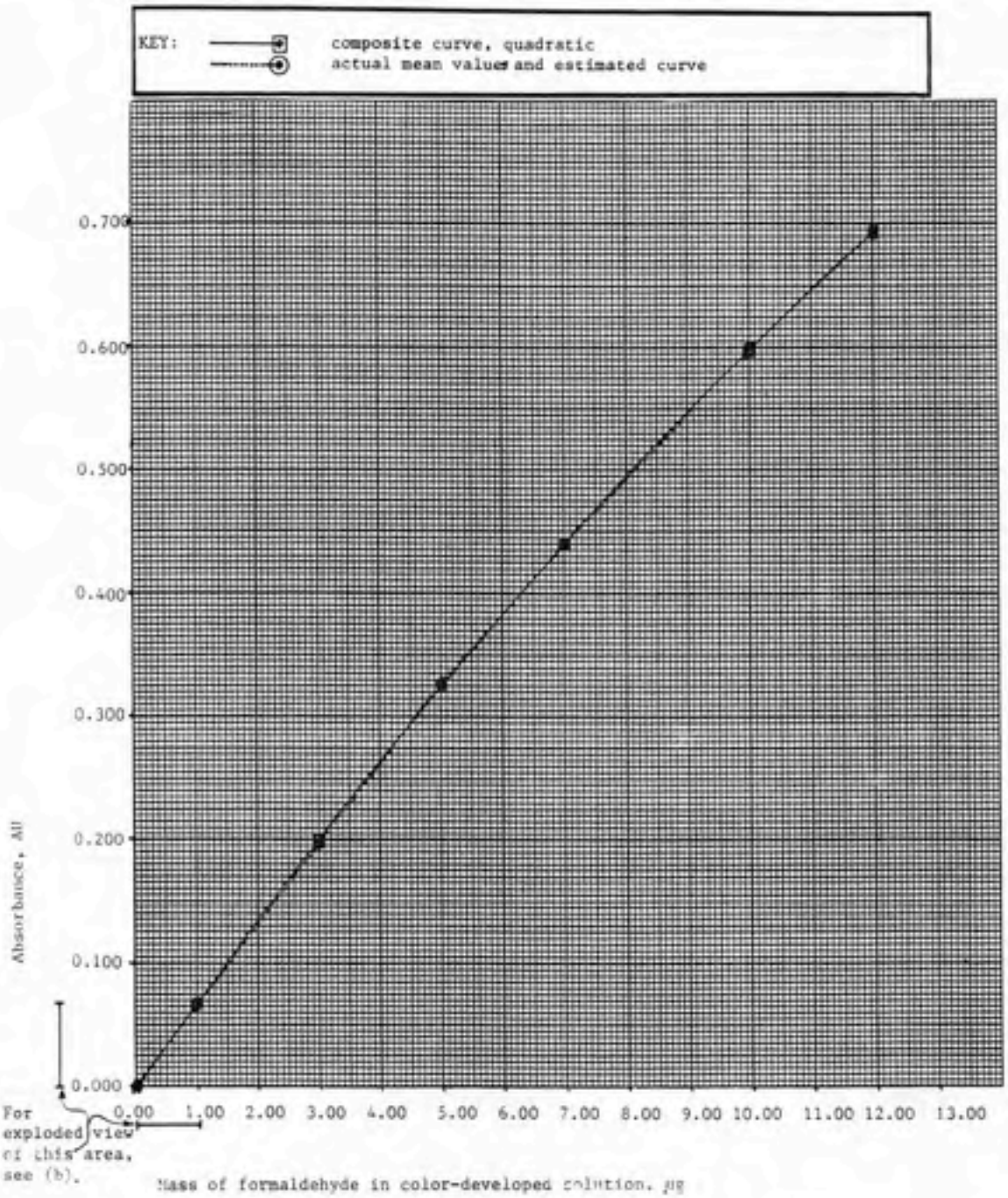
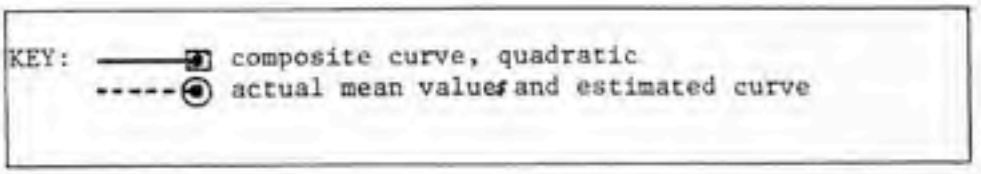
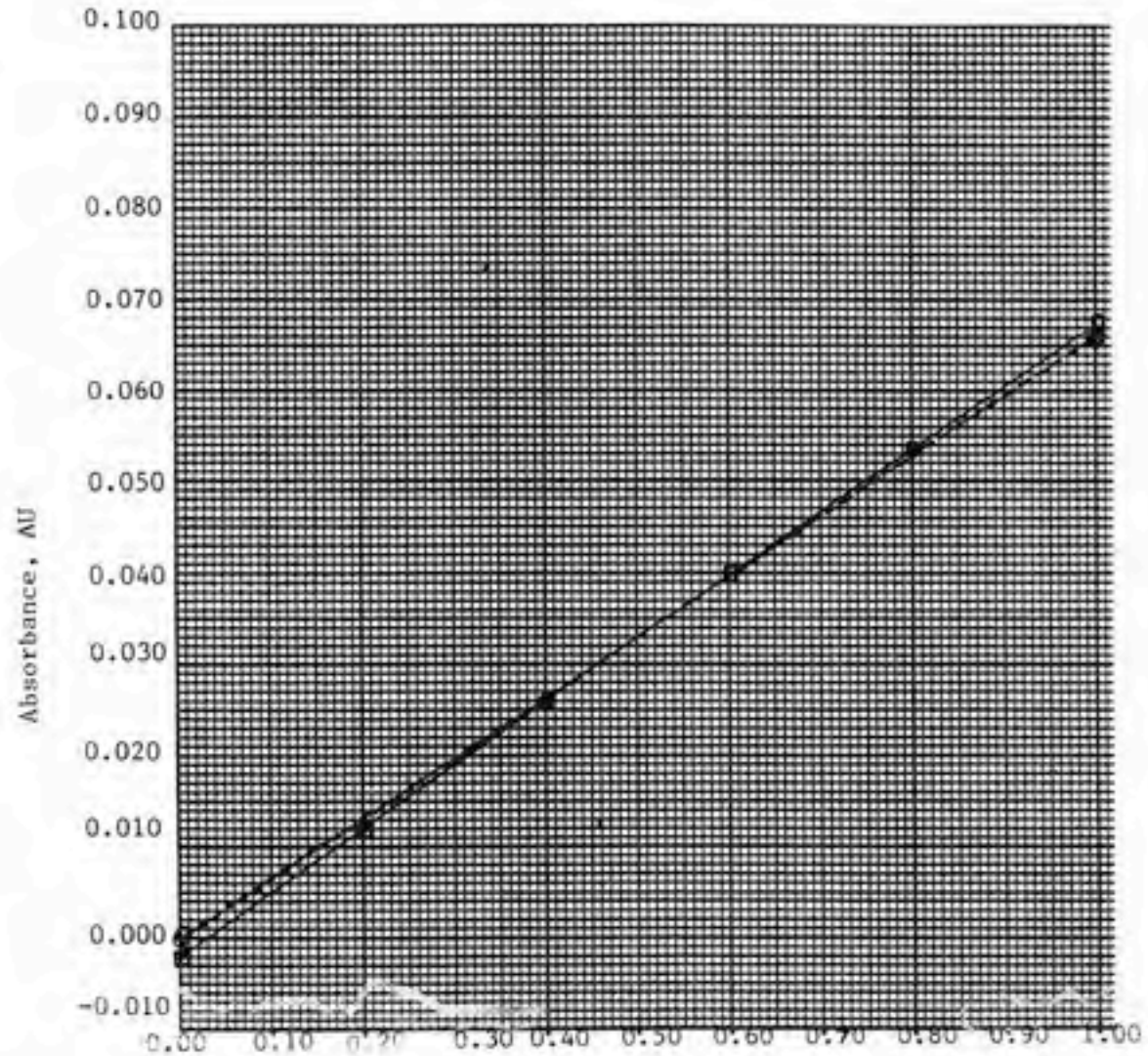


Figure VI-3. (b) Exploded View, Low Concentration. Spectrophotometric Composite Calibration Curve (with "mean-values" estimated curve).





model) did vary significantly from zero. These two findings provide substantial justification (and the latter one provides necessary justification) for selecting the quadratic model to represent the composite calibration curve. Therefore, this model was chosen.

The equation representing the chosen curve was provided by the computer program, and is given, in the form provided, in Appendix A. The curve is plotted in Figure VI-3, along with an estimated curve based on the mean values from Runs 2 through 5 (these values are from Table A-2 in Appendix 2) for comparison. When rearranged to allow its use to determine, from absorbance values, the values of formaldehyde mass in samples, the equation becomes: $x = 33.6 - \sqrt{1120 - 952y}$, where x = mass of formaldehyde in the color-developed solution (ug) and y = absorbance (AU). The composite calibration curve is valid between 0.000 and 0.693 AU, corresponding to 0.00 through 12.0 ug formaldehyde.

The use of the quadratic-estimated curve at very low levels presents a problem because its calculated y-intercept is not exactly zero (see exploded view [b] of Figure VI-3). Therefore, when samples are analyzed, the companion line in that Figure, a linear segment connecting the points (0.00, 0.000) and (1.00, 0.066), and representing the mean values for Runs 2 through 5, is

used whenever the absorbance reading is less than 0.033 AU, the approximate point where these curves cross. Between 0.000 and 0.033 AU, the "mean of the Runs" curve has more physical relevance because it crosses the origin as the "true" curve must (see discussion in Appendix A). Although this adjustment allows the curve to be used essentially down to 0.000 AU, values below 0.010 AU can be greatly affected by electronic "noise" and/or zero drift in the spectrophotometer. These respective items can sometimes affect the reading by 0.001, and up to 0.002 or 0.003 AU (10%, and 20 to 30%, respectively, at 0.010 AU). In fact, any reading below about 0.050 AU could be imprecise by up to 8% due to these effects.

2. General Operation of the Generation, Sampling, and Analysis Systems

a. Generation

Prior to the startup of the generating system for a "run" (or a group of runs), a formaldehyde-containing injection solution is prepared if a fresh supply having the desired formaldehyde concentration is not on hand. The injection solution is made by diluting formalin (of known concentration) with high-purity distilled water, and the resulting solution has the proper formaldehyde

concentration to provide the desired vapor-phase concentration when injected at a constant rate of 0.072 uL/min into the carrier gas flowing at a constant rate of 3.02 L/min.

Startup begins by turning on the mass flowmeter and allowing it several minutes to warm up. The valve on the gas tank is opened to the pressure regulator, and the output pressure is adjusted (with the output valve closed) to a low pressure, slightly above atmospheric, approximately 5 psig. This pressure is more than sufficient to move the gas through the entire system. The exhaust valves of the system (including the main, sample port, and bypass) are opened, the regulator output valve is opened, and then flow through the heated injection block is begun by slowly opening the valve at the mass flowmeter.

The heating element is then energized by turning on the electrical power to the Variac controller. The needle (control) valve at the base of, and upstream from, the rotameter is then slowly opened until a volumetric flow rate of 2.97 L/min is indicated, by the rotameter, through the portion of the system which bypasses the injection block. A volumetric flow rate of 52.7 cc/min (0.0527 L/min) through the injection block, as measured by the mass flowmeter, is then established. The

indicated total flow through the system is then about 3.02 L/min. The temperature of the heated injection block is monitored using the thermocouple, and is manually regulated to 173°C (±3°C maximum) using the Variac to control the current.

While the injection block temperature is rising toward its set point, the 10-uL syringe is filled with injection solution. (More than 10-uL of solution is drawn into the syringe, and the extra volume of solution in the ungraduated portion of the syringe barrel is used during the system conditioning phase [below] so that plenty of solution will remain in the graduated portion when the sampling portion of the run begins). Care is taken to assure that no air bubbles are present. The syringe is clamped to the holder on the syringe pump. When the block temperature reaches 173°C, the syringe and pump are moved forward so that the syringe needle pierces the septum on the injection block, and the needle's tip is close to the center of the heating element, and the thermocouple end, in the block. The movable block of the syringe pump is then placed so that it is in contact with the syringe plunger, the pump is switched on, and the movable block begins moving at an approximate rate of 2.6 cm/hr; for the Hamilton syringe used, this provides a liquid discharge rate of approximately 4.3 uL/hr (0.072 uL/min).

The generation system is now operating. It is allowed to proceed this way prior to the start of sampling for a conditioning period of at least 30 min. During this time the dilute formaldehyde-in-air mixture fills the system and has time to approach equilibrium (135), in terms of wall effects and any other considerations, so that a steady-state concentration is being provided to the sampling ports when sampling begins. All relevant parts of the system are in contact with the formaldehyde-containing air, except for the small portion of the sampling ports downstream of the shut-off clamps, and the impinger stems themselves.

When sampling is to begin, the impingers are connected to the sampling ports and the sampling port exhaust clamps are closed. Then, in rapid sequence, the sampling port clamps are opened, the pumps are connected to the impinger output tubes, the syringe volume is read and recorded, and the time is recorded. The injection block temperature and the flow rates through the mass flowmeter and rotameter are continually monitored and adjusted when necessary during the sampling period. Also, static pressures at the five pressure taps are intermittently checked and recorded so that any changes in pump performance or other problems can be detected, as well as to allow for any pressure corrections needed. The maximum pressure elevation above atmospheric is found at

the rotameter; the highest reading at that point has been 0.8 in H_2O.

When the sampling period is complete, and sampling is to be ended, in rapid sequence the syringe pump is shut off, the pumps are disconnected from the impingers, and the time is recorded. Then, the syringe is very carefully removed from the syringe pump's hold-down clamp and its volume is read and recorded. The sampling port clamps are then closed, and the clamps on the sampling port exhausts are opened. If another sampling run at the same concentration is to be conducted, the syringe is quickly refilled (to a volume exceeding 10 uL, as before) and injection is restarted so that the equilibrium concentration is quickly reestablished. If another sampling run at a higher concentration is to be conducted and the higher-concentration injection solution is ready, immediate restart may also be employed (but in this case the time must be noted, as a conditioning period at the higher concentration must be allowed) after the syringe has been rinsed with distilled water and the new solution. If the system is to be shut off or run at a lower concentration, it must be purged with clean gas for at least as long as the original conditioning period. During the purge, all exhaust clamps are left open, the heat is left on, and the flow rates are kept the same as during generation operation.

When the system is to be shut down following a purge period, the heating element in the injection block is first turned off. The gas flow through the block continues until the temperature is substantially reduced. Then, the gas flow through the entire system is stopped by turning off the output valve of the pressure regulator. As soon as the residual pressure in the system has dissipated (the pressure differential at the rotameter returns to zero), the exhaust clamps are all closed; then the flow control valves at the flowmeters are closed, and the gas cylinder valve is shut.

