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## ***Formaldehyde Measurements in Canadian Homes Using Passive Dosimeters***

by C.J. Shirtliffe, M.Z. Rousseau, J.C. Young et al

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### RÉSUMÉ

L'efficacité des dosimètres que l'on trouve sur le marché et des dosimètres passifs expérimentaux a été évaluée après des expositions s'échelonnant de deux à quatre jours et de sept jours. Les effets du transport, de l'entreposage, de l'humidité et de la vitesse de l'air sur des appareils témoins et sur l'efficacité globale ont été soigneusement étudiés.

Les modifications apportées à la conception, la manipulation, la suppression de la contamination et au contrôle de la production, ont amélioré la reproductibilité des essais et les appareils témoins, et ont rendu les dosimètres presque aussi précis que les prises d'échantillon.



# Formaldehyde Measurements in Canadian Homes Using Passive Dosimeters

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*Formaldehyde dosimeters have been tested in urea-formaldehyde foam insulated Canadian homes in which formaldehyde levels range from 0.02 to 0.2 ppm. Performance of commercial and experimental passive dosimeters was evaluated over 2- to 4- and 7-day exposures. Effects of transport, storage, humidity, and air velocity on blanks and overall performance were investigated. Modifications have improved reproducibility and blanks. Changes have involved design, handling, removal of contamination, and production control. The changes have resulted in the precision of dosimeters becoming almost equal to that of impingers. Devices under development are discussed. Design requirements include precision, accuracy, cost, use by untrained personnel, and blanks. Design requirements identified in the work for low-level dosimeters are discussed. Studies and the types of devices used in each are tabulated.*

**D**URING 1980-84 SEVERAL HUNDRED THOUSAND formaldehyde (HCHO) measurements were made in Canadian homes. Most of the measurements were in homes that contain urea-formaldehyde foam insulation (UFFI). During 1980 and early 1981, following a ban on UFFI sales in Canada, most measurements were made by technicians with the NIOSH P&CAM 125 chromotropic acid method and water-filled impingers (bubblers) to collect the formaldehyde over 1-2 h (1). In late 1980 a change was made to 3- and 4-h collection periods, sodium bisulfite solutions in the impingers, and improved analytical procedures (2). In September 1981 the Federal Government of Canada initiated a 10-week survey and study of 1978 UFFI

homes and 383 non-UFFI homes spread across Canada (3) (the "2300-home" survey). The collection and analysis were done by five commercial firms. The program started with the modified NIOSH chromotropic acid procedure and 3-h impinger collection, with 1% sodium bisulfite solution, after a 24-h preconditioning of the house. The latter part of the program included measurements with two 1-day and one 7-day type of passive formaldehyde dosimeters that sampled by permeance or diffusion. The results showed that the dosimeters were not subject to the wide variations found in the impinger measurements, and that they tended to give mean values approximately 25% higher. The differences in duplicate impinger readings, even with quality control, varied from 38% at the 0.1-ppm level, to 54% at the 0.05-ppm level, to 100% at the 0.015-ppm level (3).

Smaller studies followed in which the sodium bisulfite solution in impingers was replaced by molecular sieve to produce dry impingers. Studies were also made in which results from several types of long-term formaldehyde dosimeters were compared to repeated short-term measurements. Development of new formaldehyde dosimeters and improvement of existing dosimeters were initiated. The results of the measurements with passive dosimeters were promising even for the levels of 20–200 ppb by volume (0.02–0.20 ppm by volume) normally encountered in homes. The precision of dosimeter measurements was similar to that of active sampling techniques used in previous large studies (Figure 1). The tendency with the dosimeter was to indicate somewhat more formaldehyde than was present;

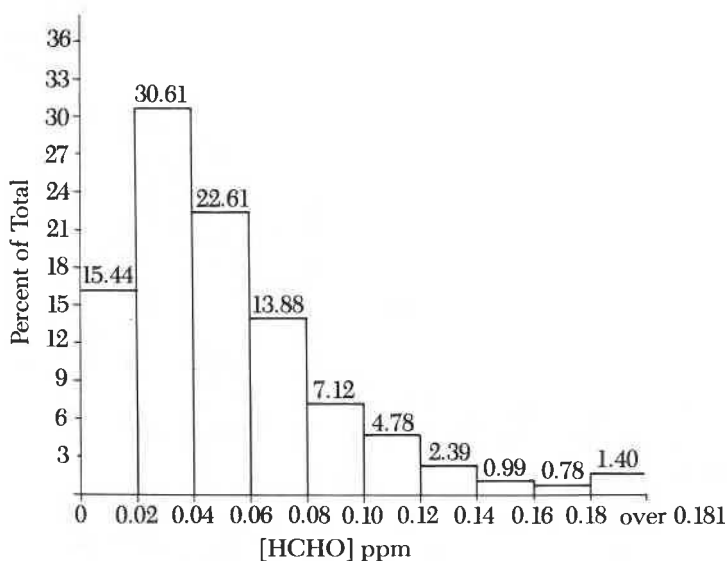


Figure 1. Distribution of HCHO levels in houses (national testing survey).

that is, additional formaldehyde was absorbed in shipment rather than that already sampled lost, and field blank readings were higher than those of laboratory blanks (3). The potential long-term exposure to gaseous formaldehyde could be measured in homes with the dosimeter over the basic 7-day family living cycle.

Short-term measurements were given lower priority because observations of diurnal and annual variations in UFFI homes indicated that formaldehyde concentrations in some homes responded rapidly to changes in the UFFI cavity environment and therefore to meteorological conditions. Peak-to-peak variation by factors of 2-4 and occasionally 10 had been measured (Table I). Peaks occurred in the evening (4) and during the autumn, and minimums occurred in late winter (Figure 2) when the formaldehyde concentration in the walls dropped by a factor of as much as 4 and occasionally 10. Diurnal and seasonal variations were generally larger in UFFI than in non-UFFI homes. Similar variations occurred in the wall cavities.

The Federal Government of Canada initiated an assistance program for homeowners in December 1981. The program involves several dosimeter measurements of formaldehyde in up to 80,000 UFFI homes during the period 1982-86. The deployment, collection, and analysis of dosimeters are to be done primarily by commercial laboratories and the Federal Government of Canada is to handle all collection of data. Houses entering the program are given a pretest in which dosimeters are sent to and returned from the homes by mail. Houses in the program have formaldehyde concentrations measured by a pair of 7-day dosimeters one to four additional times during the program, depending on their routing through the program and the results of previous tests. Thus, a relatively inexpensive but precise and accurate device to permit comparisons between results is needed.

As of February 1984, some 150,000 to 200,000 formaldehyde dosimeters had been used in the program and in related research. The majority of these were specially ordered, commercially manufactured units. Units that originally had a marginal performance have evolved into reasonably reliable devices. The evolution is continuing, along with development of improved new devices. Some devices are evolving into higher precision reference units and others into low-cost, somewhat less precise or accurate devices for use in larger studies.

**Table I. Diurnal Variations in Formaldehyde Levels (ppm)**

<i>House Number</i>	<i>10:00 A.M.</i>	<i>2:00 P.M.</i>
24	0.04	0.36
24	0.08	0.16
19	0.16	0.092
49	0.13	0.29

NOTE: All results are from Study 9 of Table IV.

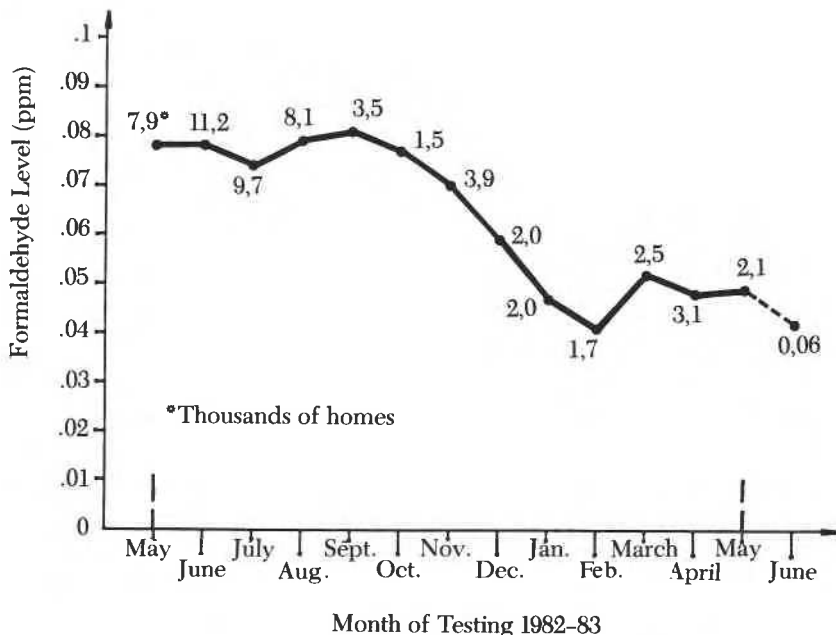


Figure 2. Average formaldehyde measurements in UFFI homes (seasonal variation Canadian UFFI-ICC program).

pollutants to much the same extent as the primary device. This technique has not been widely used. Field and laboratory blanks are of most use when

The UFFI program has provided a rare opportunity to examine details of many types of equipment and methods for measuring low-level air pollutants. The data collected from the homes in the UFFI program may be useful in defining the average and extremes in exposure of occupants to formaldehyde under different weather conditions and at different times of the year. The evolution phase has involved an extensive review of the fundamentals of what might be called indoor air dosimetry.

Many of the findings about the design, manufacture, use, and analysis of dosimeters and about the performance of other measurement devices are directly applicable to other studies or surveys of low-level pollutants.

An overview of the experience gained in Canada during the studies up to early 1984 will be presented in five sections.

### *Dosimeters for Measuring Air Pollutants*

**Definition of a Dosimeter.** Dosimeters are devices for collecting one or more substances in air; subsequent analysis is usually required to indicate quantities collected, which in turn allow calculation of exposures. There

are two basic types: passive dosimeters for gaseous pollutants (less often dust or spores) and active dosimeters for particulate matter, aerosols, and gaseous pollutants. Passive dosimeters are also called personal samplers, and active dosimeters are often called sampling tubes or, when filled with liquid, impingers or bubblers.

**Description of a Dosimeter System.** Dosimeters collect the molecules or particles of a pollutant from a known volume of air over a given period of time. The components of a dosimeter system can be some or all of the following: the collection medium, or media, including desiccant layers or a liquid-coated matrix; the primary container with nipples to allow collected air to flow through openings or the pollutant gas to diffuse into the collection medium; caps or an outer-sealed container to prevent the device from sampling before the sampling period begins; screens, porous plugs, or membranes to hold the collection medium in place or to prevent spillage; screens, porous plugs, or membranes to filter out dust entering the device; screens, porous plugs, or membranes to guide or control the air flow or sampling at the input to the device; for an active dosimeter, a pump and flowmeter or flow controller; for a passive dosimeter, one or more columns of air of known dimensions to control the rate of diffusion and therefore the rate of sampling of the pollutant gas or gases from the surrounding air; components to suspend or support the device during deployment; seals for openings in the containers and packages for shipment; and labels for identifying the device and recording its exposure.

**Fundamental Need for Field Blanks.** Dosimeters become activated when they are produced, so they collect pollutant material from the surrounding environment by diffusion or mass transfer during production; from the surfaces of the components after production; from and through the components during storage and shipment; by diffusion and mass transfer, caused by pressure and temperature cycles, through leaks in the caps or outer container or other joints during storage and shipment; and during the eventual analysis.

In such cases, the measurement made with the exposed primary measuring device must always be compared with an identical secondary device that has the same occasions for collection as the primary measuring device, except during the sampling period. The secondary device must also have an identical aging period. The secondary device is called a field blank and differs from a laboratory blank. A laboratory blank is a testing device that has never left the laboratory; it has had a similar aging period but has not had identical occasions to collect the gas as the primary device or the field blank. Alternatively a field blank may have a period of exposure to the same atmospheres as the primary device but for a shorter duration. The collection medium of the field blank is exposed to water vapor and other

the variations of the blanks are small compared to the changes from sampling and aging.

Some dosimeters are activated only after deployment and can only sample from that time until the device is analyzed. If the medium is analyzed immediately, blanks may not be required or may be of lesser importance.

The equation for conversion of the mass of gas collected in a dosimeter and the field blank to the equivalent parts per million by volume is given in Appendix 1.

**Collection Medium in a Dosimeter.** The collection medium (or media) is the heart of the dosimeter. The forms of medium vary from simple to complex: a liquid that absorbs and stores the gas, gases, or dust by forming a simple solution; a solid medium such as a filter bed for dust; a desiccant for water vapor or adsorbent bed such as a molecular sieve for gases and vapors; a solid bed of dry chemicals or a film of viscous liquid chemicals, including water films, which chemically rather than physically trap the pollutant (reactions may form adducts or derivatives); and liquid solutions that contain chemicals.

For some dry collection media the presence of water vapor may be essential or may affect the collection rate or the recovery rate.

The collection medium may not be 100% effective; all the pollutant may not be collected from the volume of air sampled, or the collection medium may re-release pollutant to the air. Passive devices may not respond linearly to changes in concentration of the gas because of the establishment of a pollutant vapor pressure over the collection medium. Failure to achieve 100% collection may be partially compensated for in the calibration process; this compensation may be reliable provided it is under 10%. Chemical reactions may convert the gases to other chemicals that are not recovered in the analysis. Biological activity in the medium may consume the gases or break down dust collected. No simple way to compensate for such losses is known, so they must be minimized by the selection of a reliable medium.

Molecules of formaldehyde may be stored in their original form, dissolved in a liquid, stored as adducts as with sodium bisulfite solutions, reacted directly with chemicals to form derivatives as with triethanolamine or 2,4-dinitrophenylhydrazine, or reacted directly with chemicals to produce a colorimetric reaction in the solution or film as with chromotropic-sulfuric acid solution. The derivatization or reactions to produce an immediate colorimetric reaction are least subject to loss during storage.

**Factors Affecting the Accuracy of Dosimeters for Gas Measurement.** The collection medium is not the only component that can affect the accuracy of the dosimeter. Dosimeters are such simple devices that their operation is often taken for granted; major sources of both random and fixed errors are often overlooked, especially errors involving the com-

plete dosimeter package including shipping materials. Calibration techniques and approximations adequate for minimizing errors that arise in the measurement of occupational levels of gases may be inadequate for measurement of levels inside homes. When collecting a gas that has unpredictable and relatively complex behavior, such as formaldehyde, at levels approaching outdoor levels, large and highly significant errors can occur. Small changes in design, manufacture, deployment, and analysis can introduce unexpected random or fixed errors.