After complete shutdown, the system is inspected visually, both externally and, where glass components are used, internally. Particular attention is given to any evidence of solid paraformaldehyde formation (due to the problems encountered in the earlier runs before heating of the injection area was used [see Section 4]). Frequently after a run (but not necessarily after every run), the injection block is removed from the system, disassembled, inspected for any evidence of solid paraformaldehyde formation (especially in the glass liner), cleaned, and reinstalled.

The calculated generation-system concentration is actually the average concentration for the sampling period, based on the ideal gas law (assuming standard

temperature and pressure, which are fixed throughout this study at 25°C [298.2 K] and 760 mm Hg [406.7 in H_2O], respectively), the total mass of the formaldehyde injected, and the total volume of air (at standard temperature and pressure) into which it went. The total mass of the formaldehyde injected is determined from the concentration of the injection solution, which was previously calculated (above), and the volume injected (from the volumes in the syringe at the beginning and end of sampling). The total volume of air (corrected to standard temperature and pressure) is found by multiplying the sampling time by the total air flow rate (corrected to standard temperature and pressure). This is obtained by correcting to standard temperature and pressure the flow rate through the rotameter, and adding that figure to the indicated flow rate through the mass flowmeter (no correction needed). The actual gas temperature used in the correction is the ambient temperature, because no significant effects on gas temperature were found due to expansion from the gas tank or from the heating element (presumably due to the mass of the apparatus through which the gas flows acting as a heat sink, and, for the latter only, the insignificant mass of the heated air compared to that of the unheated air). The actual gas pressure used in the correction is based on the measured pressure differential above atmospheric at the rotameter, and the

barometrically-measured atmospheric "corrected station pressure." All of the above calculations are shown in Appendix F. Although only an average concentration is determined it is assumed that the concentration does not vary greatly during the sampling period because experience with the syringe pump indicates that it has a reasonably constant rate of movement (and changes in motor speed can be heard), and a constant air flow rate can be assured by careful monitoring of the flowmeters and adjustment of the flow rates when needed.

b. Sampling

Prior to the startup of the sampling system for a "run," a sodium bisulfite absorbing solution is prepared if no fresh supply is on hand. The absorbing solution, which is used in the impingers as the formaldehyde-collecting medium, is prepared by dissolving a known mass of sodium bisulfite, a crystalline solid, with high-purity distilled water to a known total volume. These quantities are calculated to provide a 1% solution by weight. The specifications for this material are provided in Table VI-2. Approximately 20 mL of this solution are placed in each clean impinger; the impingers are then capped and placed in their positions adjacent to the sampling ports of the generation system.

Also prior to sampling the sampling pumps are calibrated to the desired volumetric air-flow rate (see Appendix D for a description of this procedure). The pumps are left running after calibration so that they are "warmed up" when sampling begins, and are moved to their positions near the sampling ports of the generation system. There they are connected to their battery chargers so that changing battery voltage, which could cause the flowrate to vary, does not occur during sampling.

Each air sample utilizes two impingers connected in series by a piece of Teflon^{R} tubing. Just before sampling commences, the impingers are uncapped, and for each sample, the above connection is made, the tube to the sample pump is attached to the downstream impinger outlet (but not yet to the pump; a quick-connect fitting is still disconnected at the pump), and the upstream impinger inlet is connected to the sampling port. Then, as noted in Subsection a, above, when sampling is to begin, the sampling port clamp is opened, the pump is connected to the impinger outlet tube at the quick-connect fitting, and the time is recorded. The static pressure at each pump-inlet pressure tap is intermittently checked and recorded during the sampling period so that any changes in pump performance or other problems can be detected; these readings are not used for pressure corrections for the pump flow rates, however.

Due to the constant-flow design of the pumps used, which provides for flow compensation for small changes in pump static pressure (such as the difference between the calibration system and generation system back pressures), no mathematical correction for pressure changes are needed for the pump flowrate. The maximum pressure depression below atmospheric at the pumps has been 8.2 in H_2O.

After the sampling period is complete, and sampling is to be ended, the pumps are disconnected from the impingers at the quick-connect fittings, and the time is recorded. Then, the impingers are disconnected from the sampling hoses and sampling ports, the sampling port clamps are closed, and the impingers are capped. After the generation system is properly shut down as described in Subsection a, above, the final volume of the solution in each impinger is measured in a 25-mL graduated cylinder. Each solution is then transferred to a labelled, glass-stoppered 25-mL Ehrlenmeyer flask, or left in the graduated cylinder in which it was measured (each of these is also glass-stoppered). The ground-glass joints are wrapped with Parafilm^R, and the vessels are placed in the refrigerator until they are to be analyzed.

The sampled concentration for any sample is actually the average sampled concentration for the sampling period,

based on the ideal gas law (assuming standard temperature and pressure), the volume of air sampled (at standard temperature and pressure), and the total mass of the formaldehyde collected; the latter is the combined total of the individual masses obtained from the separate analyses of the primary (upstream) and back-up (downstream) impinger solutions for the sample. The volume of air sampled (corrected to standard temperature and pressure) is found by multiplying the sampling time by the sampling air flow rate (the calibration of which, as noted above, was corrected to standard temperature and pressure, and automatically compensates for changing conditions). All of the above calculations are shown in Appendix F. Although only an average sampled concentration is determined it is assumed that the sampled concentration does not vary greatly during the sampling period from the actual concentration because experience with the sampling pumps, and careful monitoring of the pump static pressure readings, indicates that the pumps have a very constant rate of air flow.

c. Blanks

A "blank," a sample through which no gas is drawn, is prepared for each run of the generation system. This is done by pouring approximately 25 mL of absorbing solution

into a 25-mL glass-stoppered Ehrlenmeyer flask at the same time as the impingers are filled for sampling (described in the previous subsection). The stopper is placed on the flask, and the flask is kept near the impingers when they are placed in their locations for sampling. After sampling is completed, and the impinger solution volumes have been measured, and the solutions transferred to flasks, the ground-glass joint on the blank's flask is, like those for the samples, wrapped with Parafilm^{R} and the flask is placed in the refrigerator along with the samples. They are all analyzed during one session. The analytical result of a blank will be zero (within the precision of the analysis) unless some contamination occurs or some other problem manifests itself. The purpose of the blank is to detect such problems. If a positive blank value is detected, the analytical results may be adjusted by this value; see Subsection d, "Analysis," for further discussion of this.

d. Analysis

Analysis of collected samples does not need to be performed immediately. Although refrigerated samples are stable for at least 8 days (as discussed in Part II.F.3), in this study analysis is performed within 2 days of collection. Prior to analysis, any refrigerated samples are removed from the refrigerator and allowed to return

to room temperature. During this time, power to the spectrophotometer is turned on and the unit is allowed to warm up. Then, the spectrophotometer calibration is verified by conducting the absorbance-accuracy portion of the spectrophotometer instrument-performance tests described in Appendix D (at 590 nm only), as discussed in Section 1.b, to insure the continued validity of the standard analytical curve.

Each sample is prepared for analysis essentially as in NIOSH Method 3500 (45) (see Appendix E). A 4-mL aliquot of the sampling solution is pipetted into a clean, dry 15-mL glass-stoppered test tube, and 0.1 mL of 1% chromotropic acid is added. Then 6 mL of concentrated H_2SO_4 is slowly added, with caution exercised due to the exothermic reaction. However, rather than providing additional heat to raise the temperature to 95°C, the heat from the exothermic reaction is employed to bring the reaction to completion, as traditionally recommended (as in NIOSH P&CAM 125 [93]). The stoppers are placed on the test tubes during this time to protect the solutions and guard against spattering, but they are not firmly seated, so that pressure can escape. The reaction forms the purple chromogen (discussed in Part II.F.3) to be measured. After the reaction, time is allowed for cooling before analysis.

When the analytical result using a 4-mL aliquot of sampling solution (for the first step of the sample preparation) is expected to be outside of the absorbance range of the standard analytical curve of Section 1.b, a diluted solution may be prepared by using a 2- or 1-mL aliquot (instead of a 4-mL aliquot) and making up the remaining volume to 4 mL with fresh $NaHSO_3$ absorbing solution; the standard volumes (noted above) of the other reagents are then used. Likewise, if the analytical result of a color-developed solution is found to be outside of the proper absorbance range, this dilution procedure may be used with a second, smaller aliquot of sampling solution to prepare a new color-developed solution for analysis.

A reagent blank is also prepared for use in zeroing the spectrophotometer, using fresh $NaHSO_3$ absorbing solution (and larger volumes of this and the other reagents, in a 25-mL glass-stoppered flask).

All transfers are made by pipette; usually, the Eppendorf 4710 Automatic Pipette is used for volumes of 0.1 to 1.0 mL, while various glass volumetric (and, when necessary, graduated) pipettes are used for the larger volumes.

For analysis, the Beckman spectrophotometer is adjusted to 580 nm; then, its reference cell cuvette and automatic-feed sample cell cuvette are both filled with the reacted solution of reagent blank, and the instrument baseline, or "zero," is set. Solution is simply poured into the reference cuvette, but is drawn by vacuum into the sample cuvette with the automatic-feed system. Air bubbles can form in the cuvettes, and will affect the zero setting. Both cuvettes are allowed to sit for a time, to allow the bubbles to form and be removed, before the zero is set. The bubbles may be removed from the light beam area by gently tapping the cuvette along its non-transparent side. With the automatic feeder, the lamp need not be turned off after setting the zero before the first chromagen-containing sample solution is introduced, or between samples. Rather, distilled water is used to flush out the blank or previous sample while the absorbance reading is monitored, and the sample compartment need not be opened. The chromagen-containing sample solution to be measured is then introduced and sufficient volume is used to flush out the distilled water. The absorbance at 580 nm is read and recorded.

Frequent checks for zero drift are made by re-introducing additional reacted solution of reagent blank and checking the zero. At this point, the opportunity is taken to shut off the lamp and inspect the cuvettes for air

bubbles (while reagent blank solution is in the sample cell, since inspecting the cuvette requires removing it and subsequently resetting the zero), which will also affect the absorbance of sample solutions, even if no zero drift is apparent. The "field" blanks that were originally prepared at the time of sampling are prepared and analyzed in similar fashion to the impinger samples.

The absorbance of a chromagen-containing sample solution is compared with the standard analytical curve in Section 1.b, and the mass of formaldehyde per 4-mL aliquot is obtained. This mass is adjusted by the appropriate "field" blank value if necessary, and the result is multiplied by the ratio of the total sample volume (measured in Subsection b, Sampling) and the aliquot volume to give the mass of formaldehyde collected in the impinger that the sample analysis represents. The sum of the masses in the primary (upstream) and secondary (downstream) impingers represents the total mass of formaldehyde in the air sample.

3. Specific Operation of the Generation, Sampling, and Analysis Systems during the Evaluation of the Generation System

The study design discussed in Part V, and the design of this phase of the study (the generation system evaluation)

discussed in Appendix B.1, permit certain statements to be made about the operation of the systems during this phase. Since the generating efficiency of the generation system is to be tested against the "known" efficiency of the collection procedure as documented in Part III.B.2, the sampling systems will be run only at the volumetric flowrate of 1 L/min and for the maximum time of 60 min traditionally recommended (93); these conditions are among the best-documented in Part III.B.2. Since the Statistical Design in Appendix B.1 calls for two samples for each generation system run, and the samples require 1 L/min each, more than 2 L/min of formaldehyde-containing gas is required to be generated if there is to be an excess to guard against starvation. This requirement is met in the procedures discussed in Section 2.a, above, as the system generates about 3.02 L/min. Since each run involves the collection of two samples, both sampling ports in the generation apparatus ("A" and "B") are used on every generation run.

As also stated above, the syringe has only 10 uL of measurable volume; however, this is more than sufficient for 60 min (1 hr) at an the specified injection rate of 4.3 uL/hr. The statistical design of Appendix B.1 also specifies that four concentration levels be used, and the general design discussed in Part V.B.1 calls for the study to cover the range of about 0.1 to 6.4 ppm (so the generation system should be effective over this range); therefore,

concentrations of 0.1, 0.4, 1.6, and 6.4 ppm were used in this part of the study.

Generally, then, the operating procedure for the generation-system-evaluation phase of the study is essentially as described in Section 2, above, as supplemented by the information in this section.

4. Evaluation of the Generation System

The generation system performance was evaluated, using data generated with the procedures of Section 3. The design of this evaluation, the calculations used, an analysis and discussion of the data, and conclusions and recommendations regarding the generation system are fully discussed in Appendix B.

It was concluded that the system precisely, and with reproducible accuracy, generates formaldehyde concentrations between 0.4 and 6.4 ppm. The combined generation and collection efficiency (which represents the generation efficiency multiplied by the collection efficiency) in this range is 87.3%. From Part III.B.2, it is known that the collection efficiency under the sampling conditions used has been determined experimentally to be from 92 to 100% (60, 87, 135), averaging 96%; therefore, the generating efficiency is calculated to be 91%, a figure judged to be

acceptable considering the high precision. The combined generation and collection efficiency at 0.1 ppm is only 80%; this was found statistically to be significantly different from the 87.3% at the higher concentrations, and the magnitude of the difference was found to exceed the criteria set in the design of this evaluation (in Section 1 of Appendix B). Therefore, it was concluded that the system is adequate for use in the range of 0.4 to 6.4 ppm, but should not be used to generate levels below 0.4 ppm.

5. Specific Operation of the Generation, Sampling, and Analysis Systems during the Experimental Sampling

The study design discussed in Part V permits certain statements to be made about the operation of the systems during this phase of the study. Since the Statistical Design in Section 2 of Part V.B calls for only one sample for each generation system run, and the maximum sampling flowrate to be tested is 1 L/min, only something over 1 L/min of formaldehyde-containing gas is required to be generated if there is to be an excess to guard against starvation. This requirement is, of course, met (as was noted in Section 3, above) in the procedures discussed in Section 2.a, above, as the system generates about 3.02 L/min. No difference was noted in the results of the generation-system evaluation for samples collected from the two different sampling ports in the generation apparatus ("A" and "B"), but for the

experimental phase port "A" is used on every generation run. During this phase, the sampling-port clamp on port "B" is never opened, while the exhaust-port clamp is opened when the system is in the conditioning and purge phases, as before, but is also left open during the sampling phase. The use of only one sampling system and one sampling port, as described here, represents a modification of the procedure described in Section 2, above.

As also stated above, in Section 2.a as well as Section 3, the syringe has only 10 uL of measurable volume; since the Study Design calls for sampling times at least as long as 4 hr (and the Statistical Design calls for two levels of time; 1 hr and 4 hr were chosen), this volume is insufficient for the specified injection rate of 4.3 uL/hr. The procedure of Section 2.a is therefore further modified as follows, when the 4-hr samples are to be collected: The startup is conducted as before, with the additional stipulation that sampling should be begun as soon as possible after the syringe first reads 10 uL. After 2 hr of sampling, about 8.6 uL of the available 10 uL will have been injected. The syringe pump is shut off (while sampling continues), and the syringe is quickly removed, read, refilled to exactly 10 uL, and reinstalled. The needle is pushed through the septum, the syringe pump's movable block is placed touching the plunger, and the syringe pump is restarted. The syringe now contains enough solution to finish the remainder of the

sampling period without further attention, and at the end of the period the procedure is the same as previously described in Section 2. The refilling operation can be accomplished in less than 1 min, so the upset of the concentration equilibrium is short lived. The calculated generation-system concentration is determined based upon the sum of the two injection volumes, and reflects the average concentration during the entire sampling period (taking into account the decline in concentration during this operation, since the gas flow continues and the volume that flows during this time is included in the volume used for the concentration calculation). The sampled concentration, also reflecting the average, will not be improperly affected.