The accuracy of dosimeters can be affected by factors that influence the collection, storage, and release of gases from the collection medium. Some of the same factors and some additional ones will affect the sampling rate of the dosimeter, in particular the diffusion rate to the collection medium. The presence of dust, aerosols carrying the gases, and polymerized gas molecules can increase the sampling rate. Some factors that can affect the accuracy of dosimeters for gas measurement are listed in Table II along with the effect caused and a very approximate estimated error rating, which is given only as a prioritization parameter for error studies. In evaluating the performance of a dosimeter or in searching for causes of inaccuracies in results, the factors in Table II should not be overlooked. These factors cannot be precise because they depend on the design and deployment of the dosimeter, the gas being measured, and the environment of the sampling.

Formaldehyde is a very reactive gas, and this reactivity makes it difficult to establish reliable sampling rates. Many environmental factors affect the results. Some of the factors are discussed in later sections.

The errors involved in the colorimetric analysis of the eluant from exposed dosimeters are similar to the errors for normal colorimetric analysis of formaldehyde collected in water-filled impingers. The primary differences are the small quantities of water used to elute the gas from the collection medium and the need to remove particulate matter from the solution. The elution process must be checked for its effectiveness at recovering the correct amount of formaldehyde. Discussion of the analytical procedures has been for the most part excluded from the following discussion on dosimeter development, although considerable work has been done on the chromotropic, pararosaniline, and 2,4-dinitrophenylhydrazine methods to improve their performance and to adapt the methods for use in homes.

### *Adaptation of Commercially Available Dosimeters for Use in Homes*

Three commercial formaldehyde dosimeters were evaluated as they became available and were modified in cooperation with the manufacturers to improve their performance for measurements in homes. Each of these dosimeters is discussed in detail in this section. A comparison of the various devices is given in Table III.

**Pro-Tek C-60 Du Pont Dosimeter.** BACKGROUND. The Pro-Tek

Table II. Some Factors That Affect Accuracy of Dosimeters

<i>Factor</i>	<i>Type of Medium Affected<sup>a</sup></i>	<i>Effect</i>	<i>Estimated Error Rating<sup>b</sup></i>
High absolute humidity	dry	capacity reduction	1
Low absolute humidity	wet	evaporation	3
Large humidity variations	dry	loss from media	3
Large temperature changes	dry	loss from media	2
	both	sampling rate changes	4
Barometric pressure variations ( $\pm 10\%$ )	both	diffusion rate changes	4
	dry	vapor pressure on medium changes	3
Diffusion of other gases to surface	both	small changes in sampling rate	4
Adsorption of gas on diffusion tube	both	nonconstant sampling	3
High face velocity (turbulence)	both	increased sampling rate	3
	both	decreased sampling rate	1
Low face velocity	both	decreased sampling rate	1-2
Swelling of permeance membrane (dimethyl silicone)	both	decreased sampling rate	1-3
Dust collection at mouth of device (on screen)	both	increased sampling rate at low concentrations	1-2
Sampling of aerosols	both	increased sampling rate by adsorbed gas	?
Sampling of gas polymers	both	changed sampling rate	?
Development of vapor pressure over medium (back desorption)	dry	collection not true integration	1-2
	both	loss of collected gas	2-3
	both	reduced sampling rate	2-3
	both	calibration impossible	2-3
	wet	similar to dry, but effect generally less	1-2

<sup>a</sup>"Both" indicates both wet and dry media.

<sup>b</sup>The estimated error ratings are defined as follows: 1, 50-100%; 2, 25-50%; 3, 10-25%; 4, 0-10%; and ?, impossible to assess from data so far.

C-60 formaldehyde dosimeter [Du Pont (6)], composed of a single blister unit, was selected for initial studies as it was the only personal monitor specifically developed for measurement of formaldehyde that was commercially available in 1981. A review of the data indicated that the Du Pont formaldehyde dosimeter had considerable potential for low-level measurements and 7-day exposures. It was designed for occupational levels and had a capacity of 2-50 ppm · h. Du Pont had done extensive laboratory and some field evaluation of the device. Most of the data were for exposures of 8 h and concentrations of approximately 0.5-10 ppm. The mean blank

Table III. Formaldehyde Dosimeters Studied

Device	Material <sup>a</sup>					Sampling Rate (cm <sup>3</sup> /min)	Collection Medium	Colorimetric Method Used		Special Considerations for Analysis	Recommended Exposure Duration (days)
	Reser- voir	Dif- fuser	Cap	Inner Bag	Outer Bag			Basic Method <sup>b</sup>	Modification in Analysis		
Du Pont Pro-Tek	serlin plastic	PE	PE	PE	foil	2.27	sodium bisulfite solution	CTA	Du Pont-Beak	precise make-up of evaporation	5-7
AQRI	glass	glass	PE	PE <sup>c</sup>		3.95	sodium bisulfite	CTA	AQRI-Beak	centrifuging	4-7
3M	PE	PE	PE		PE <sup>d</sup>	65.9	on glass fiber sodium bisulfite	CTA	3M-Beak	filtration	1-7 <sup>e</sup>
Concord	PE	PE	PE	PE		4.16	on cellulose mol. sieve 13X (1/16 in. pellets)	PRA	Concord	filtration	7
NAE-NRCC	glass	glass	PE	PE		4.03	mol. sieve 13X (beads)	CTA	NAE-Beak	filtration	3-4

<sup>a</sup>PE is polyethylene.<sup>b</sup>CTA is chromotropic acid; PRA is pararosaniline.<sup>c</sup>Unsealed.<sup>d</sup>Semisealed.<sup>e</sup>Insufficient documentation to establish well.

absorbance and variation were quality controlled so that accuracies of  $\pm 25\%$  could be achieved within that range at a 95% confidence level.

**VERSION I: INITIAL DESIGN: A SINGLE BLISTER UNIT.** The device consists of a diffusion strip that contains 34 holes approximately 0.6 mm in diameter and 6 mm long (the face velocity effect is eliminated by using these multiple small-diameter holes and low sampling rate per hole [length-to-diameter ratio is 10]); a diffusion membrane between the diffusion strip and the adsorbent medium to prevent leakage and to act as a separator for dust; a wet adsorbent medium, 2.4 mL of a 1% sodium bisulfite solution held in the diffusion blister; a plastic shell that covers and protects the plastic blister against breakage and UV light and supports the blister while it is being exposed; an aluminum pouch and two plastic closures that act as sealing materials for the device after exposure (no cap for the diffusion strip was used); some labels (stickers) for user identification, lot identification; and recording data; and instructions for analysis by colorimetry and Du Pont-modified NIOSH P&CAM 125 chromotropic acid method.

*Field Studies.* In 1981, the Federal Government of Canada conducted the 2300-home survey (Study 2, Table IV, and Ref. 3). Three-hour impinger tests were run on the first day of a 7-day measurement. Pro-Tek C-60 monitors were used in approximately 900 homes as a first trial for indoor air quality use. The dosimeters were deployed by technicians, exposed for 7 days, then mailed by homeowners to a laboratory in Toronto. Although the devices did meet manufacturer's specifications, neither the blank values nor the confidence level was adequate for studies in homes. Various problems had to be resolved to improve the performance of the Pro-Tek C-60 dosimeter for the monitoring of low levels of formaldehyde. These problems were as follows:

**Problem 1:** High field blank readings with large random error varying from lot to lot.

**Cause:** Contamination of the monitor inside the pouch.

Large self-adhesive labels had been placed on the outside of the plastic shell of unexposed badges; these labels were inside the pouches during the journey back to the analytical laboratory (2–20 weeks) and caused contamination of the sampling blister unit. Adhesive used for the sticker and ink used on the label, especially from felt marker pens used inadvertently, emitted various gases and contaminated the solution in the blister (Table V).

**Problem 2:** High and variable laboratory blank readings.

**Cause:** Inadequate control over the cleanliness of the production line.

A contributing factor to the contamination of the pouch was an inadequate control over the cleanliness of the production line and of the storage of components before assembly. Further laboratory experiments showed

Table IV. Formaldehyde Measurement Studies

Study	Number of Buildings	Objectives	Date	Formaldehyde Measurement Technique: Number of Devices per Building per Trial					Active Device
				Du	Pont	AQRI	3M	NAE	
1. National survey, pilot run	100	Monitor levels in UFFI homes where health problems identified.	fall 1981	3					2 Impinger 1 Impinger(O) <sup>a</sup>
2. National survey <sup>b</sup>	2300	Monitor levels in homes across Canada: 1978 UFFI homes and 383 non-UFFI controls.	fall 1981	3 <sup>c</sup>		2			2 AORST <sup>d</sup> 1 AORST(O) <sup>a</sup>
3. New Brunswick survey	83	Repeat of homes from Study 2 because of QA-QC problems.	fall 1981	2		2			2 AORST 1 AORST(O) <sup>a</sup>
4. University of Western Ontario	28	Monitor seasonal variations in levels in UFFI and non-UFFI homes. Each home monitored up to five times.	1982-84	3 <sup>c</sup>		3 <sup>e</sup>	3 <sup>f</sup>	2 <sup>g</sup>	1 AORST 1 Impinger
5. Lavoie study	2	Monitor levels and investigate effects of varying exposure duration.	Aug. 1982	20		20			2 or 3 AORST
6. Building 88 study	1	Comparison of performance of monitors.	1982-83	80		80	20	10	1 Impinger 1 AORST 1 DNPH <sup>h</sup> 1 Impinger
7. SHQ study	1	Monitor elevated levels and compare devices.	1983-84	5 <sup>i</sup>		5 <sup>j</sup>			
8. AQR study	2	Compare performances of two lots of AQR devices with Du Pont at various formaldehyde levels.	mid-1983	45		45			
9. St. John's study <sup>k</sup>	50	Determine levels and compare techniques in UFFI and non-UFFI homes.	summer-fall 1981	2 or 3					MIRAN <sup>j</sup> 1 Impinger

Continued on next page.

Table IV (continued)

Study	Number of Buildings	Objectives	Date	Formaldehyde Measurement Technique: Number of Devices per Building per Trial				
				Du Pont	AQRI	3M	NAE	Active Device
10. Newfoundland study								
a.		Determine levels in homes and schools and compare techniques.	summer-fall 1981	33	45		33	
b.		Compare 3M version II to AQRI version II and AORST.	summer-fall 1981		2-3	2-5		1 or 2 AORST
11. Du Pont study	5	Evaluation of Du Pont double blister device.	winter 1982-83	5-8	2			
12. MacLaren study								
a.	12	Measure levels in non-UFFI homes (19 wk).	winter 1981-82	4 <sup>m</sup>				1 Impinger
b.	10	Measure levels in some air-conditioned homes (10 wk).	summer 1982	4 <sup>m</sup>				2 Impinger <sup>u</sup>
13. PRL study								
a.	50	Measure relationship between levels and airtightness in non-UFFI homes.	1982	2				
b.	46	Measure levels in non-UFFI homes with low air-change rates.	Jan. 1983	2				

14. Canadian study <sup>a</sup>	200	Compare performances of experimental and commercial devices.	summer 1983	3	2	8	
15. UFFI Homeowner Assistance Program <sup>b</sup>							
a. Screening pretest	40,000	Establish levels in UFFI homes before any remedial measures.	1982-86		2		
b. Premeasure (full scale)	13,000	Establish levels before major remedial measures.	1982-86		2		15-30 Detector tubes
Premeasure (medium scale)	14,000	Establish levels before lesser remedial measures.			2		15-30 Detector tubes
c. Postmeasure	17,000	Confirm adequacy of separation between occupants and cavities.	1982-86		2		5 Detector
16. Schools							
a.	18	Establish levels in UFFI and new non-UFFI schools.	1981-82	15-35	0-15	0-12	Impingers <sup>c</sup> AORST <sup>d</sup> DNPH <sup>e</sup>
b.	2	Compare levels in schools to exposure of pupils. Six students per school.	1982		3	3 <sup>f</sup>	

<sup>a</sup> (O) indicates reading taken outdoors. <sup>b</sup> The 2300-home survey; surveys 1 and 2 together are sometimes referred to as the 2400-home survey. <sup>c</sup> In 450 homes only, 2 inside and 1 outside the home. <sup>d</sup> AORST denotes active Oak Ridge sampling tube. <sup>e</sup> Sets of 3 devices, deployed on 5 or more separate occasions. <sup>f</sup> Sets of 3 devices, deployed on 2 or more separate occasions. <sup>g</sup> Single time deployment of a pair of devices. <sup>h</sup> DNPH denotes 2,4-dinitrophenylhydrazine sampling tube. <sup>i</sup> Sets of 5 devices, deployed on 9 separate occasions. <sup>j</sup> Sets of 5 devices, deployed on 13 separate occasions. <sup>k</sup> Program of Health and Welfare Canada. <sup>l</sup> MIRAN denotes continuous IR monitor. <sup>m</sup> Two devices deployed inside the home and 2 deployed outside. <sup>n</sup> One impinger inside the home and one outside. <sup>o</sup> Four Concord devices and 8 Concord wall cavity devices were also used per building per trial. <sup>p</sup> Ongoing program; total program registration as of March 1984 was 60,000. <sup>q</sup> Varying numbers of devices were used in different homes. <sup>r</sup> Each student wore 3 consecutive badges for times of 2, 2, and 1 day.

that released gases increased the contamination of the chemical medium in the diffusion blister (Table V).

**Problem 3: Leakage of chemical adsorber solution from the blister.**

**Cause:** Failure of the diffusion membrane over the diffusion strip, evaporation of the blister solution, or inadequate control in filling the blister with the chemical solution.

Spillage of the chemical solution was observed in the foil pouch upon receipt in the laboratory. Some blisters were empty with only a slight solid deposit left. Diffusion membranes were broken, and the solution spilled out and sometimes evaporated; this result was assumed to be induced by squeezing of the device during transportation. The device was relatively fragile. Padded envelopes had been selected because their use permitted faster and far less expensive shipping than the use of small boxes. In many cases, the volume of the chemical collection medium that remained in the blister was small; adjustments had to be made during the analysis of the dosimeter, and thus a source of error was introduced.

**Problem 4: Improper usage by homeowner or technician.**

**Cause:** Complicated deployment procedures.

The dosimeter was complicated for use by homeowners and even trained technicians. Pouches were received that were improperly sealed, labels were either not completed at all or not properly completed. Opening, sealing, and labeling operations were necessary prior to exposure. The design of the plastic closures used to seal the foil pouch made it difficult to seal and even more difficult to reopen after exposure and reseal once the

**Table V. Formaldehyde Contamination Inside Pro-Tek Version I Pouch: Test Results**

<i>Components Tested for HCHO Emission</i>					<i>Conditions</i>		<i>Equivalent ppb for 7-day Exposure</i>	
					<i>Heating 55 °C (h)</i>	<i>Cooling 5 °C (h)</i>	<i>Diffusion Blister</i>	<i>Sealed Blister</i>
<i>D.B.U.</i>	<i>Shell</i>	<i>Pouch</i>	<i>Collector</i>	<i>Label</i>				
					69	27	27	7
•	•	•			69	17	25	9
					69	27	19	9
•	•				69	27	16	7
					64	23	17	4
		•	•		64	23	32	9
					64	23	121	9
•	•	•		•	64	23	129	6
					64	23	39	7
•	•	•	•	•	64	23	37	5

NOTE: The components tested for HCHO emission are defined as follows: D.B.U., double blister unit with diffusion strip; shell, white plastic shell to hold blister unit; pouch, tedlar-coated aluminum foil pouch to hold badge; collector, dilute sodium bisulfite solution; and label, large: 1 in. × 2 in., hand written, and small: 1/4 in. × 3/4 in., machine numbered.

dosimeter was placed inside. The overall difficulty in using the device generated various field-related problems.