The Statistical Design also specifies that three concentration levels be used, and the generation-system evaluation discussed in Section 4, above, and in Appendix B limits the study to the range of 0.4 to 6.4 ppm; therefore, concentrations of 0.4, 3.4, and 6.4 ppm were used in this part of the study. Also specified is the use of three sampling flowrates, which should range between 0.1 and 1.0 L/min according to the Study Design. This specification was followed for the 1-hr samples, in which flowrates of 0.1, 0.5, and 1.0 L/min were used. For the 4-hr samples, excessive dilution of the samples before analysis would be required for 1.0 L/min samples of 6.4-ppm atmospheres, so a

range of 0.1 to 0.5 L/min (specifically, 0.1, 0.3, and 0.5 L/min) was used for the flowrates tested.

Except for the modifications described in this section, the operating procedure for this phase of the study is essentially as described in Section 2, above, as supplemented by the additional information in the previous paragraph. Since samples of 0.4 and 6.4-ppm atmospheres were collected at 1.0 L/min for 1 hr during the generation-system evaluation, these samples were not duplicated during the experimental phase of the study; rather, the earlier data was re-used.

VII. RESULTS

The raw data from the experimental sampling (main experimental phase of the study) are presented in Appendix C. Table VII presents a summary of these results.

Table VII. Results summary

Nominal sampling time, hr	Nominal formaldehyde concentration level, ppm	Nominal air-sampling flowrate, L/min	Replicate "Run" number	Formaldehyde concentration, ppm (corrected to standard conditions [25°C, 760 mmHg]) generated (calculated)	sampled	Combined generation and collection efficiency, %	Calculated collection efficiency,** %
1	0.4	0.1	-	0.401	0.372	92.8	102
		0.5	-	0.402	0.345	85.8	94
		1.0	1	0.403	0.347*	86.1 } $\bar{x}$ = 87.5	95
			2	0.399	0.358*	89.7	99
			3	0.404	0.350*	86.6	95
	3.4	0.1	-	3.46	3.15	91.0	100
		0.5	1	3.46	3.00	86.7 } $\bar{x}$ = 91.0	95
			2	3.47	3.31	95.4	105
		1.0	-	3.36	2.88	85.7	94
	6.4	0.1	1	6.44	6.09	94.6 } $\bar{x}$ = 92.2	104
			2	6.44	5.78	89.8	99
		0.5	-	6.49	5.65	87.1	96
		1.0	1	6.50	5.72*	88.0	97
			2	6.36	5.70*	89.6 } $\bar{x}$ = 88.5	98
			3	6.41	5.64*	88.0	97
4	0.4	0.1	-	0.399	0.400	100	110
		0.3	-	0.400	0.334	83.5	92
		0.5	1	0.393	0.382	97.2 } $\bar{x}$ = 97.4	107
			2	0.406	0.396	97.5	107
	3.4	0.1	1	3.40	2.95	86.8 } $\bar{x}$ = 84.5	95
			2	3.31	2.72	82.2	90
		0.3	1	3.39	2.80	82.6 } $\bar{x}$ = 82.4	91
			2	3.40	2.79	82.1	90
		0.5	-	3.36	2.69	80.1	88
	6.4	0.1	-	6.27	4.40	70.2	77
		0.3	-	6.20	3.97	64.0	70
		0.5	-	6.47	6.27	96.9	106

* Average of two samples

** Based on a calculated generation efficiency of 91% (See Part VI.B, Section 4).

VIII. ANALYSIS AND DISCUSSION

The summary statistics for the data in Table VII of Part VII appear in Table VIII-1. As indicated in Table VIII-1, the mean combined (generation and collection) efficiency for all data is 87.4%, essentially unchanged from the generation system evaluation where it was 87.3%; this leads to a calculated mean collection efficiency for all data of 96%, unchanged from the average value taken from the literature (see Section 4 of Part VI.B for information on these values). However, an examination of the results of the individual observations (in Table VII of Part VII) and of the means shown in Table VIII-1 reveals obvious variation in the data set above and below the overall mean, so an analysis was undertaken to determine if this variation is purely random or is correlated with changes in the values of the factors under investigation (the sampling conditions of sample time, formaldehyde vapor concentration, and volumetric flowrate of air). Throughout the following statistical analysis, the combined (generation and collection) efficiencies are used in the statistical calculations in place of the calculated collection efficiencies (these quantities are, of course, proportional) for convenience and because the former are in fact what were actually measured.

Table VIII-1. Summary statistics for results

Description of data set	Number of values	Combined generation and collection efficiency, % mean	Combined generation and collection efficiency, % sample standard deviation	Calculated mean collection efficiency,* %
All data	27	87.4	7.9	96
All 1-hour data	15	89.1	3.1	98
All 4-hour data	12	85.3	11.2	94
All 0.4-ppm data	9	91.0	6.1	100
All 3.4-ppm data	9	85.8	4.9	94
All 6.4-ppm data	9	85.4	11.0	94
All 0.1-L/min Data	8	88.4	9.0	97
All 0.3-L/min data (4-hr only)	4	78.0	9.4	86
All 0.5-L/min data	8	90.8	6.7	100
All 1.0-L/min data (1-hr only)	7	87.7	1.6	96
1-hour, 0.4-ppm data	5	88.2	3.0	97
1-hour, 3.4-ppm data	4	89.7	4.4	99
1-hour, 6.4-ppm data	6	89.5	2.7	98
4-hour, 0.4-ppm data	4	94.6	7.5	104
4-hour, 3.4-ppm data	5	82.7	2.5	91
4-hour, 6.4-ppm data	3	77.0	17.5	85

*Based on a calculated generation efficiency of 91% (see Section 4 of Part VI.B)

A. Statistical Analysis

DIFFERENCES AMONG MEANS, Full Factorial Model - As a first step in this analysis, the data presented in Table VII were also subjected to several analyses of variance (ANOVAs), performed with the aid of the General Linear Models Procedure of the Statistical Analysis System (SAS), a mainframe computer package. The first two of these, one using the raw data and the other using the data in log-transformed form, were performed to test for significant differences among the mean combined (generation and collection) efficiencies for the various levels of each of the main effects (concentration, flowrate, and sampling time), each of the three two-way interactions (e.g., concentration level and sampling time), and the three-way interaction (all three main effects combined). Variation due to generation imprecision ("run"-to-"run" variability) is included in the error term (because the replicate generation "run"-number level is the lowest level available for the analysis and therefore cannot be tested by a lower level), as is variation due to sampling and analytical imprecision, or any other unknown variables. These ANOVAs were performed as planned in the study design (see Section 2 of Part V.B), and some additional information about them is provided in that Section. The log-transformed data were generated because it was suspected that the experimental data were distributed in a fashion more closely resembling a log-normal than a normal distribution.

The ANOVA tables for these two analyses are provided in Tables VIII-2 and VIII-3. An examination of these tables reveals significant differences among the mean combined efficiencies for the various levels of each of the main effects ($p < 0.001$) except for sampling time, each of the two-way interactions ($p < 0.004$) except for the sampling time and flow rate combination using the non-transformed data ($p = 0.0057$), and the three-way interaction ($p < 0.0018$). Also shown is that the r^2 value (r = correlation coefficient) for the log-transformed data is somewhat greater than for the non-transformed data, which indicates that the log-normal distribution is a better representation of the distribution of the data than the normal distribution. Therefore, the ANOVA using the log-transformed data (Table VIII-3) is considered the definitive illustration of the presence (and strength) of significant differences among the means of the various parameters for the full factorial model, and the log-transformed data were selected for use in a subsequent ANOVA described below.

In the interpretation of the ANOVA results in Table VIII-3, it was necessary to consider that there are many missing cells in this ANOVA since not all of the flowrates were used for each sampling time. This situation can be a cause of instability, where there is apparently excessive, statistically significant fluctuation of means from level to level of a factor, for almost all factors (investigated parameters). Furthermore, the precision (reproducibility) in the data set, as indicated by the

Table VIII-2. Analysis of Variance (ANOVA) of Raw Data with Full Factorial Model, for Differences in Means

Source	Degrees of Freedom	Sum of Squares	f value	p value
Time	1	0.00118810	1.54	0.2460
Concentration	2	0.02543559	16.49	0.0010
Flowrate	3	0.03498815	15.12	0.0007
Time*Concentration	2	0.02272697	14.73	0.0015
Time*Flowrate	1	0.01004890	13.03	0.0057
Concentration*Flowrate	6	0.03525418	7.62	0.0040
Time*Concentr*Flowrate	2	0.02144591	13.90	0.0018
Error	9	0.00694283		

r^2 = 0.957154 C.V. = 3.1776%

Table VIII-3. Analysis of Variance (ANOVA) of Log-Transformed Data with Full Factorial Model, for Differences in Means

Source	Degrees of Freedom	Sum of Squares	f value	p value
Time	1	0.00275902	2.88	0.1241
Concentration	2	0.04109599	21.42	0.0004
Flowrate	3	0.05093359	17.70	0.0004
Time*Concentration	2	0.02931737	15.28	0.0013
Time*Flowrate	1	0.01428483	14.89	0.0039
Concentration*Flowrate	6	0.05294803	9.20	0.0020
Time*Concentr*Flowrate	2	0.03039808	15.85	0.0011
Error	9	0.00863270		

$r^2 = 0.963985$

3.2% coefficient of variation (properly calculated from the non-transformed data; see Table VIII-2) is so good that even very small differences in combined efficiency are detected as statistically significant. Taken together, the above two items indicate that the analysis has a very high power to detect small differences that in turn may be present due to the instability. The magnitude and real-world meaning of the detected differences was investigated to help determine if they were important or merely a statistical anomoly.

The magnitude of the detected differences was investigated by an examination of the mean combined efficiencies for each main effect, in Table VIII-1, which reveals that among the means for the concentration levels (one of the main effects for which significant differences among means were detected) is one which is noticeably greater than the other; the converse situation (one mean noticably lower) exists among those for the levels of flow rate. These differences are, evidently, those detected by the ANOVA. It should be noted that, for the latter case, the low mean corresponds with one of the flow rates that was used at only one sampling time (leaving empty cells at the other sampling time), and it is based on relatively few samples compared with those corresponding with the other flow rates.

The magnitude of the differences detected is not extreme, with the maximum difference between any two means for concentration levels being less than 6 percentage points, and for flow rates

less than 13 percentage points. The means for the most highly significant two-way interaction (time and concentration combinations) are also shown in Table VIII-1, and the maximum difference among them is somewhat larger at almost 18 percentage points. The means for the three-way interaction are simply the means for all cells (all sets of unique sampling conditions), which can be seen in Table VII in Part VII as the combined efficiency results (and the indicated means of the replicates for those cells with replicate "runs"). Although there are large differences among some of the means of the cells, the fact that many contain only one value means that random variation may account for a portion of this, so this finding lacks importance.

Of greater importance than the maximum differences among means is the maximum difference between any mean and the combined efficiency under previously documented sampling conditions (determined in the generation system evaluation phase; see Section 4 of Part VI.B) of 87.3%. The statistical design (Section 2 of Part V.B) was intended to detect any decline from this figure in excess of 15 percentage points (which had been calculated to occur if collection efficiency declined below 80%), based on the idea that such a decline would be excessive. For the main effects, the maximum difference between any mean and the 87.3% is only about 9 percentage points. This indicates that the sampling performance is acceptable, at least, for all sampling conditions investigated; however, the related question is then posed as to whether the detected differences are true indicators

of trends which may be of sufficient importance to require, for example, the use of correction factors under certain sampling conditions, or of some other measure to account for them.

DIFFERENCES AMONG MEANS, Reduced-Size (n = 16) Model - To further investigate the nature of the detected differences in means, a separate data set of reduced size (n = 16) was created by eliminating (from the full factorial model) the data associated with the flow rates that are not in common with each sampling time, so that there are no empty cells. This removed the source of instability discussed above. This data was log transformed and the analysis was repeated. The ANOVA table is presented in Table VIII-4. An examination of this table reveals no significant differences among means associated with the main effects. This finding implies that the differences detected using the full factorial model may have been largely caused by the instability. However, all but one two-way interaction and the three-way interaction still have significant ($p < 0.05$) differences detected. It should be noted, though, that this analysis, while more ideal than that for the full-factorial model, is still "unbalanced" (i.e., unequal numbers of observations per cell) and may therefore still be somewhat unstable.

The overall mean combined efficiency for the reduced-size model, and means for the most highly significant two-way interaction (time and concentration combinations) are also shown in

Table VIII-4; the means for the three-way interaction are simply the means for all cells in the model and can be seen in Table VII in Part VII, as discussed above for the full factorial model, by ignoring the data for the 0.3- and 1.0-L/min flow rates (as they were excluded from the reduced-size model). These means were examined, to help determine the importance of the significant differences detected, in a fashion similar to that described above for the two- and three-way interactions in the full factorial model. Similar findings resulted.

Interpretation of the importance of the detected differences for the interactions was difficult, given their uncertain physical meaning and possible relationship to the presence of an unbalanced analysis. Even if these differences were to be dismissed as unimportant, it would not be valid to solely consider the lack of significant differences among the main effcets for the reduced-size model as the definitive finding while ignoring those found for the full factorial model because, although the r^2 value for the former (see Table VIII-4) suffers only slightly compared to the latter, the latter still has the obvious flaw of not using all of the data.

Therefore, it was desirable to seek further information to help clarify the nature of the differences among means for the main effects with the full factorial model (i.e., are they "real," or an anomoly of the unstable analysis) and to help interpret their physical significance. Even if the differences are "real," the

Table VIII-4. Reduced-Size (N=16) Model with No Empty Cells, using Log-Transformed Data, for Differences in Means

Analysis of Variance (ANOVA)

Source	Degrees of Freedom	Sum of Squares	f value	p value
Time	1	0.00275902	1.49	0.2895
Concentration	2	0.02226378	6.01	0.0624
Flowrate	1	0.00114024	0.62	0.4767
Time*Concentration	2	0.02931737	7.91	0.0407
Time*Flowrate	1	0.01428483	7.71	0.0500
Concentration*Flowrate	2	0.02344538	6.32	0.0577
Time*Concentr*Flowrate	2	0.03039808	8.20	0.0385
Error	4	0.00741504		

$r^2 = 0.940411$

Means

Description of data set	Number of values	Mean combined (generation and collection) efficiency, %
All data	16	89.6
1-hour, 0.4-ppm data	2	89.3
1-hour, 3.4-ppm data	3	91.0
1-hour, 6.4-ppm data	3	90.5
4-hour, 0.4-ppm data	3	98.2
4-hour, 3.4-ppm data	3	83.0
4-hour, 6.4-ppm data	2	83.6

magnitudes are still below the stated criteria, and are at discreet points without obvious trends. It would be physically implausible, though certainly not impossible, for significant changes in collection performance to occur in the middle of a range of a given factor as implied by the findings of the full factorial model, since a linear or curvilinear relationship seems likely in this situation; therefore, a determination of whether significant trends exist in the data would provide further information on the nature of these differences, and their importance to the actual use of the collection method in the field. For example, even if it were found to be acceptable under the criteria to use the method throughout the studied ranges of the various factors, a determination of the presence of significant trends would indicate if collection performance declines occur over certain ranges and thus if correction factors are needed across and/or outside of certain ranges, or if other precautions should be recommended.

INVESTIGATION OF TRENDS, Informal Examination of the Means - The initial step taken to determine the presence of trends in the data was an informal look, by reexamination of the means in Table VII of Part VII and Table VIII-1. Some possible trends were found. For example, possible trends can be seen in Table VIII-1 among the means for the concentration levels and time levels (there is variation among the flowrate-level means but no apparent trend) and for the two-way interaction of time and concentration; however, no trend certain to be statistically

significant was obvious. This finding led to a need to formally determine trends.

INVESTIGATION OF TRENDS, Formal Determination - To formally determine trends, the data presented in Table VII were subjected to four additional analyses of variance (ANOVAs), for regression analyses, treating each factor as a continuum (as each of these factors are). These were: an ANOVA using the full model (main effects, two-way interactions, and three-way interactions); an ANOVA of the log-transformed data, using the full model; an ANOVA of the log-transformed data, for the main effects and two-way interactions; and, an ANOVA of the log-transformed data, for the main effects only.

The purpose of these ANOVAs was to test the data for statistically significant trends in combined (generation and collection) efficiencies associated with each of the main effects (concentration level, sampling time, and flowrate), with each two-way interaction (e.g., concentration level and sampling time), and with the three-way interaction (all three main effects combined). To find such trends, the models were used to determine, for all main effects and interactions included in each particular model, if the line of best fit that could theoretically be plotted to represent combined efficiencies across the investigated range of a particular main effect or interaction had a significant slope. More specifically, the null hypothesis for each such line is that its slope is equal to zero,

and the testing determines if its slope varies significantly from zero. The rationale behind testing for trends in this manner is that the combined efficiency would ideally exhibit a flat (no-slope) response over the investigated range of a given factor, and it is desirable to know if that is not the case.

Insufficient data were available to properly test for significant higher-order coefficients (e.g., quadratic), which, if present, would of course indicate the presence of higher order relationships, because only three levels were measured for each factor and more than three would be needed to do this. However, it was believed that the most likely trends would exhibit at least some linearity and would thus still be detected.

The individual ANOVA models chosen were selected to allow the most conservative assessment of each level of analysis (main, two-way, etc.) by not using the statistical power of the levels below; these lower levels are instead included in the error term. In other words, the most conservative assessment of the main effects is provided by the ANOVA for the main effects only; if a significant source of variation is one of the main effects, then a simple model relating variability in the data to one or more individual physical parameters can be confidently applied.

The log-transformed data were generated for the same reason as with the first two ANOVAs (for differences in means) described in this Part: because it was suspected that the experimental data

were distributed in a fashion more closely resembling a log-normal than a normal distribution. After the ANOVAs of both the non-transformed and the log-transformed data were generated using the full model, they were compared to determine which distribution was more closely resembled by the distribution of the data; the log-normal distribution was selected as the better representation of the distribution of the data (the rationale for this selection is noted below, and was discussed previously with respect to the two ANOVAs for differences in means). Based on this selection, the log-transformed data were used for the two remaining ANOVAs (for the main effects and two-way interactions, and for the main effects only). In all of these ANOVAs, variation due to generation imprecision ("run"-to-"run" variability) is included in the error term, since the replicate generation "run"-number level is the lowest level available for the analysis and therefore cannot be tested by a lower level; variation due to sampling and analytical imprecision, or any other unknown variables, is also included in the error term.

Tables VIII-5 through VIII-8 contain the ANOVA tables from these analyses. A comparison of the r^2 values in Tables VIII-5 and VIII-6 indicates that the log-normal distribution is a better representation of the distribution of the data than the normal distribution, since the r^2 from the ANOVA of the log-transformed data is the greater of the two. Therefore, the log-transformed data were selected, as noted above, for use in the subsequent two ANOVAs (for the main effects and two-way

Table VIII-5. Analysis of Variance (ANOVA) Table for Regression Analysis of Raw Data with Full Model, for Trends (Non-Zero Slopes)

Source	Degrees of Freedom	Sum of Squares	f value	p value
Time	1	0.00344725	0.94	0.3439
Concentration	1	0.00533195	1.46	0.2422
Flowrate	1	0.00002463	0.01	0.9355
Time*Concentration	1	0.03163825	8.65	0.0084
Time*Flowrate	1	0.00128864	0.35	0.5599
Concentration*Flowrate	1	0.00610554	1.67	0.2120
Time*Concentr*Flowrate	1	0.01517688	4.15	0.0559
Error	19	0.06952686		

r^2 = 0.576147 C.V. = 6.9203%

Table VIII-6. Analysis of Variance (ANOVA) Table for Regression Analysis of Log-Transformed Data with Full Model, for Trends (Non-Zero Slopes)

Source	Degrees of Freedom	Sum of Squares	f value	p value
Time	1	0.00525230	1.01	0.3267
Concentration	1	0.00795828	1.54	0.2303
Flowrate	1	0.00000148	0.00	0.9867
Time*Concentration	1	0.04735473	9.14	0.0070
Time*Flowrate	1	0.00221540	0.43	0.5210
Concentration*Flowrate	1	0.00898586	1.73	0.2035
Time*Concentr*Flowrate	1	0.02224266	4.29	0.0521
Error	19	0.09844079		

$r^2 = 0.593963$

Table VIII-7. Analysis of Variance (ANOVA) Table for Regression Analysis of Log-Transformed Data, Main Effects and Two-Way Interactions Only, for Trends (Non-Zero Slopes)

Source	Degrees of Freedom	Sum of Squares	f value	p value
Time	1	0.00142898	0.24	0.6318
Concentration	1	0.00014385	0.02	0.8788
Flowrate	1	0.01490209	2.47	0.1318
Time*Concentration	1	0.02938001	4.87	0.0392
Time*Flowrate	1	0.01445910	2.40	0.1373
Concentration*Flowrate	1	0.00280262	0.46	0.5034
Error	20	0.12068346		

$r^2 = 0.502219$

Table VIII-8. Analysis of Variance (ANOVA) Table for Regression Analysis of Log-Transformed Data, Main Effects Only, for Trends (Non-Zero Slopes)

Source	Degrees of Freedom	Sum of Squares	f value	p value
Time	1	0.02013796	2.26	0.1464
Concentration	1	0.01869058	2.10	0.1610
Flowrate	1	0.00175909	0.20	0.6610
Error	23	0.20494538		

$r^2 = 0.154665$

interactions, and for the main effects only), and the three ANOVAs based upon the log-normal distribution, for which Tables VIII-6, VIII-7, and VIII-8 are the ANOVA tables, are considered the definitive illustration of the presence or absence of significant trends in the data.

As shown in Tables VIII-6 and VIII-7, for the full model and for the model with main effects and two-way interactions, respectively, significant ($p < 0.04$ in both cases) variation is associated with the two-way interaction of time and concentration level, indicating a trend in combined efficiencies associated with the combination of time-and-concentration levels. In the full-model ANOVA, a non-significant trend of variation associated with the three-way interaction (concentration, time, flowrate) was detected ($p > 0.05$). No significant trends are associated with any of the main effects in any of the three models. The ANOVA table for the non-transformed data (Table VIII-5) indicates a coefficient of variation (C.V.) of only 6.9%. The C.V. is associated with the error term (which, as noted earlier in this Part, includes variation in the data due to generation imprecision, sampling and analytical imprecision, or any other unknown variables), and this low value indicates that variation due to these items is small, giving good overall precision.

As noted in Section 2 of Part V.B, it was intended that the data presented in Table VII also be subjected to an analysis by response-surface determination; this type of analysis, normally

computer generated, provides two-dimensional contour-map diagrams of the response of a selected parameter at a selected level of significance, with respect to two other parameters selected as the axes. However, there since there is no significant association between variability in the combined efficiency and any single factor such as sampling flowrate, and because the significant variability associated with the two-way effect has no clear physical meaning (this is discussed two paragraphs hence), this type of analysis would not provide any useful information for this data set and so was not used.

Generally, the results of the ANOVAs indicate that the collection efficiency of the method is fairly constant throughout the tested ranges of sampling time, air-sampling flowrate, and airborne formaldehyde concentration. As noted at the beginning of this Part, the calculated mean collection efficiency for all of the data is 96% (see Table VIII-1), the same as previously documented for limited ranges of sampling time and flowrate (see Section 4 of Part VI.B). However, the meaning of the significant variation in the results associated with the two-way interaction of sampling time and concentration must be assessed.

An examination of the data in Table VIII-1 reveals the trend responsible for the significance of the two-way interaction of sampling time and concentration: the collection efficiency is stable across concentration levels for 1-hr samples but declines sharply with concentration for 4-hr samples. However, the

interaction does not have any obvious physical significance, in terms of why it would be a factor affecting collection efficiency. Increasing these parameters together does not necessarily lead to a large total sample volume or collectable mass of analyte, as a low flow rate could be used to offset these parameters. In fact, the data in Table VII in Part VII indicate that a much higher combined efficiency was measured at the highest flowrate, than at the other flowrates, for the highest concentration at the longest time.

The amount of variation in the data from the 4-hr, 6.4-ppm "runs" is rather large, and one might speculate that some difficulty was encountered in keeping the generation system controlled under these conditions. In fact, the variation within most of the 4-hr data is relatively large. Perhaps all of the 4-hr data are somewhat imprecise, allowing for random error, and perhaps there was increased generation-system difficulty at the highest concentration (6.4 ppm) over the 4-hr period causing an apparent low efficiency. It may be noticed that if the rather variable, 4-hr, 6.4-ppm data, which also have a rather low calculated mean collection efficiency, were excluded, the collection performance would "appear" essentially constant. Nevertheless, there is no evidence outside of speculation that the detected trend is an artifact of increased generation system imprecision. So, the ANOVA found the trend to be significant, and, despite the fact that no "common sense" reason is apparent, it must be assumed that the trend does reflect an actual (although relatively small)

loss of collection performance at the highest concentrations over the longest times.

SUMMARY - The investigation of trends in the data, by revealing no significant trends among the main effects, clarifies the nature of the differences among means for the main effects with the full factorial model (detected in the first ANOVA in this Part) as most likely being an anomoly of the unstable analysis; this is due to the physical implausibility of significant changes in collection performance occuring in the middle of a range of a given factor (as implied by the findings of the full factorial model) when the factor has no significant trend across its range. As noted earlier, even if the differences at discreet points are "real," the magnitudes are still below the stated criteria. Similar reasoning is used for the interactions found in the "differences among means" analysis that are not confirmed by the investigation of trends. Therefore, a judgement has been made that, with respect to the actual use of the collection method in the field, special consideration need only be given to the apparent loss of collection performance at the highest concentrations over the longest times, noted in the previous paragraph, detected by the investigation of trends.

B. Other Considerations

In Part III.B, it was concluded that chemical reaction will account for most of the absorption which occurs when

formaldehyde-containing gas is collected with aqueous sodium bisulfite, but that absorption by solution must be considered as a possible secondary mechanism. A list was developed, in Section 1 of Part III.A, of eight factors influencing the collection efficiency performance, for absorption by solution, of a gas absorber. Some of these were varied during this study: the degree of contact between the gas and the absorbent (determined by bubble size, which, for a midget impinger, is affected by the rate of gas flow); the duration of contact (also affected by the rate of gas flow); the volume of gas sampled (also affected by the rate of gas flow, as well as by the sampling time); and, the concentration of the contaminant in the gas. In Section 2 of that Part, a similar list was developed for absorption by chemical reaction. Some of these were varied during this study: the first two items in the above list; and, the molar quantity of contaminant to be collected and reacted (determined by the concentration of the contaminant in the gas and the volume of air sampled [in turn determined by the rate of gas flow and the sampling time]).

The current study has essentially been unable to detect changes in collection performance for the investigated system related to changes in the factors listed above. (Recall that the apparent loss of collection performance detected at the highest concentrations over the longest times does not appear to be related to high total volume or high molar quantity of contaminant collected and reacted, because the loss occurs among

the lower flow rates, not the highest one). The best explanation for this fact is that, for each of the factors varied in the study, the range of values over which the factor was varied did not cause any of the underlying factors in the list above to be placed outside of the range in which they provide near-maximal absorption of formaldehyde from air into the absorbing liquid. This may be because some of the other factors listed in Part III.A, which are not among those listed above as being varied in the study (some because they are fixed properties inherent to the physical system used), are so strongly favorable to absorption that declines in absorption performance caused by varying the factors which were varied were too small to detect. Specifically, high rates of diffusion and reaction, and a high solubility of both formaldehyde and the sodium formaldehyde-bisulfite compound, are possible factors that could strongly favor absorption.

IX. CONCLUSIONS

It may be concluded from this study that the collection efficiency, for airborne formaldehyde, of midget impingers containing about 20 mL of aqueous 1% sodium bisulfite is about 96% when volumetric airflow rates between 0.1 and 1.0 L/min are used for 1 hr, or when volumetric airflow rates between 0.1 and 0.5 L/min are used for 4 hr, for airborne formaldehyde concentrations between 0.4 and 6.4 ppm. A possible exception to this statement is evidence of an unexplained decline in collection efficiency when concentrations near 6.4 ppm are sampled for 4 hr.

The evaluation of the dynamic generation system developed for this study led to a conclusion that the generation system can generate levels of airborne formaldehyde between 0.4 and 6.4 ppm with an efficiency of 91% and high precision (see Appendix B).

X. RECOMMENDATIONS

A. Recommendations regarding the Sampling Method

1. Recommendation for the Use of the Sampling Method

It is recommended that midget impingers containing about 20 mL of aqueous 1% sodium bisulfite be used with volumetric airflow rates between 0.1 and 1.0 L/min for 1 hr, or with volumetric airflow rates between 0.1 and 0.5 L/min for 4 hr, for airborne formaldehyde concentrations between 0.4 and 6.4 ppm. A possible exception to this statement occurs when concentrations near 6.4 ppm are sampled for 4 hr, due to evidence of an unexplained decline in collection efficiency under these conditions. If concentrations of that magnitude are anticipated, limiting the sampling time to 1 hr is recommended (which would not ordinarily create a problem, since long-term exposure to such high concentrations is rare today).

2. Recommendations for Future Research regarding the Sampling Method

a. It is recommended that additional research be conducted to determine the nature of the problem discussed above regarding possible reduced collection efficiency at 6.4 ppm for 4-hr samples.

b. It is recommended that additional research be conducted to determine the collection efficiency of the system between 0.1 and 0.4 ppm over the time and flowrate ranges used in this study.

B. Recommendations regarding the Dynamic Generation System

1. Recommendation for the Use of the Dynamic Generation System

It is recommended that the system be used to generate airborne formaldehyde concentrations between 0.4 and 6.4 ppm (see Appendix B).