**DESIGN MODIFICATIONS FOR VERSION II.** Arrangements were made for the following changes to be made in a single lot of Pro-Tek C-60 dosimeters: (1) A sealed blister was added to the blister unit above the diffusion blister. The chemical adsorbent solution in the sealed blister was isolated from any inside-the-pouch contamination. Its analysis could be used to evaluate the effects on the chemical solution of aging and cycling of temperature during transportation. The aim of this change was reduction of the high mean blank value. (2) The instructions for its use were modified so that only one small factory-printed identification sticker was put into the aluminum pouch. This procedure eliminated unknown inks and labels from the pouch. The production line was cleaned prior to production of the modified devices. The aim of this change was reduction of contamination.

**VERSION II: THE DOUBLE BLISTER UNIT.** *Field Studies.* In early 1982 a field study in 83 homes was carried out in New Brunswick (3). It compared the Pro-Tek C-60 double blister with the Air Quality Research (AQR) PF-1 version I (to be described later) and an active sampling technique based on a molecular sieve collection medium.

Also, several hundred devices were used for surveys in schools insulated with UFFI (Table IV). The problems and observations recorded during these studies are as follows:

**Problem:** Field blank values much higher than laboratory blank values.

**Cause:** Solution aging and pouch contamination.

Analysis of blisters from unopened pouches showed that the sealed blister had a much lower background formaldehyde level than the diffusion blister and could not act as a representative field blank (Table VI, Version II). This result indicated that a major contamination source in the pouch had not yet been eliminated. The white plastic shell that held the device in place and provided a clip with which to suspend it was one possible source of contamination: formaldehyde sticking to the surface of the pouch could be released in high levels that could be absorbed by the chemical solution during extended transportation periods.

The effects of the storage conditions and handling of the diffusion blister were unknown. Laboratory simulation of temperature cycling during transportation and storage was necessary to determine the magnitude of the effect.

The following conclusions were reached as a result of the simulation: The absorbance of the sodium bisulfite solution in the sealed blisters of 25 dosimeters aged at 50 °C increased according to the following equation, where  $t$  denotes the time of exposure (in hours), and  $r$  is the correlation coefficient:

$$\begin{aligned}\text{absorbance} &= 0.0078 + 0.000177 t & r &= 0.93 \\ \text{equivalent parts per billion for 7-day exposure} &= 3.2 + 0.074 t\end{aligned}$$

The absorbance of the sodium bisulfite solution in the diffusion blister that sampled the air in the coated foil pouch increased according to the following equation:

$$\begin{aligned}\text{absorbance} &= 0.030 + 0.00365 t & r &= 0.83 \\ \text{equivalent parts per billion for 7-day exposure} &= 12 + 1.5 t\end{aligned}$$

The difference in the second term gives an approximate measure of the contribution of the pouch at 50 °C and equals  $0.0019t$  or  $0.79t$  ppb. The difference in the first term gives an approximate measure of the collection by diffusion from the pouch prior to the aging test and equals 0.022 absorbance units or 9 ppb.

Deviation of 24 of the 25 data points from the equation was less than 0.012 absorbance units (5 ppb). The data indicate a positive correlation with both solution aging and pouch contamination.

Table VI. Blank Analyses for Various Versions of Pro-Tek C-60 Dosimeters

<i>Dosimeter</i>	<i>Quantity of Blisters Analyzed</i>	<i>Geometric Mean (ppb)</i>	<i>Standard Deviation (ppb)</i>	<i>Range of Readings (ppb)</i>
Version I				
Nine production lots	425	10-43	2-9	6-67
Version II				
Diffusion blister				
Lot 16 <sup>a</sup>	73	29	24	14-55
Lot 19	20	9	2	7-16
Lot 14-2	21	14	3	10-23
Lot 15-8	14	17	3	13-33
Sealed blister				
Lot 16 <sup>a</sup>	75	6	2	3-13
Lot 19	20	6	1	3-8
Lot 14-2	21	5	2	3-11
Lot 15-2	14	9	2	6-12
Version III (Lot 12)				
Diffusion blister	88	12	6	7-39
Diffusion blister	176	16	7	7-57
Sealed blister	42	7	2	4-14
Sealed blister	58	8	6	3-41
Sealed blister	48	7	2	4-16

NOTE: Measured absorbances have been converted to equivalent parts per billion for 7-day exposure.

<sup>a</sup>New Brunswick survey.

Various small experiments were also carried out to isolate possible contamination sources in the pouch. Table V gives results for formaldehyde collected from different combinations of the dosimeter components when exposed for 64 or 69 h at 50 °C, expressed in equivalent parts per billion for a 7-day exposure. The labels inside the pouch are the major source of formaldehyde, and the plastic shell and even the inside liner of the foil pouch are significant sources of uncontrolled contamination.

**DESIGN MODIFICATIONS FOR VERSION III.** A new batch of devices was produced with modifications arrived at in discussions with the Du Pont production department. These were as follows: (1) Another blister unit having both sealed and diffusion blisters was added to the pouch. One of the diffusion blister units was to remain in the pouch from the production stage to the laboratory analysis and was meant to monitor the formaldehyde level in the pouch. The formaldehyde concentration was to be subtracted from that present in the diffusion blister that was exposed to the room air. The other two sealed blisters were to provide information on storage conditions and could be used for evaluating the reproducibility of the analysis combined with constancy of production. The pouch containing the extra blister unit was to be resealed and suspended in close proximity to the exposed blister unit. (2) The white plastic shells were eliminated to reduce contamination. Blister units would be less protected against physical abuse and UV light but would have better protection during shipping.

**VERSION III: TWIN DOUBLE BLISTER UNITS WITHOUT PLASTIC SHELL.**  
*Field Studies.* Field comparisons with other commercial dosimeters were conducted in schools and homes to evaluate reproducibility of results with the dosimeters and to determine the adequacy of the field blanks. The following observations were made:

**Problem:** Field blank readings not sufficiently low and reproducible.

**Cause:** Diffusion blister sampling during storage and transportation.

The sources of contamination were reduced to a minimum but there was no mechanism to reduce the diffusion blister sampling during storage and transportation in case of accidental puncture of the pouch or contamination during the long period of storage before deployment or after sampling. These could all increase the amount of formaldehyde absorbed by the blanks (Table VI, Version III).

**DESIGN MODIFICATIONS FOR VERSION IV.** A large batch of dosimeters was purchased with the following changes: numbers were embossed on each blister unit to avoid use of labels inside the pouch; a cap was placed on the diffusion strip during production, and it was to be removed before exposure and replaced afterwards; individual blister units were sealed into polyethylene bags during production; and white plastic shells were sealed in separate aluminum pouches. Shells were only to be used when excessive exposure to light occurred during the measurement after exposure.

After exposure, the two blister units were to be placed in one of the polyethylene bags and sealed inside the pouch with the same closures as for the pouch.

**VERSION IV: VERSION III WITH DIFFUSION STRIP CAPS AND SEALED BAGS.** *Field Studies.* Evaluation of Version IV has not been completed. One general observation is possible.