2. Recommendation for Future Research regarding the Generation System

It is recommended that additional research be conducted to determine the source of the reduced generation efficiency of the system in the 0.1-ppm range.

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APPENDICES

Appendix A. Spectrophotometric Standard Analytical ("Calibration") Curve

Table A-1. Spectrophotometric Calibration Curve - Raw Data*

Mass of formaldehyde in color-developed solution, ug	Absorbance, AU				
	Run 1,** 1-29-85	Run 2, 1-31-85	Run 3, 1-31-85	Run 4, 2-8-85	Run 5, 2-8-85
0.00	0.000	0.000	0.000	0.000	0.000
1.00	0.054	0.065	0.067	0.064	0.066
3.00	0.186	0.201	0.194	0.195	0.197
5.00	0.290	0.329	0.322	0.331	0.330
7.00	0.495	0.449	0.434	0.432	0.440
10.0	0.580	0.620	0.584	0.602	0.589
12.0	---	---	---	0.695	0.689
15.0	0.812	0.852	0.815	0.820	0.829
20.0	0.987	1.029	1.015	---	---

* These data are plotted in Figure A-1.
** Excessive "zero drift" was detected after data generation was completed.

Figure A-1. Spectrophotometric Calibration Curve: Raw Data

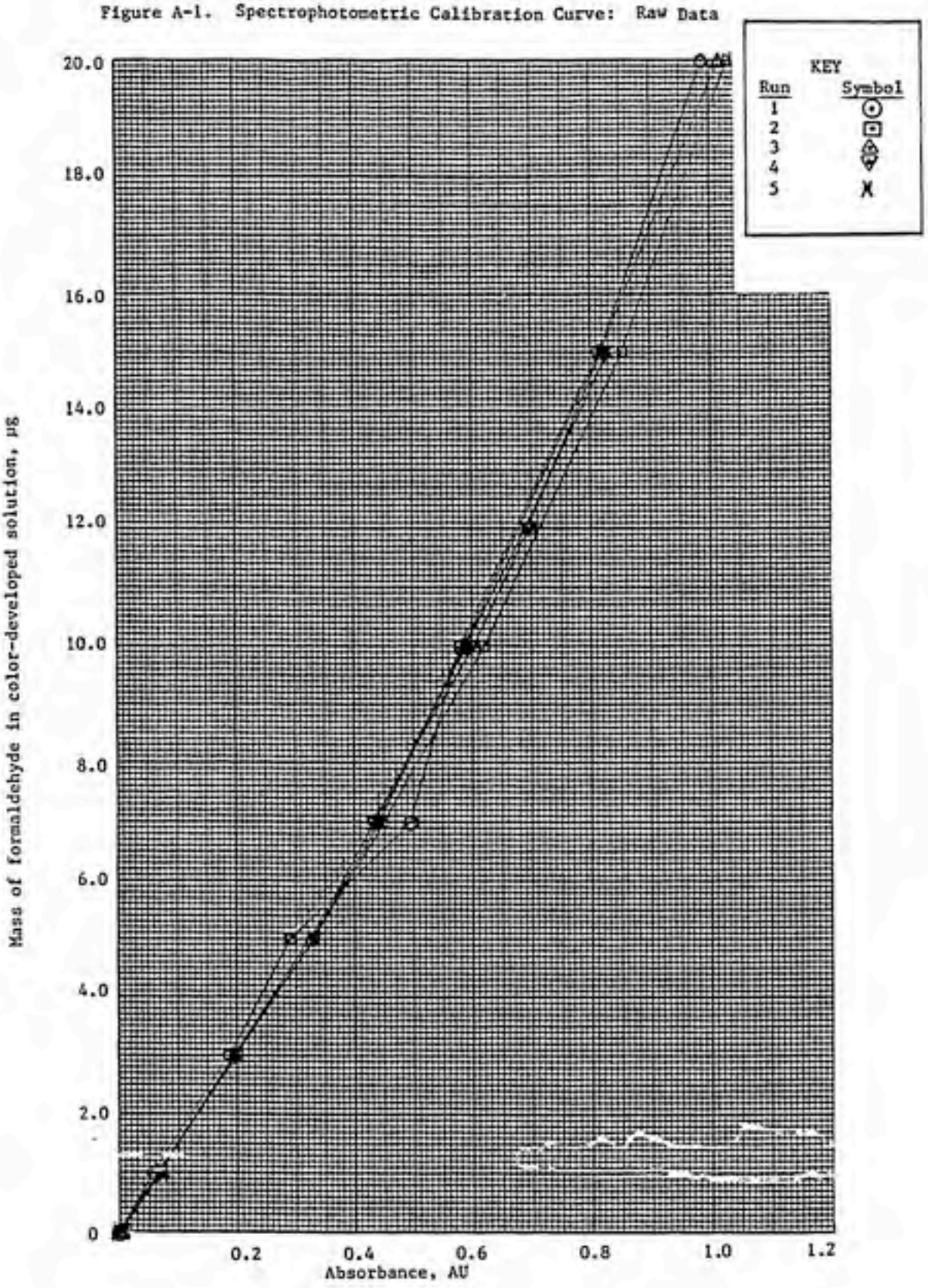
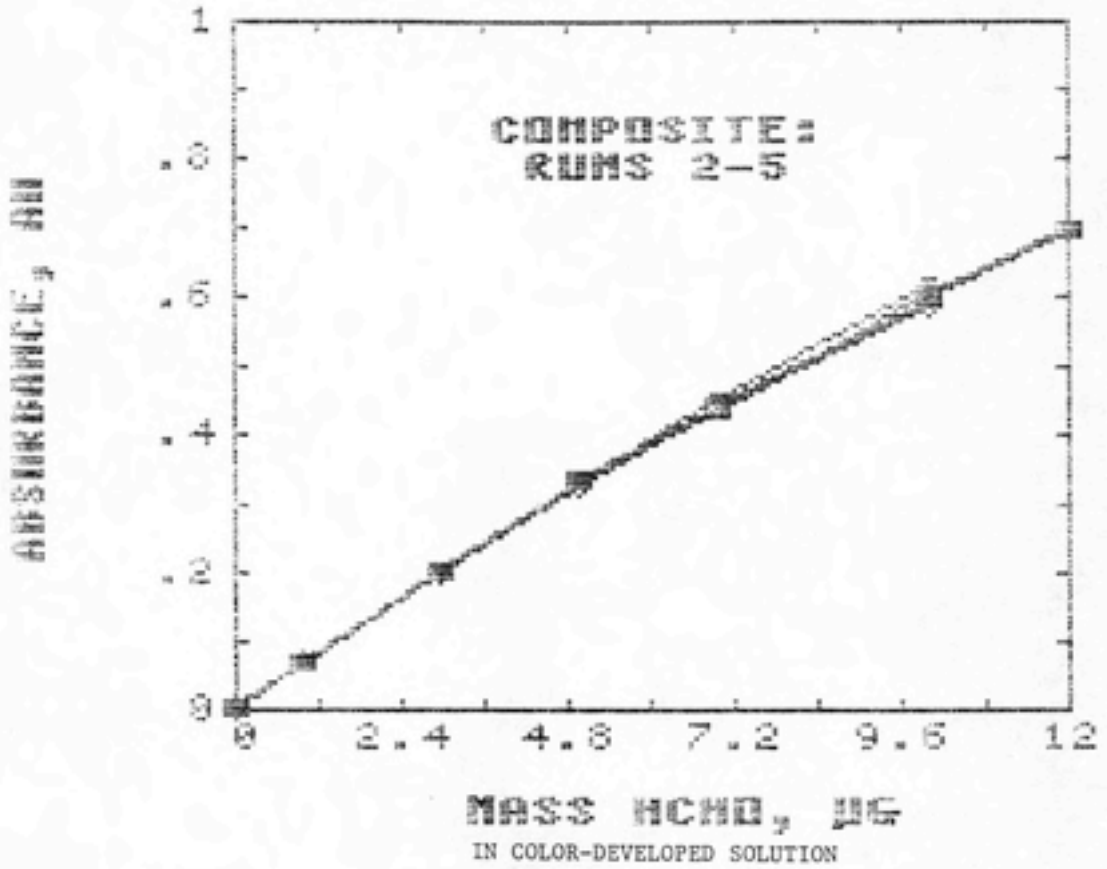


Table A-2. Spectrophotometric Calibration Curve - Final Data Used

Mass of formaldehyde in color-developed solution, ug	Absorbance, AU				
	Run 2, 1-31-85	Run 3, 1-31-85	Run 4, 2-8-85	Run 5, 2-8-85	Mean, Runs 2 through 5
0.00	0.000	0.000	0.000	0.000	0.000
1.00	0.065	0.067	0.064	0.066	0.066
3.00	0.201	0.194	0.195	0.197	0.197
5.00	0.329	0.322	0.331	0.330	0.328
7.00	0.449	0.434	0.432	0.440	0.439
10.0	0.620	0.584	0.602	0.589	0.599
12.0	---	---	0.695	0.689	0.692

Figure A-2. Spectrophotometric Calibration Curve - Final Data Used



Statistical Analysis and its Interpretation

The data presented in Table A-2 were subjected to a two-way analysis of variance (ANOVA) without interactions, performed with the aid of the General Linear Models Procedure of the Statistical Analysis System (SAS), a mainframe computer package. The purpose of this was to test for variation in the data due to "run number." The model took account of "run" and concentration. Table A-3 contains the ANOVA table from this analysis. As shown in Table A-3, highly significant ($p = 0.0001$) variation is associated with concentration; this would be expected, of course, since the very purpose of the curve is to illustrate the concentration dependence of the absorbance. Of greater value here is the finding that the variation with "run" is not significant ($p = 0.0829$). This finding permits the final decision to pool the data from all of the runs to create a composite calibration curve.

The combined data were then subjected to regression analyses, both first and second order (linear and quadratic forms, respectively) as noted in the main body of this report. These analyses were also performed with the aid of the General Linear Models Procedure of SAS. The purpose of these analyses was to provide the estimated line or curve of best fit for the data that conforms to each of the forms specified, and to provide an estimate of the predictive value of each line or curve.

The estimated first-order line of best fit is described by the following linear equation: $y = 0.014 + 0.059x$ where y = absorbance (AU) and x = mass of formaldehyde in the color-developed solution (ug). The y-intercept (0.014) was found to be significantly different from zero ($p = 0.0095$). This is undesirable because the "true" curve must have an intercept of zero, since the absorbance is arbitrarily set to zero ($y = 0$) using the blank (zero mass of formaldehyde, or $x = 0$) solution. This finding can be interpreted as evidence of at least some lack of accuracy in the region of low concentrations. As expected, the slope, or linear-term coefficient (0.059), was found to be significantly different from zero ($p = 0.0001$). This is expected because the "true" curve should have a non-zero slope to reflect the theoretically proportional relationship between concentration and absorbance. The correlation coefficient is a very good 0.996, indicating strong correlation and thus predictive value overall.

The estimated second-order curve of best fit is described by the following quadratic equation: $y = -0.00216 + 0.07050x - 0.00105x^2$ where y and x are defined as in the preceding paragraph. The y-intercept (-0.00216) was not found to be significantly different from zero ($p = 0.45$). This is desirable because, as noted above, the "true" curve must have an intercept of zero. As also noted above, the "true" curve should have a non-zero linear-term coefficient ("slope") to reflect the theoretically proportional relationship between concentration and absorbance. This coefficient (0.07050) was indeed found to vary significantly from zero ($p = 0.0001$). Of much greater

importance is the fact that the quadratic-term coefficient (-0.00105) was also found to vary significantly from zero ($p = 0.0001$), meaning the quadratic term is, by definition, significantly different from zero (except when $x = 0$). This indicates that there is significant curvature in the data, which is necessary and substantial justification for using the quadratic model. Also, the correlation coefficient is an excellent 0.999, indicating very strong correlation and thus predictive value overall.

Table A-3. Spectrophotometric Calibration Curve - Analysis of Variance (ANOVA) on the Data.

Source	Degrees of Freedom	Sum of Squares	f value	p value
Run	3	0.00035	2.67	0.0829
Concentration	6	1.34454	5115.56	0.0001
Error	16	0.00070		

r^2 = 0.9995 C.V. = 2.2%

Appendix B. Evaluation of the Generation System.

1. Design

In Part V.A, the overview of the study design, the need for, and the purpose of, an evaluation of the generation system was discussed, with respect to the complete study design. The basic strategy for evaluating the generation system was also discussed. The generation and sampling requirements for this evaluation were determined both by the requirements of the overall study as set forth in Part V.B, Section 1 (these affected the actual operation of the apparatus during this phase and thus are further discussed in the Methods, Part VI.B.3), and by the following statistical design.

STATISTICAL DESIGN OF THE GENERATION-SYSTEM EVALUATION: The following two assumptions were used to formulate the design: a sampling error of 5% (based on typical portable sampling pump performance); and, an analytical error of 5% (based upon a documented three-laboratory comparison [45]). The following criteria were also used to formulate the design: an 80% power of detecting a difference of 5 percentage points in generator efficiency for one or more concentration levels from the average generator efficiency. The design was based upon varying the following parameters: the number of concentration levels; the number of replicate generations ("runs") per concentration level; and, the number of replicate samples collected per "run." The objective of this last item was to provide a measurement of sample-to-sample variability (including differences between sample

ports in the apparatus, and sampling and analytical imprecision) which would be included in the ANOVA's error term (representing overall imprecision from factors not isolated in the analysis). This source of variability would be included in the error term of the analysis so that it would not be included in any variability detected in the higher levels (concentration level, and "run"-number within concentration level). Further discussed below is why this source of variability cannot be individually measured.

A family of four proposed study designs was developed. Each design, consisting of a proposed numerical value for each of the three parameters noted above, was subjected to a power calculation of the Analysis of Variance (ANOVA) type. More specifically, a hierarchical design for a nested ANOVA was intended to be used, and the power calculations reflected this.

The ANOVA around which the proposals were designed was intended to test for significant differences in generation efficiencies between concentration levels (the main effect) and between "run"-number levels within concentration levels (the nested effect). The ANOVA was not intended to test for differences between overall "run"-number levels because they would have no physical meaning (since generation "runs" sharing the same number have nothing but the number in common). The ANOVA cannot test for differences between sample-code ("A" or "B") level because this is the lowest level in the design; variation in the data due to differences between these levels (which would indicate differences between

sampling ports "A" and "B" in the experimental apparatus [see Part VI.A]) would be included in the error term, as would variation due to sampling and analytical imprecision, or any other unknown variables.

As implied in the previous paragraph, the basic hierarchical design placed concentration level at the highest level in the intended ANOVA; below that was generation "run" number within concentration; the next, and lowest, level was the error term. The hierarchical nature of the design provides for determination of whether the component of variation associated with the second lowest level of the ANOVA (in this case, "run" within concentration) is significantly greater than that associated with the lowest level (error). Then, the combined component of variation of these two levels would be similarly compared to the next highest level (which is concentration level).

The power calculations used the number of degrees of freedom available from: the number of levels of concentration; the number of levels of generation "run" within concentration (i.e., the number of "runs" per concentration level); and, the error term containing the remaining degrees of freedom needed to allow for the total number of samples called for in the specific proposed design. Only the main effect was required to meet the power criteria (therefore, the power to detect the nested effect may have been less than 80%). The most practical design containing a sufficient number of degrees of freedom to provide statistical power meeting the above criteria was selected.

The following design was selected and used:

4 concentration levels of airborne formaldehyde

3 generation "runs" per concentration level

2 air samples collected from each generation "run"

---

24 air samples, total

2. Methods

The equipment and procedures used to conduct the evaluation of the generation system are the same as those used for the main collection-efficiency study (see Part VI); the few exceptions to this statement can be found in Section 3 of Part VI.B, "Specific Operation During Generation System Evaluation."

When the study was initially undertaken, the heated injection block was not included in the generation-system apparatus; rather, the injection was conducted at ambient temperature. A special glass "T" fitting, with the vertical branch of the "T" shaped to hold the septum and the horizontal branches carrying the gas flow, was used in its place in the apparatus. In this configuration, the apparatus pictured in Figure VI-1 in Part VI.A, Section 1, also differed in that the full volume of gas flowed through this "T" rather than being split, and that there was no mass flowmeter (all of the gas was passed through and metered by the rotameter), nor was there a need for a thermocouple or power supply controller. Of course, the operating procedures were slightly different, simply reflecting these changes only. As shown in the next section of this Appendix, the attempt to use the system as described here was unsucessful, and the equipment and operations were then modified to the specifications described in Part VI.

3. Results

The raw data from the initial trials of the generation system without the heated injection block and associated items (see Section 2, above, of this Appendix) are presented in Table B-1. Table B-2 presents a summary of these results. The mean of the combined (generation and collection) efficiencies is 66%, and the sample standard deviation is 15% (n = 14). The mean of the calculated generation efficiencies is 69%. As noted in Table B-2, the validity of the results of six of the samples is doubtful; recalculation of the above summary statistics excluding these data results in a mean of 55% (sample standard deviation = 6.3%, n = 14) for the combined (generation and collection) efficiencies, and thus a mean of 57% for the calculated generation efficiency.

An obvious problem of low and variable generator efficiency is apparent from the data in Table B-2 and these statistical parameters. In fact, data collection was suspended when the problem was discovered, although two concentration levels had not yet been investigated. White solid residue was noted to be forming on the injection needle tip. (It was visible through the glass "T-fitting" used in place of the heated injection block for the initial generation "runs.") The cause of the problem, apparently, is that some paraformaldehyde polymer formation occurred, rather than complete evaporation of the formaldehyde in the solution (70). Possibly, this is due to the methanol in the solution vaporizing sooner, leaving nothing to stabilize against polymerization (70).

Table B-1. Raw Data, Evaluation of the Generation System, Initial Generation "Runs" Without Heated Injection Block

Date (time) of generation "run"	"Run" code		Conditioning elapsed time, min	Sampling and measured-injection elapsed time, min	Measured-injection volume, uL	Injection solution concentration of formaldehyde, mg/mL	Generation system volumetric gas flowrate, std. L/min	Calculated generated concentration of formaldehyde, ppm	Sample code
	nominal formaldehyde concentration level, ppm	replicate "run" number							
2-4-1985	0.1	1	12	60.0	4.46	5.17	3.00	0.105	A
									B
2-6-1985	0.1	2	60	60.0	4.47	5.17	2.98	0.105	A
									B
2-7-1985	0.1	3	45	60.0	4.41	5.17	3.00	0.103	A
									B
2-12-1985 (10:41 am)	0.4	1	43	60.0	4.37	20.7	2.96	0.415	A
									B
2-12-1985 (3:40 pm)	0.4	2	36	60.0	4.42	20.7	2.96	0.419	A
									B
2-13-1985	0.4	3	30	60.0	4.40	20.7	2.98	0.415	A
									B
2-19-1985	0.4	4	55	60.0	4.43	20.7	3.01	0.413	A
									B

Table B-2. Results Summary, Evaluation of the Generation System, Initial Generation "Runs" Without Heated Injection Block

Generation "Run" code						
Nominal formaldehyde concentration level, ppm	Replicate "Run" number	Calculated generated formaldehyde concentration, ppm*	Sample code	Sampled formaldehyde concentration, ppm*	Combined generation and collection efficiency, %	Calculated generation efficiency,** %
0.1	1	0.105	A	0.056	53	55
			B	0.061	58	60
	2	0.105	A	0.054	51	53
			B	0.054	51	53
	3	0.103	A	0.075***	73***	76***
			B	0.098***	95***	99***
0.4	1	0.415	A	0.36***	87***	91***
			B	0.33***	80***	83***
	2	0.419	A	0.32***	76***	79***
			B	0.32***	76***	79***
	3	0.415	A	0.22	53	55
			B	0.22	53	55
	4	0.413	A	0.29	70	73
			B	0.22	53	55

* Corrected to standard conditions (25°C, 760 mmHg)

** Based upon a collection efficiency under these sampling conditions of 96% (see Part VI.B.4 for a discussion of this documented collection efficiency)

*** Possible contamination of injection area and system by polymerized HCHO (paraformaldehyde) solid from prior injections on 0.1 ppm (nominal) run 3 and 0.4 ppm (nominal) runs 1 and 2.

As a solution to the above problem, based upon advice received (70), the apparatus and procedures were revised by the addition of the heated injection block to the system and the use of it to heat the injection area to at least 170°C, to prevent polymer formation (or, to decompose it as it forms [70]).

The apparatus and procedures were then as described in Part VI, Methods. The generation system evaluation was then begun again; this time it was completed without apparent problems. The raw data from the evaluation of the generation system are presented in Table B-3. Table B-4 presents a summary of these results.

4. Analysis and Discussion

The summary statistics for the data in Table B-4 appear in Table B-5. Also based on the data in Table B-4 is Figure B-1, a plot of the mean combined (generation and collection) efficiencies for each generation "run" (based on the results of the two samples collected during each "run") against the nominal concentration levels. The data presented in Table B-4 were also subjected to a nested analysis of variance (ANOVA) with multiple comparisons, performed with the aid of the General Linear Models Procedure of the Statistical Analysis System (SAS), a mainframe computer package. The purpose and design of this ANOVA was identical to that which was planned during the design of this phase of the study, and it is fully described in Section 1 of this Appendix; some of the key points noted in Section 1 are restated in the following paragraph.

Table B-3. Raw Data, Evaluation of the Generation System

Date (time) of generation "run"	"Run" code: nominal formaldehyde concentration level, ppm	"Run" code: replicate "run" number	Conditioning elapsed time, min	Sampling and measured-injection elapsed time, min	Measured-injection volume, uL	Injection solution concentration of formaldehyde, mg/mL	Generation system volumetric gas flowrate, std. L/min	Calculated generated concentration of formaldehyde, ppm	Sample code	Sample (pump) volumetric gas flowrate, std. L/min	Impinger number (1=primary, 2=backup)
4-10-1985	0.4	1	40	60.0	4.45	20.0	3.00	0.403	A	0.985	1
									B	0.995	1
											2
4-11-1985 (am)	0.4	2	45	60.0	4.42	20.0	3.01	0.399	A	0.987	1
									B	1.01	1
											2
4-11-1985 (pm)	0.4	3	59	60.0	4.48	20.0	3.01	0.404	A	0.997	1
									B	1.01	1
											2
4-16-1985	6.4	1	51	60.0	4.49	315	2.99	6.50	A	0.994	1
									B	0.994	1
											2
4-17-1985 (am)	6.4	2	47	60.0	4.42	315	3.01	6.36	A	0.993	1
									B	0.993	1
											2
4-17-1985 (pm)	6.4	3	40	60.4	4.46	315	3.01	6.41	A	1.00	1
									B	1.01	1
											2
4-30-1985 (9:40 am)	0.1	1	44	60.0	4.39	4.94	3.00	0.0991	A	0.986	1
									B	0.996	1
											2
4-30-1985 (12:40 pm)	0.1	2	75*	60.0	4.55	4.94	3.00	0.103	A	0.980	1
									B	0.984	1
											2
4-30-1985 (3:10 pm)	0.1	3	61*	60.0	4.59	4.94	3.00	0.104	A	0.975	1
									B	0.973	1
											2
5-2-1985 (10:00 am)	1.6	1	35	60.0	4.41	79.8	2.99	1.60	A	0.972	1
									B	0.984	1
											2
5-2-1985 (12:00 noon)	1.6	2	68*	60.0	4.43	79.8	2.99	1.60	A	0.968	1
									B	0.980	1
											2
5-2-1985 (3:00 pm)	1.6	3	56*	60.0	4.46	79.8	2.99	1.62	A	0.965	1
									B	0.977	1
											2
7-17-1985 (11:00 am)	0.0	1	NA	60.0	0.00	0.0	3.01	0.0	A	0.976	1
7-17-1985 (5:00 pm)	0.0	2	40**	60.0	0.00	0.0	3.02	0.0	A	0.978	1

* Conditioning included continuous operation from previous "run," approximate 5 min period without injection, and further condition

** operated previously at 6.4 ppm, then purged for this time.

1 Corrected for "zero drift."

2 Corrected for blank value.

Table B-4. Results summary, Evaluation of the Generation System

Generation "Run" code						
Nominal formaldehyde concentration level, ppm	Replicate "Run" number	Calculated generated formaldehyde concentration, ppm*	Sample code	Sampled formaldehyde concentration, ppm*	Combined generation and collection efficiency, %	Calculated generation efficiency,** %
0.0	1	0.0	A	0.028	NA	NA
	2	0.0	A	0.0	NA	NA
0.1	1	0.0991	A	0.076	77	80
			B	0.075	76	79
	2	0.103	A	0.082	80	83
			B	0.079	77	80
	3	0.104	A	0.085	82	85
			B	0.088	85	89
0.4	1	0.403	A	0.357	88.6	92.3
			B	0.337	83.6	87.1
	2	0.399	A	0.355	89.0	92.7
			B	0.360	90.2	94.0
	3	0.404	A	0.357	88.4	92.1
			B	0.343	84.9	88.4
1.6	1	1.60	A	1.44	90.0	93.8
			B	1.38	86.2	89.8
	2	1.60	A	1.42	88.8	92.5
			B	1.38	86.2	89.8
	3	1.62	A	1.32	81.5	84.9
			B	1.34	82.7	86.1
6.4	1	6.50	A	5.32	81.8	85.2
			B	6.12	94.2	98.1
	2	6.36	A	5.70	89.6	93.3
			B	5.70	89.6	93.3
	3	6.41	A	5.70	88.9	92.6
			B	5.59	87.2	90.8

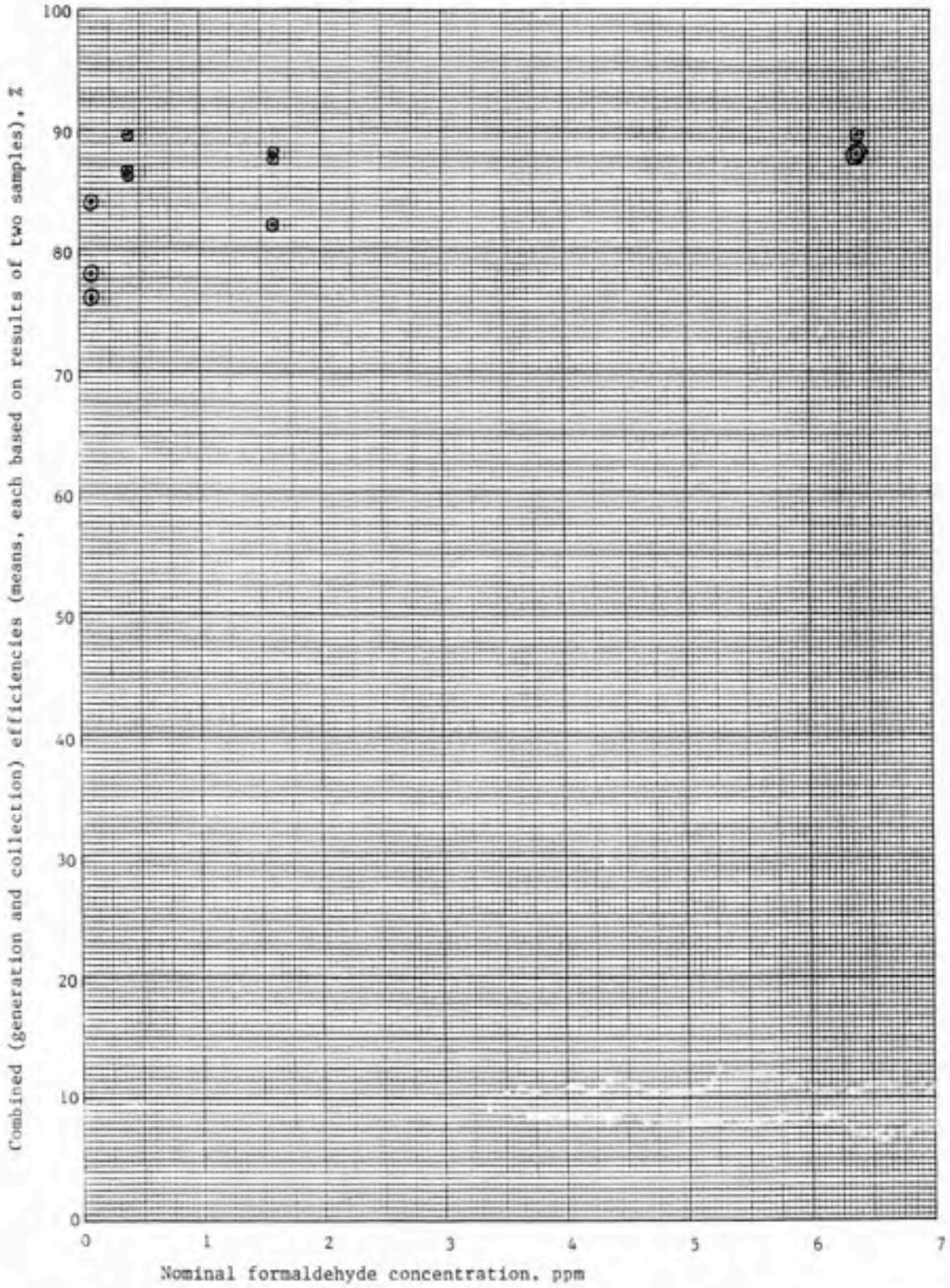
* Corrected to Standard conditions (25°C, 760 mmHg)

** Based upon a collection efficiency under these sampling conditions of 96%
(See Part VI.B.4 for a discussion of this documented collection efficiency)

Table B-5. Summary Statistics for Results, Evaluation of the Generation System

		Combined generation and collection efficiency	
	Number of values	Mean	Sample standard deviation
All data	24	85%	4.8%
All data excluding 0.1-ppm level	18	87.3%	3.4%
0.1-ppm level	6	80%	3.5%
0.4-ppm level	6	87.5%	2.6%
1.6-ppm level	6	85.9%	3.3%
6.4-ppm level	6	88.6%	4.0%

Figure B-1. Additional Summary of the Results, Evaluation of the Generation System



The purpose of the nested ANOVA was to test for variation in the data associated with concentration level (the main effect), and with "run" number within concentration levels (the nested effect). More specifically, the model tested for significant differences in combined (generation and collection) efficiencies between concentration levels and between "run"-number levels within concentration levels. The ANOVA did not test for differences between overall "run"-number levels because, as noted previously in this Appendix, they have no physical meaning (since generation "runs" sharing the same number have nothing but the number in common). Also, as discussed previously, it could not test for differences between sample-code ("A" or "B") level (which could indicate differences between sampling ports "A" and "B" in the experimental apparatus) because this is the lowest level in the design; variation in the data due to differences between these levels would be included in the error term, as would variation due to sampling and analytical imprecision, or any other unknown variables.