The ease of use of the device has decreased with every added complication in the design; simplicity has been sacrificed for an overall improvement in performance. The cost has also increased. The device has become the high-reliability reference dosimeter in field surveys conducted by trained personnel.

**AQRI PF-1 Monitor.** **BACKGROUND.** A second commercial dosimeter was selected in 1982 for use in the UFFI Homeowner Assistance Program. The device was originally designed for monitoring of indoor air quality levels over 7-day periods. It also underwent evolutionary changes. To reduce the number of changes that might be required, a visit was made to the plant and extensive discussions were held on production techniques and quality control. The changes that were subsequently required relate to the selection of formaldehyde-free components, details of production, and improvement of analytical procedures, rather than to changes in form.

**VERSION I: INITIAL DESIGN.** The AQR PF-1 monitor (Air Quality Research International [AQRI]) consists of a glass vial that provides the diffusion column, sized to reduce face velocity effects for indoor conditions; a dry chemical collection medium consisting of a glass fiber filter pad coated with sodium bisulfite and situated at the bottom of the vial; a plastic snug-fit cap that is placed on the closed end of the vial during sampling; on the outside of the bottle, a label that identifies the production lot number; attached to the vial, a ribbon that suspends the inverted device during sampling; and directions for the analysis that is to be initiated in the vial. The collection medium eluent is centrifuged and analyzed by colorimetry by using an AQR-modified NIOSH P&CAM 125 chromotropic acid method.

*Field Studies.* A certain number of devices were analyzed as laboratory blanks as part of the Quality Assurance-Quality Control (QA-QC) program for the UFFI Homeowner Assistance Program. The problems found and observations made in early 1982 are as follows:

**Problem:** High contamination of the device after use of a few lots.

**Cause:** Change in components.

After producing several lots that had good performance, the manufacturer changed to a more precise type of vial and new cords to suspend the device. These vials had a slightly smaller diameter, and, therefore, the original caps were not as tight. In addition, the new cords emitted formaldehyde at levels of several parts per million and escaped checks made on the original cord. The formaldehyde entered the vials during shipment and

storage and produced a serious contamination that was not detected during the manufacturer's QA-QC procedures.

**DESIGN MODIFICATIONS FOR VERSION II.** Caps and precision vials were carefully sized. Low formaldehyde emission ribbons were obtained and checked for formaldehyde emission. The manufacturers improved their QA-QC program. The blank values became acceptably low and more reproducible within lots.

*Field Studies.* In 1982-83, the Lavoie study and the AQRI study (Table IV) were conducted. The first aimed at comparing Pro-Tek C-60 Version II with AQR Version I for various exposure times ranging from 3 to 10 days. The second study included UFFI houses and particle board buildings in which formaldehyde levels varied from 0.04 to 0.8 ppm. In this study, two AQR Version II dosimeters of different lots and one Du Pont Version I were exposed for a 7-day period. The problems observed were as follows:

Problem: Sampling rate not constant.

Cause: Not determined.

The sampling rate decreased after approximately 5 days at formaldehyde levels of approximately 0.1 ppm. At higher concentrations, between 0.15 and 0.4 ppm, the recovery rate of the device compared to the Pro-Tek C-60 Version I was approximately 50%. The sampling rate was different between different production lots.

The cause of the problem could not be positively identified, so a review of available laboratory data on the device was initiated.

In the meantime, the manufacturer recommended that the duration of exposure be reduced to 4 or 5 days; this modification was considered unacceptable to the Canadian UFFI Homeowner Assistance Program.

**DESIGN MODIFICATION FOR VERSION III.** The manufacturer increased the capacity of the device for formaldehyde collection by increasing the amount of bisulfite on the coated glass filter pad. Also the manufacturer modified the analytical procedure to increase its sensitivity and the recovery capability of the dosimeter.

Problem: Calibration factor uncertainty.

Cause: Not determined.

The measurements with the AQRI device were still lower than those of the Du Pont device. Further investigation of possible causes was performed, and the calibration data was reviewed.

**DESIGN MODIFICATION FOR VERSION IV.** The manufacturer increased the calibration factor by 9% after a review of the data and calculation procedure. Where measurements have been made in the same houses before

and after the change in calibration factors, an adjustment must be made to one of the readings.

**VERSION V: THE FUTURE.** Some questions are not completely resolved, and these may require additional modifications to the device. First, the effects of environmental factors such as air moisture content on the recovery and the stability of the sodium formaldehyde bisulfite adduct are not well understood, especially in regard to their effect on absorption under conditions of varying concentration. Also, accuracy in measuring the formaldehyde level when other gases are present needs to be documented. Controlled calibration chamber exposures do not simulate exposure to other gases, dust, and cycling of environmental factors. Only carefully monitored field studies or more complex simulations can improve the knowledge of real-life performance of the monitors. Finally, an indicator is needed to show clearly if the cap has been removed.

**Use of 3M Formaldehyde Monitor 3750 in Canada and Subsequent Modifications.** **BACKGROUND.** The 3M formaldehyde monitor 3750 was originally designed as a personal monitor for occupational areas where relatively high formaldehyde levels are present. Initial devices were supplied with data of extensive laboratory evaluations and some field evaluations.

The objective of the study in Canada was to determine if the device could provide adequate field performance over 168 h in order to be part of the Canadian UFFI Homeowner Assistance Program.

**VERSION I: INITIAL DESIGN.** The 3M formaldehyde monitor 3750 consists of a plastic enclosure measuring 12 × 33 mm (length/diameter = 2.8); dry chemical absorption media consisting of a sodium bisulfite impregnated cellulose disc at the bottom of a vial; a microporous plastic screen at the mouth of the vial to control turbulence effects and to prevent dust entry, held in place with a snap-on ring; a clip for attaching to a cord or ribbon; a snap-on cap that replaces the snap-on ring after exposure and during initial analysis; and instructions for analysis by a 3M-modified P&CAM 125 chromotropic acid method with the elution in the badge but analysis completed outside the monitor.

**Field Studies.** A small-scale field study done in 1982 consisted of deploying the Pro-Tek C-60, AQR PF-1, 3M, and experimental dosimeters side by side in a room where the formaldehyde level was known to be approximately 0.2 ppm. The 3M monitors were exposed for various times from 6 to 72 h. This procedure was to determine the period of constant sampling rate. At that time, the recommended exposure duration for the 3M monitor was 1–2 days. The test was repeated in the same room while a small fan circulated the air.

**Problem:** Actual sampling rate lower than that measured in laboratory.

**Cause:** Probably face velocity effect.

A face velocity effect could partly explain the low sampling rate. The sampling rate increased while the fan was working (Figure 3).