Table B-6 contains the ANOVA table from this analysis. The combined (generation and collection) efficiencies are used in the calculations in place of the calculated generation efficiencies (these quantities are, of course, proportional) for convenience and because the former are in fact what were actually measured. As shown in Table B-6, the component of variation associated with the generation "run" number (within the concentration levels) is not significantly greater than that associated with the error

Table B-6. Analysis of Variance (ANOVA) of Results, Evaluation of the Generation System

Source	Degrees of Freedom	Sum of Squares	f value	p value
Concentration	3	0.02950500	6.95	0.013
Run(concentration)	8	0.01131600	1.43	0.277
Error	12	0.01184900		

r^2 = 0.775033 C.V. = 3.6817% Combined efficiency mean = 0.85350000

term ($p = 0.277$). However, the component of variation associated with concentration level is significantly greater ($p = 0.013$) than the combined component of variation associated with error and with "run" number within concentration levels.

The latter finding, more simply stated, is that there is variation significantly associated with concentration level, indicating that one or more concentration levels have combined efficiencies that are significantly different from that of the remaining levels. The former finding, more simply stated, is that there is no variation associated with "run"-number within concentration levels, indicating good "run"-to-"run" reproducibility. The ANOVA table indicates a coefficient of variation (C.V.) of only 3.7%. The C.V. is associated with the error term (which, as noted earlier in this Appendix, includes variation in the data due to differences between sampling ports "A" and "B" in the experimental apparatus, sampling and analytical imprecision, or any other unknown variables), and this low value indicates that variation due to these items is small, giving very good overall precision. It should also be noted that an examination of the data in Table B-4 reveals no apparent differences in combined efficiency associated with sample-code ("A" or "B") level, so the sample ports to which these codes refer are unlikely as a source of systematic error.

To determine which concentration level(s) showed significantly different combined efficiencies from those of the other levels, the multiple comparisons test was employed. The combined efficiency at

the 0.1-ppm nominal level differed significantly ($p < 0.05$) from those of the remaining three levels. The combined efficiencies for the other three levels do not vary significantly in this way. Thus, the combined (generation and collection) efficiency is significantly reduced at the 0.1-ppm concentration level. As shown in Table B-5, the efficiency at the 0.1-ppm nominal level is only 80%, which is over 8% less than the 87.3% figure for the 0.4- to 6.4-ppm-level range. This exceeds the 5% maximum for this difference that was chosen in the design phase of the evaluation (see Section 1 of this Appendix). This is a substantial difference because a very high generating precision with predictable accuracy is required if the generation system is to be adequate for use in the collection efficiency study; this finding instead indicates a lack of these qualities at the lowest concentration.

At this point, consideration was given to testing for the presence of a significant trend in the data by determining if the line of best fit for a plot of the combined (generation and collection) efficiencies for each generation "run" against the nominal concentration levels has a significant slope (more specifically this test would determine if the slope of this line were significantly different from zero). Trends in the data first were visually examined by consulting Table B-5 and Figure B-1. A strong dichotomy was seen between the 0.1-ppm-concentration level and all other concentration levels in terms of combined efficiency, rather than any indication of a gradual decline of combined efficiency with concentration level. Although a gradually sloped line would

appear to fit the plot in Figure B-1, if the 0.1-ppm-level points were removed, a very flat response would be seen (especially if one point [1.6 ppm, 82.1%] is momentarily ignored as appearing to be a possible outlyer) through the remaining concentration range of 0.4 to 6.4 ppm. There are no data between the 0.1- and 0.4-ppm levels to indicate whether there is a gradual decline in efficiency from the 0.4-ppm level down to the 0.1-ppm level and below, or to indicate the shape of the curve describing the decline. Therefore, instead of formally testing for trends in the overall data as described above, it was decided to eliminate the data at and around the 0.1-ppm level as having unacceptably reduced efficiency, and to simply not use the generation system below the 0.4-ppm level known to be in the apparent region of flat response.

Table B-5 and Figure B-1 were again examined for the presence of a significant trend in the remaining data (for the 0.4- to 6.4-ppm range); the combined efficiency level is very flat throughout this range, as noted in the previous paragraph, and no formal testing to verify this was considered necessary.

As discussed in Part VI.B.4, the collection efficiency of the method under the sampling conditions used has been found to average 96%. If the generation efficiency of the system were 100%, the combined efficiency would average 96%. The results above document a mean value of only 87.3% (for the concentration range 0.4 to 6.4 ppm). Using Student's t-test, the latter was found to be significantly less than the former ($p < 0.05$). The mean bias, or

average generating efficiency, is 91% (found by dividing the mean combined efficiency by the calculated collection efficiency) in this range.

5. Conclusions and Recommendations

The following conclusions about the generation system performance were reached:

1. Precise, reproducible concentrations of formaldehyde vapor, equalling about 91% of the calculated concentration, can be generated using this generation system.

2. An exception to the above statement must be made when levels around 0.1 ppm are desired, as low generator efficiency occurs in this range.

3. Losses of formaldehyde vapor in the system, due to wall effects becoming quantitatively important at the lowest levels, must be suspected.

The following are recommendations regarding the use of the generation system, and further work indicated from this part of the study:

1. The generation system may be used to produce formaldehyde vapor concentrations of 0.4 to 6.4 ppm for collection efficiency

studies of the aqueous bisulfite impinger method at $\leq$ 1 L/min and/or $\geq$ 1 hr.

2. Further work is needed to determine the source of the lowered generator efficiency in the 0.1-ppm range.

Appendix C. Raw Data

Table C. Raw data

Date (time) of generation "run"	"Run" code: nominal sampling time, hr	nominal formaldehyde concentration level, ppm	nominal sampling flowrate, L/min	replicate "run" number	Conditioning elapsed time, min	Sampling and measured-injection elapsed time, min	Measured injection volume, uL	Injection solution concentration of formaldehyde, mg/mL	Generation system volumetric gas flowrate, std. L/min	Calculated generated concentration of formaldehyde, ppm	vo f st
6-26-1986 (11:00 am)	1	0.4	0.1	-	34	60.0	4.43	20.0	3.00	0.401	
6-26-1986 (1:00 pm)	1	0.4	0.5	-	32*	60.0	4.44	20.0	3.00	0.402	
6-26-1986 (4:00 pm)	1	3.4	0.1	-	45	60.0	4.50	170	3.00	3.46	
6-26-1986 (5:30 pm)	1	3.4	0.5	1	15*	60.0	4.50	170	3.00	3.46	
6-27-1986 (10:00 am)	1	3.4	1.0	-	50	60.5	4.47	170	3.00	3.36	
6-27-1986 (12:00 noon)	1	6.4	0.1	1	39	60.0	4.44	319	3.00	6.44	
6-27-1986 (2:00 pm)	1	6.4	0.1	2	17*	60.0	4.44	319	3.00	6.44	
6-27-1986 (4:00 pm)	1	6.4	0.5	-	18*	60.0	4.50	319	3.00	6.49	
7-11-1986 (5:00 pm)	1	3.4	0.5	2	1*	51.5	3.87	170	3.00	3.47	
7-2-1986 (12:30 pm)	4	0.4	0.1	-	30	229.0	16.84	20.0	3.00	0.399	
7-3-1986 (9:00 am)	4	0.4	0.5	1	30	245.0	17.79	20.0	3.00	0.393	
7-3-1986 (2:00 pm)	4	0.4	0.5	2	5*	226.0	16.89	20.0	3.00	0.406	
7-8-1986 (3:30 pm)	4	0.4	0.5	-	30	224.0	16.45	20.0	2.99	0.400	
7-9-1986 (3:00 pm)	4	3.4	0.1	1	43	222.0	16.33	170	2.99	3.40	
7-10-1986 (9:30 am)	4	3.4	0.3	1	40	228.5	16.71	170	2.99	3.39	
7-10-1986 (2:00 pm)	4	3.4	0.3	2	1*	235.0	17.33	170	3.00	3.40	
7-11-1986 (12:30 pm)	4	3.4	0.5	-	29	222.5	16.32	170	3.02	3.36	
7-15-1986 (2:00 pm)	4	6.4	0.5	-	44	223.0	16.67	319	3.00	6.47	
7-16-1986 (9:30 am)	4	3.4	0.1	2	51	228.0	16.39	170	3.01	3.31	
7-16-1986 (2:00 pm)	4	6.4	0.1	-	5*	224.0	16.32	319	3.02	6.27	
7-17-1986 (1:00 pm)	4	6.4	0.3	-	39	223.0	16.08	319	3.02	6.20	

* Conditioning included continuous operation from previous "run," approximate 5 min period without injection, and further condi

1 Corrected for "zero drift."

2 Corrected for blank value.

Appendix D. Calibrations and Other Measurements of Equipment Parameters

This appendix is divided into three sections. The first contains descriptions of the procedures used to calibrate and/or make other measurements of equipment parameters (except for the development of the spectrophotometer standard analytical curve, which is covered in Section 1.b of Part VI.B in the main body of this report, and supplemented in Appendix A). The second section provides the equations used to make the calculations relevant to these procedures, and the third provides specifications for the equipment and materials used exclusively for these procedures.

Descriptions of Procedures Used

- Sampling Pump Calibration

The volumetric air-flow rate of each sampling pump was measured before and after each use using a bubble tube and conventional industrial hygiene field-sampling technique. The ambient temperature and pressure were measured during each calibration check, and were used to correct the measured flowrate to standard conditions (1 atm, 25°C). Refer to equation (1) for the correction calculation used. The sampling pumps used are designed to maintain constant flow even when pressure changes occur, so it is unnecessary to account for slight differences in pressure between calibration (ambient) and actual use.

- Rotameter Calibration

The rotameter was calibrated by directing pressurized carrier gas (purified nitrogen) through the rotameter to a bell-type spirometer. Constant volumetric flow was maintained by adjustment of a valve upstream from the rotameter to keep the rotameter ball steady. The volume of gas introduced to the spirometer and the elapsed time were used to calculate the exact flowrate. The temperature and absolute pressure (at the rotameter ball) were recorded, and used to correct the measured flowrate to standard conditions. Refer to equation (2) for the correction calculation used. This procedure was replicated three times at each ball setting measured.

- Mass Flowmeter Calibration

The mass flowmeter was calibrated by directing pressurized carrier gas (purified nitrogen) through the mass flowmeter to a soap-bubble meter. Constant volumetric flow was maintained by adjustment of a valve upstream from the mass flowmeter to keep the mass flowmeter indicator needle steady. The ambient temperature and absolute pressure were recorded, and used to correct to standard conditions the measured volume of gas moved through the soap-bubble meter. Refer to equation (3) for the correction calculation used. The corrected volume of gas moved through the soap-bubble meter and the elapsed time were used to calculate the exact corrected flowrate. This procedure was replicated at least three times at each needle setting measured.

- Syringe and Automatic Pipette Calibrations

The syringe and automatic pipette were volumetrically calibrated using similar procedures. Indicated volumes of filtered/distilled water were carefully discharged into tared weighing trays, and the weight change was measured so that the true mass could be determined. The ambient temperature was measured so that the density of the water could be precisely stated from published data (134), and the mass and density were used to calculate the true discharged volume. Correction factors were developed for each device that did not have exactly equal indicated and actual volume discharges. An analytical balance was used to make the weight measurements for the automatic pipette calibrations, while a micro analytical balance was used to make the weight measurements for the syringe calibrations.

- Impinger Nozzle-to-base Distance Measurement

The distance between the tip of the nozzle and the base of the impinger was measured for numerous combinations of unmatched stems and vials from the supply available for use. Several combinations were found to have a measurement of 5.0 mm for this dimension; only these were used to collect air samples for this study. The distance between the nozzle tip and the base for a given set was determined by the insertion of a wire into the impinger stem until it stopped against the base of the impinger. The wire had been marked with graduations in the form of notches at regular intervals by using a micrometer, and the distance was determined by observation through the glass impinger.

- Spectrophotometer Performance Check-out Procedures

The Beckman Model 25 Spectrophotometer performance was checked initially, and quarterly thereafter, in accordance with the Beckman Instructions (105). Proper performance was verified by checking out the wavelength calibration, absorbance accuracy (or span), and photometric linearity.

The wavelength calibration was checked by using a holmium oxide filter as a wavelength standard. Holmium oxide glass has a number of sharp absorption bands which occur at precisely known wavelengths, which are published in the Instructions. A comparison of these wavelengths (and the allowable tolerances around each) with the indicated (by the instrument) wavelengths of the absorbance peaks was made by manually scanning the wavelengths using the Wavelength Control. The instrument was found to be within specified tolerances initially and at quarterly intervals.

The absorbance accuracy was checked by using Standard Reference Materials (SRM) 930 filters. Each of the three stable, neutral-density filters in the SRM 930 set, for which absorbance certification is provided by the National Bureau of Standards (NBS), was used to verify the absorbance accuracy at a specific absorbance value for each of four different wavelengths. The indicated absorbance for each filter at each wavelength was compared to the relevant certified value provided by NBS for the specific filter set (each set is unique). Each indicated value initially was found to be

very close to the relevant certified value (no tolerance limits were provided, however), and, more importantly, the values showed almost no changes (and no trends among the changes) at quarterly intervals. SRM 930D Set 641 was used for these tests.

The photometric linearity was checked using known-concentration solutions of potassium chromate (K_2CrO_4) in aqueous 0.05 N potassium hydroxide (KOH). The absorbance of each solution was measured at 370 nm (using the absorbance of plain 0.05 N KOH as the reference), and these values were plotted against the concentration values. Ideally, the plot would be perfectly linear; the actual plot was very close, with a very slight deviation from linearity at the highest concentration level. The performance was judged to be acceptable (no specific tolerance limit was provided in the Instructions).

Calculations

- Sampling Pump Calibration - Correction to Standard Conditions

$$Q_S = Q_A \frac{P_A T_S}{P_S T_A} = Q_A \frac{P_A \cdot 298.15K}{406.7 \text{ in } H_2O \cdot T_A} \quad (1),$$

where Q_A is the measured flow rate at ambient conditions, P_A is the ambient pressure, and the other variables and constants are defined in Appendix F.

(Derived from ideal gas law [108])

- Rotameter Calibration - Correction to Standard Conditions

$$Q_S = Q_R \left[\frac{P_R T_S}{P_S T_R}\right]^{1/2} = Q_R \left[\frac{P_R \cdot 298.15K}{406.7 \text{ in } H_2O \cdot T_R}\right]^{1/2} \quad (2),$$

where the variables are defined in Appendix F.