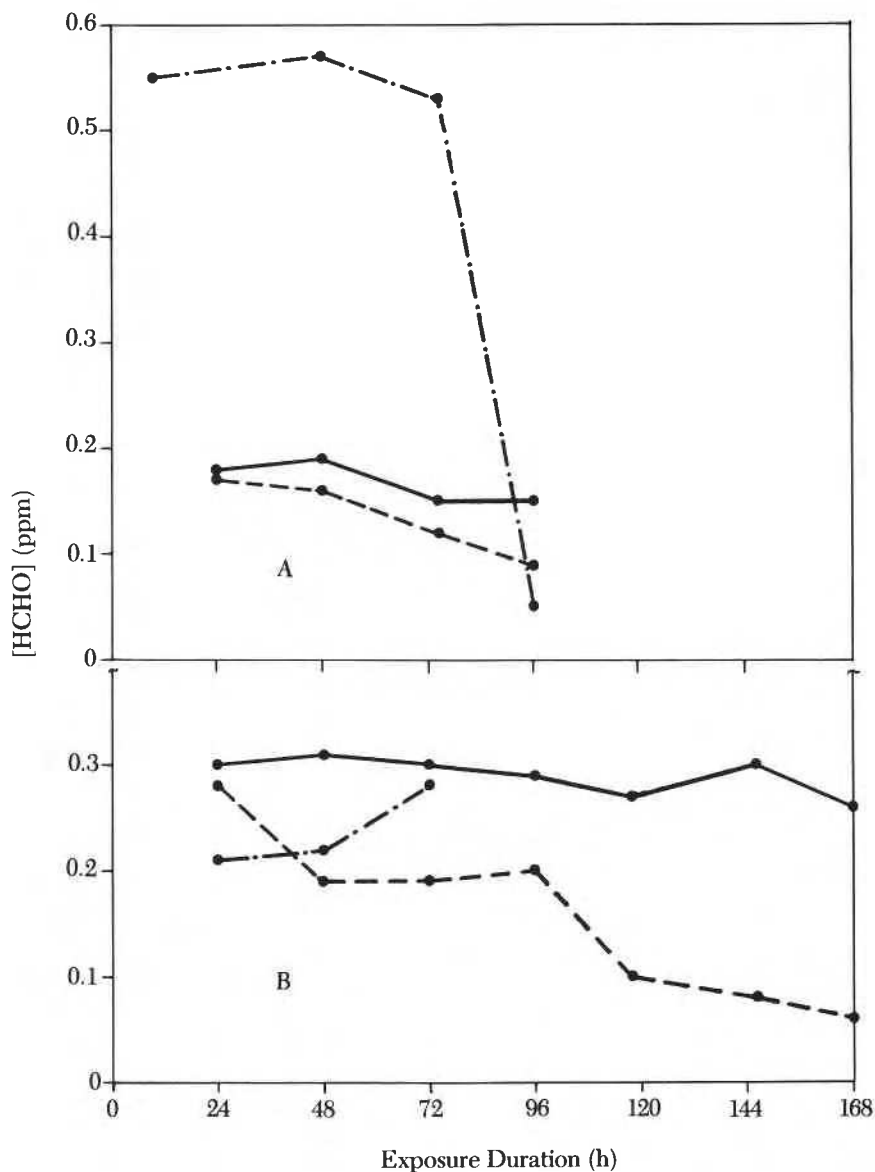


Figure 3. Effect of air velocity on collection rate. Key: A, static air (no fan); B, fan running (air circulating); —, Pro-Tek C-60; ---, AQR PF-1; and - · - ·, 3M.

Data supplied by the manufacturer state that the 3M monitor sampled within 25 % accuracy with air velocities greater than 0.1 m/s. Between 0.05 and 0.1 m/s, the sampling rate decreases by 25 %. Between 0.04 and 0.05 m/s, the rate decreases by an additional 25 % of its original value. The face velocity measured in the room rather crudely was the order of 0.1 m/s and could explain the low result.

**Problem:** Deactivation after about one day of exposure.

**Cause:** Probably insufficient collection medium for the sampling rate.

The 3M device failed to collect formaldehyde after 1-day exposure and appeared to lose formaldehyde if exposed for a longer period.

**Problem:** Complicated procedure for sealing after exposure of the dosimeter.

**Cause:** Poor design.

The snap ring and protective screen must be removed after exposure, and a complex snap cap must be installed. Dexterity is required to place the snap cap on the dosimeter, and many users were unable to accomplish the installation without training.

The identification label at the back of the device is too small.

**DESIGN MODIFICATIONS FOR VERSION II.** The manufacturer tackled the problem of increasing the sampling period and reducing the sampling rate by adding a perforated plastic disc between the chemical medium and the screen to provide face velocity and dust protection.

**Field Study.** A small number of the 3M devices were deployed for 168 h at the same time as a small number of the C-60 Version III (Table IV, Study 6). The results were promising but were obscured by contamination of the absorbent discs at the plant; this contamination gave higher and more variable blank readings.

**FUTURE.** The manufacturer was requested to provide further laboratory evaluation and QA-QC data for the new device before further field testing could be undertaken.

A change in the application would require a complete redesign of the device; this redesign was not contemplated by the manufacturer. Use of the 3M was discontinued except for short-term exposures and research projects.

### *Evaluation of Existing Experimental Devices*

**Active Oak Ridge National Laboratories Dosimeter (Sampling Tube).** The experimental active sampling tube system designed by Oak Ridge National Laboratories (ORNL) was first used as designed (7). It was then modified, and extensive work was undertaken to check its performance and to obtain low and reproducible laboratory blank readings. The original design specified standard polyethylene dryer tubes filled with molecular sieve 13X and held in place with metal screens. Either 30 or 60 L of air was drawn through the devices over a 15- or 30-min period with a sonic orifice

and a timer-controlled pump. Either a specially modified pararosaniline or the chromotropic acid methods were used for analysis (2). These samplers displayed various advantages over the liquid impinger method, including increased sample retention after sampling, ease of use and transportation, and improved reproducibility. The modified system was especially suitable for large studies and for obtaining reliable values in relatively stable conditions against which to compare the results from the passive dosimeters. Problems were encountered with obtaining consistently low blanks when several commercial laboratories were asked to apply a standard procedure. Rather than instituting the special training required, we eliminated the device from the larger studies. The study did indicate that the same technology might be applicable to passive devices and provided valuable information for their development.

**Passive Oak Ridge National Laboratories Dosimeters (Permeance Membrane).** Two experimental passive devices were tested during one 1981 field survey of approximately 80 homes (Table IV, Study 3). Both were based on the ORNL water-filled passive dosimeter design (8). Dimensions were approximately 35 mm in diameter by 15 mm high. A 25- $\mu$ m membrane of dimethyl silicone was placed over the mouth of the polyethylene devices; the adsorbent was water in one case and molecular sieve 13X in the other. The devices were exposed for 24 h, analyzed by the pararosaniline method, and the results were compared with those of the Du Pont dosimeter and liquid impinger values. Performance of both was erratic; good agreement was found for a minority of the devices. Concern arose over the use of the thin membrane and its sensitivity to relative humidity. The permeance of the membrane appeared to change by a significant percentage when the average humidity to which the membrane was exposed changed from 25% to 75%.

**Development of New Formaldehyde Dosimeters.** The availability and adaptability of formaldehyde dosimeters for use in homes was reviewed in 1981. The only dosimeter commercially available to monitor HCHO was the Du Pont Pro-Tek C-60 Version I, designed for monitoring at occupational levels of HCHO. The development and eventual production of a dosimeter in Canada appeared to be the only course that would result in a device uniquely suited to the long-term needs of the Canadian UFFI Homeowner Assistance Program. Achievement of the strict quality control in manufacturing and shipment that was required seemed improbable unless the device could be made under close scrutiny.

The objective of the program was to develop a dosimeter that was inexpensive and accurate and gave a reproducible measurement of formaldehyde. Furthermore, any device that was developed would have to be suited to the measurement of gases other than formaldehyde that were emitted by UFFI or UFFI-contaminated materials. The gases were not identified at that point, as only preliminary work on UFFI offgases had been per-

formed. The simplest scenario was that the same dosimeter be used for all gases. Various techniques for producing and analyzing dosimeters were considered. Investigations of effectiveness of different absorbents, constructions, materials, sampling durations, analytical methods, etc. were initiated.

Two laboratories were enlisted to undertake the development of the dosimeter. One was charged with designing a dosimeter that used gas chromatograph analysis and the other was charged with designing a dosimeter that used colorimetric analysis. Each used its specific area of expertise and experience. The solution was approached from two directions, and at the same time the evolution and use of the commercially available dosimeters described earlier was continuing. Experience gained in that activity was applied to the development of the new devices.