(Rotameter equation [108])

- Mass Flowmeter Calibration - Correction to Standard Conditions

$$V_S = V_A \frac{P_A T_S}{P_S T_A} = V_A \frac{P_A \cdot 298.15K}{760 \text{ mm Hg} \cdot T_A} \quad (3),$$

where V_A and V_S are the volumes at ambient conditions and corrected to standard conditions, respectively, P_A is is defined as for equation (1), above, and the other variables and constants are defined in Appendix F.

(Ideal gas law)

Specifications for Equipment and Materials Used

Table D-1 provides specifications for the equipment used exclusively for these procedures, as does Table D-2 for the materials.

Table D-1. Specifications for the Equipment used Exclusively in the Procedures of Appendix D

Item	Manufacturer, Model Name and Number	Size or Measurement Range	Serial Number	Specifications
Spirometer, bell type	American Meter Company	150L	4135	Correction factor: 0.993
Micro Analytical Balance	Metler Instruments Corp., Model AE 163	0 to 9.99999g	C19902	-------
Holmium oxide glass filter	Beckman Instruments, Inc., Part No. 96157	----	M950	Absorption peaks at following wavelengths (nm): 279.3, 287.6, 360.8, 418.5, 453.4, 536.4, 637.5
SRM 930 filter set	National Bureau of Standards, Certified Standard Reference Materials (SRM) 930D filter set	----		Absorbance

Wavelength (nm):	440	465	590	635
1-641	1.018	0.962	1.083	1.052
2-641	0.697	0.659	0.741	0.720
3-641	0.534	0.497	0.562	0.556

Bubble tube, large	Kimax	1000mL	----	Glass
Bubble tube, small	Kimax	100mL	----	Glass

Table D-2. Specifications for the Materials used Exclusively in the Procedures of Appendix D

Item	Specifications
Potassium hydroxide solution, aqueous 0.05N (KOH)	Ingredients: "Baker Analyzed" A.C.S. Reagent Grade KOH (Lot 260684); filtered/distilled water
Potassium chromate solutions (K_2CrO_4)	Concentrations: 8, 16, 24, 32, and 40 mg/L of 0.05N KOH Solution. Ingredients: MCB A.C.S. Reagent Grade K_2CrO_4 (Lot 4222); 0.05N KOH Solution

Appendix E. NIOSH Method 3500 (45)

FORMULA: $H_2C=O$; CH_2O

M.W. = 30.03

FORMALDEHYDE

METHOD: 3500
ISSUED: 2/15/84

OSHA: 3 ppm; C 5 ppm; P 10 ppm
NIOSH: lowest feasible level [1]
ACGIH: C 2 ppm
(1 ppm = 1.23 mg/m³ @ NTP

PROPERTIES: gas; BP -19.5 °C;
vapor density 1.067 (air = 1.00);
explosive range 7 to 73 % v/v in air

SYNONYMS: methanal; CAS #50-00-0; formalin (aqueous 30 to 50% w/v HCHO).

SAMPLING

SAMPLER: FILTER + IMPINGERS
(1-µm PTFE membrane and 2 impingers, each with 20 mL 1% sodium bisulfite solution)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 2 L @ 1 ppm
-MAX: 100 L

SHIPMENT: transfer samples to bottles before shipping

SAMPLE STABILITY: 30 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 100 to 600 µg per sample [2]

BIAS: none identified

OVERALL PRECISION (s_r): 0.09 [2]

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: formaldehyde

SAMPLE WORKUP: note liquid volume; remove 4-mL aliquot

ANALYSIS: color development (chromotropic acid + sulfuric acid); absorbance @ 580 nm

CALIBRATION: solutions of formaldehyde in distilled water

RANGE: 2 to 40 µg per sample

ESTIMATED LOD: 0.5 µg per sample [2,3]

PRECISION (s_r): 0.03 [2]

APPLICABILITY: The working range is 0.02 to 0.4 ppm (0.025 to 0.5 mg/m³) for an 80-L air sample. This is the most sensitive formaldehyde method in the NIOSH Manual of Analytical Methods and is able to measure ceiling levels as low as 0.1 ppm (15-L sample). It is also preferred for the determination of formaldehyde in area samples at all concentrations due to its simplicity.

INTERFERENCES: Phenols, in 8-fold excess over formaldehyde, produce a -10% to -20% bias [4]. Ethanol and higher M.W. alcohols, olefins, aromatic hydrocarbons [5] and cyclohexanone also produce small negative interferences [4]. Little interference is seen from other aldehydes [4].

OTHER METHODS: This method was originally adapted from the Intersociety Committee [6] and designated P&CAM 125 [4]. For personal samples or where interferences to this method are present, use Method 2502.

Source: Reference 45

REAGENTS:

1. Chromotropic acid, 1%. Dilute 0.10 g 4,5-dihydroxy-2,7-naphthalene disulfonic acid disodium salt to 10 mL with distilled water. Filter. Store in brown bottle. Prepare fresh weekly.
2. Sulfuric acid, 96%.*
3. Formaldehyde stock solution, 1 mg/mL (See APPENDIX).
4. Formalin solution, 37%.*
5. Distilled, deionized water.
6. Sulfuric acid, 0.02 N, aqueous.
7. Sodium hydroxide, 0.01 N, aqueous.
8. Sodium sulfite, 1.13 M, aqueous.
9. Sodium bisulfite, 1%. Dissolve 1 g in distilled water. Dilute to 100 mL. Prepare fresh weekly.

*See Special Precautions.

EQUIPMENT:

1. Sampler: 37-mm filter cassette with 37-mm polytetrafluoroethylene (PTFE) membrane filter, 1- to 3-μm pore size followed by two midget impingers; inert, flexible tubing for cassette-to-impinger connection.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Bottles, screw-cap Nalgene CPE, 50-mL.
4. Spectrophotometer, visible, 580 nm.
5. Volumetric pipettes, 0.1-, 0.5-, 1-, 4-, 5-, 6- and 10-mL; 1-, 2- and 5-mL, graduated in 0.1-mL units, with pipet bulb.
6. Volumetric flasks, 10- and 100-mL, and 1-L.
7. Burets, 50-mL.
8. pH meter.
9. Pipettes, 2-mL, disposable, with pipet bulb.
10. Spectrophotometer cuvettes, 1-cm.
11. Flasks, glass-stoppered, 25-mL.
12. Graduated cylinder, 25-mL.
13. Waterbath at 95 °C.
14. Magnetic stirrer.
15. Beaker, 50-mL.

SPECIAL PRECAUTIONS: Sulfuric acid is extremely corrosive; handle while wearing acid-resistant gloves, apron and full face shield with goggles.

Formaldehyde is viewed as a potential carcinogen by NIOSH [1] and should be handled in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fill the two impingers for each sample with 20 mL 1% sodium bisulfite solution. Make cassette-to-impinger and impinger-to-sampling pump conections with flexible, inert tubing. Insert a second filter/cassette assembly in line between the sampler and sampling pump to trap any liquid which might splash over from the impingers during sampling.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 2 to 100 L.
4. Transfer the contents of the impingers to separate polyethylene bottles for shipping.

SAMPLE PREPARATION:

5. Transfer each impinger solution to a clean, dry 25-mL graduated cylinder. Note volume of solution from front impinger, V_f (mL), backup impinger, V_b (mL), and blank impinger, V_B (mL).
6. Pipette 4-mL aliquots from each sample solution into 25-mL glass-stoppered flasks.
   NOTE: Adjust aliquot size to contain between 2 and 20 μg formaldehyde for optimum absorbance.

CALIBRATION AND QUALITY CONTROL:

7. Prepare a calibration stock solution by dilution of 1 mL of 1 mg/mL formaldehyde stock solution to 100 mL with 1% sodium bisulfite solution.
8. Pipet, e.g., 0, 0.1, 0.3, 0.5, 0.7, 1.0 and 2.0 mL calibration stock solution into 25-mL glass-stoppered flasks.
9. Add 1% sodium bisulfite solution to bring the volume of each working standard to 4 mL.
   NOTE: These working standards contain approximately 0, 1, 3, 5, 7, 10, and 20 µg formaldehyde. Use the exact values based on standardization of the formaldehyde stock solution.
10. Analyze together with samples and blanks (steps 12 through 15.
11. Prepare calibration graph (absorbance vs. µg formaldehyde/4 mL).

MEASUREMENT:

12. Add 0.1 mL 1% chromotropic acid to the flask and mix.
13. Add 6 mL conc. H_2SO_4 slowly to the flask. Replace the stopper gently. Gently swirl the solution to mix.
    CAUTION: Exothermic reaction.
14. Heat the solution to 95 °C for 15 min. Cool the solution to room temperature.
    NOTE: Use caution due to the corrosive nature of hot sulfuric acid and the possible pressure buildup within the flask.
15. Read sample absorbance at 580 nm in a 1-cm cuvette.
    NOTE: If absorbance is greater than the highest standard, take a smaller aliquot, dilute to 4 mL with 1% sodium bisulfite solution, and analyze.

CALCULATIONS:

16. Calculate the mass, µg, of formaldehyde in each front impinger (M_f), back impinger (M_b) and average blank impinger (M_B). Use the appropriate aliquot factor (e.g., 4 mL aliquot/original volume from step 6) and the total sample volume noted in step 5.
    NOTE: Discard the sample if the mass found in the backup impinger exceeds 1/3 the mass found in the front impinger. Collection efficiency is <0.95 for each impinger.
17. Calculate the concentration, C (mg/m^3), of formaldehyde in the air volume sampled, V (L):

$$C = \frac{M_f + M_b - 2M_B}{V}, \ mg/m^3$$

EVALUATION OF THE METHOD:

The method was checked for reproducibility by having three different analysts in three different laboratories analyze standard samples containing between 1 and 20 µg formaldehyde. The results agreed within ± 5% [6]. This method was independently compared with the 2,4,-dinitrophenylhydrazine-coated silica gel method of Beasley et al. over the range of 0.8 to 2.2 ppm formaldehyde [8] and was found to give approximately 25% lower concentrations.In another study comparing this method, P&CAM 318 [7], and the method of Beasley, et al., all three methods were found to be statistically equivalent under laboratory test conditions and loadings from 8.2 to 22.4 µg per sample of formaldehyde [9].

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APPENDIX:

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)
Dilute 2.7 mL 37% formalin solution to 1 L with distilled, deionized water. Standardize as follows:

Place 5.0 mL 1.13 M sodium sulfite solution in a 50-mL beaker, stirred with a magnetic stirrer. Adjust pH to between 7 and 9 with base or acid. Record the pH. Pipet 10.0 mL stock formaldehyde solution into the beaker. The pH should now be about 12. Titrate the solution back to its original pH with 0.02 N sulfuric acid. (1 mL of 0.02 N sulfuric acid = 0.600 mg HCHO; about 17 mL acid needed.) Calculate the concentration, C_s (mg/mL), of the stock formaldehyde solution:

$$C_s = \frac{30.0 \cdot [(N_a \cdot V_a) - (N_b \cdot V_b)]}{V_s}$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid
V_a = volume of acid (mL) used for titration
N_b = normality of NaOH
V_b = volume of NaOH (mL) used for back titration
V_s = volume of HCHO stock solution (10.0 mL).

Appendix F. Calculations

Formalin Solution Formaldehyde Concentration

$$(y_F,\ g/mL) = \frac{(y_{F,\ A.C.S.\ Certified},\ \text{weight \%})}{100} \cdot (\rho_F,\ g/mL)$$

Injection Solution Formaldehyde Concentration

$$(y_{HCHO},\ mg/mL) = (y_F,\ mg/mL) \cdot \frac{u_F}{u_{[solution,\ total]}}$$

Total Volumetric Gas Flowrate through Rotameter:
Correction to Standard Conditions

$$Q_R = Q_C\left[\frac{P_C\ T_R}{P_R\ T_C}\right]^{1/2} = Q_C\left[\frac{406.7\ \text{in}\ H_2O\ .\ T_A}{P_R\ .\ 298.15K}\right]^{1/2} \quad *$$

$$Q_S = Q_R\ \frac{P_R\ T_S}{P_S\ T_R} = Q_R\ \frac{P_R\ .\ 298.15K}{406.7\ \text{in}\ H_2O\ .\ T_A} \quad **$$

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* Rotameter equation (108)
** Derived from ideal gas law (108)

Calculated Generated Formaldehyde Concentration

$$(x_{HCHO},\ ppm) = \left[\frac{10^6 ppm}{parts/part} \cdot y_{HCHO} \cdot \frac{1\ gmol}{30.05g} \cdot \frac{24.465L}{gmol} \cdot u_{inj}\right] \cdot \frac{1}{\dot{u}_{air[tot]} \cdot t}$$

Mass of Collected Formaldehyde, Total in (one) Impinger

$$m_{HCHO(impinger)} = m_{HCHO(aliquot)} \cdot \frac{u_{impinger}}{u_{aliquot}}$$

Sampled Formaldehyde Concentration

$$(x_{HCHO},\ ppm) = \left[\frac{10^6 ppm}{parts/part} \cdot m_{HCHO} \cdot \frac{1\ gmol}{30.05g} \cdot \frac{24.465L}{gmol}\right] \cdot \frac{1}{\dot{u}_{air} \cdot t}$$

NOMENCLATURE

Variables

m_{HCHO} = total mass of formaldehyde collected in sample

$m_{HCHO(aliquot)}$ = mass of formaldehyde in an aliquot of sample solution

$m_{HCHO(impinger)}$ = mass of formaldehyde collected in one impinger of a sample

P_R = pressure (absolute) "seen" by rotameter ball

Q = volumetric flow rate, rotameter

Q_c = volumetric flow rate, nominal from calibration curve

Q_R = volumetric flow rate, corrected to conditions at rotameter ball

Q_S = volumetric flow rate, rotameter, corrected to standard conditions

t = sampling time

T_A = temperature, ambient

T_R = temperature "seen" by rotameter ball
$= T_A$

u = volume

$\dot{u}_{air,s}$ = flow rate of air, each sample (at standard conditions)
$= Q_S$ of pump, corrected to standard conditions

$\dot{u}_{air,tot}$ = total air flow rate at standard conditions
$= Q_S + Q_{mass\ flowmeter,s}$

u_F = volume of Formalin used (in solution of interest)

u_{inj} = injection volume

x_{HCHO} = concentration of formaldehyde in air

y_F = Formalin solution formaldehyde concentration, mass-to-volume

y_{HCHO} = injection solution mass-to-volume concentration

ρ_F = density of Formalin solution, mass-to-volume

Constants

$[M.W.]_{HCHO}$ = molecular weight of formaldehyde
= 30.05 g/gmol (134)

P_c = pressure, rotameter calibration curve
= P_s

P_s = standard pressure
= 406.7 in H_2O = 760 mmHg

T_c = temperature, rotameter calibration curve
= T_s

T_s = standard temperature
= 298.15K = 25°C

V_m = molar volume of ideal gas (@ 273.15K[0°C], 1 atm)
= 0.02241383 m^3/gmol (134)

$V_{m(25°C)}$ = molar volume of ideal gas (@ 298.15K[25°C], 1 atm)
= 0.024465 m^3/gmol = 24.465 L/gmol (derived from V_m and Ideal Gas Law)

Subscripts

aliquot - refers to the portion of a sampling solution used in the analysis

impinger - refers to either the primary or back-up impinger used in a sample

C - calibration-curve conditions

R - rotameter-ball actual conditions