**Development of National Aeronautics Establishment-National Research Council of Canada Dosimeter.** The developmental work on one dosimeter (9) was undertaken at the National Research Council of Canada (NRCC) by the National Aeronautics Establishment (NAE) under the direction of L. Elias, who has experience in the measurement of trace quantities of gases in both the lab and the field using active dry sampling tubes with gas chromatographic analysis. An attempt was made to adapt these techniques to the measurement of UFFI offgases. The first phase was to adapt the device for formaldehyde, then to adapt it to other aldehydes, and eventually to other offgases. The development of the unit for formaldehyde is nearing completion and has been used in comparative studies. The design phase of the NAE-NRCC device included the following studies and selection of components:

**ADSORBENT SELECTION.** Adsorbents that were examined include Alumina, Carbosieve B, Tenax GC, Poropak T, N, and R, Chromosorb 104 and 105, OV-17 on platinum mesh, charcoal, molecular sieve 13X, and silica gel. Trapping efficiencies and recovery were investigated. Because of long experience and good initial laboratory results, silica gel was selected. Silica gel proved to have poor long-term formaldehyde storage, so a change was made to molecular sieve 13X.

**ANALYTICAL TECHNIQUES.** Thermal desorption into a gas chromatograph was originally selected as the most efficient method to sample a variety of gases. Analyses for formaldehyde were made with both flame and photoionization detectors, although photoionization detectors were found to offer little advantage for formaldehyde measurements with the types of gas chromatographs available.

Difficulties with precision of formaldehyde determinations, the greater sensitivity required, and the lack of any reference method that could deal with the small quantities collected made it necessary to change to a larger amount of collection medium in a larger device so comparisons could be made to colorimetric analysis. The better reproducibility and ac-

curacy of the colorimetric analysis for formaldehyde and increasing experience in commercial laboratories with colorimetric analysis dictated a change to such a technique. The chromotropic acid method of colorimetric formaldehyde analysis with water elution, followed by filtration before color development, was selected.

**DIMENSIONS OF DOSIMETERS.** As gas chromatography was the method initially selected, the first versions were slightly modified gas chromatographic adsorption tubes. A supported 2–3-cm length of granular adsorbent was placed in a very narrow (6.3 mm o.d.) piece of 7.5-cm long Pyrex tubing.

Although this design looked promising for high concentrations of formaldehyde typical of occupational exposure, not enough formaldehyde was collected for proper analysis of the lower levels found in UFFI dwellings. The design of the device was changed to increase the sampling rate. A glass specimen bottle approximately 2.3 cm o.d.  $\times$  5.6 cm long, having a screw cap and approximately 1-cm long neck, was employed.

The desire for greater reliability of formaldehyde measurements resulted in the choice of an even larger glass bottle approximately 2.3 cm o.d.  $\times$  8.5 cm long. A very simple screw top design was chosen for low cost. A bed 0.2 cm deep of molecular sieve was measured into the bottom of the tube, and a diffusion length of approximately 8 cm was left. The ratio of diameter to length was then approximately 1.9.

The NAE–NRCC dosimeter was first tested and calibrated in the laboratory, then was compared initially to various versions of the Du Pont and AQR dosimeters in a number of small studies (Table IV, Study 14). A number of problems were found with the performance of the initial version.

**Problem:** Collection capacity at humidities above 70% was low.

**Cause:** Tendency of the molecular sieve to collect water vapor.

The trapping and retention of formaldehyde on molecular sieve decreased with time at higher humidities. At levels of relative humidity below 50% the sampling rate did not change significantly with exposure durations of up to 120 h. However, at relative humidity levels of 70% and higher, decreases in sampling rate of approximately 6%, 12%, and 35% were found after exposure durations of approximately 1, 2, and 5 days, respectively. All experiments were performed at room temperature (22 °C).

**Modification 1.** The bed depth was increased to 0.5 cm but still did not provide adequate capacity at high relative humidities. Preconditioning the molecular sieve by exposure to a humid formaldehyde-free atmosphere did not ameliorate the situation. Cycling humidity levels could cause some of the trapped formaldehyde to be released.

**Modification 2.** The sampling duration was reduced from 7 to 3 or 4

days to reduce humidity-induced effects. This modification improved the accuracy.

Problem: Cap loosening.

Cause: Poor design.

The screw-on caps presented problems in transportation and homeowner handling. Some caps loosened during transportation and resulted in leakage of air and occasional spilling of molecular sieve.

*Modification 3.* Further experimentation with different types of snap-on and more positively locking caps is continuing.

Problem: Different deployment from other dosimeters.

Cause: Different design parameters.

The NAE-NRCC devices were originally designed to be placed up-right on top of furniture. Such placement could permit spillage of sieve and contamination from formaldehyde sources (i.e., shelving and ashtrays), which decreased the choice of placement.

*Modification 4.* For comparison with other devices, a narrow ribbon was attached to allow the devices to be hung from the ceiling.

**FUTURE WORK.** More investigations are underway to evaluate the dosimeter's performance. Field and laboratory trials are planned to test the modified units. Use for other aldehydes and other gases is being evaluated.

**Development of the Concord-NRCC Dosimeter.** Before the UFFI Homeowner Assistance Program was launched, Concord Scientific Corporation had performed work for the Ontario Government on dosimeter monitoring of SO<sub>2</sub> at levels found in homes. For Health and Welfare Canada they had also conducted studies on SO<sub>2</sub> and NO<sub>x</sub> dosimetry at indoor levels.

In 1982, as the UFFI Homeowner Assistance Program got underway, Concord Scientific Corporation was asked to assist in the development of a formaldehyde dosimeter under a contract with the National Research Council of Canada. Various requirements were established including accurate, reproducible formaldehyde measurements at low levels in UFFI houses; selection of formaldehyde-free materials and machine-tooled, tightly fitting components; and applicability of the device to monitor other UFFI offgases. Two 7-day monitors have been developed—one for room air and the other for wall cavities. The design of the Concord-NRCC dosimeter included a number of comparative studies and a selection of components.

**ADSORBENT SELECTION.** The adsorbent selected was molecular sieve 13X. The selection was based on data showing long-term stability of the adsorbed formaldehyde after sampling. The use of the sieve allowed a number of analytical methods to be used when the tube was adapted to measurement of other gases.

Desiccant beds added above the sieve beds in the modified active Oak Ridge sampling tube (AORST) to increase the capability of the device to sample at high humidities gave results that were not reproducible. The desiccant removed formaldehyde from the air along with the water vapor.

**ANALYTICAL TECHNIQUES.** The modified pararosaniline method of analysis was selected for formaldehyde measurement (2) because of higher sensitivity obtained in initial studies in which comparisons were made with chromotropic acid analysis. The pararosaniline method was modified beyond Miksch's modification and optimized for the configuration of the dosimeter (e.g., volume of water used in the solution, etc).

**DIMENSIONS OF THE DOSIMETER.** Various prototypes were constructed with sampling tubes and bed diameters of 8 and 15 mm and lengths of 100 to 300 mm. The ratio of diameter to length was determined for each. In addition, water uptake tests were performed and were followed by actual field measurements of formaldehyde where results were compared with those from other devices.

Sampling rates were determined for the prototype devices, and a diffusion length of 8 cm was chosen as optimum for the device.

**SELECTION OF MATERIALS.** For reasons of cost, ease of manufacture, reproducibility of dimensions, and tightness of fit, the components of the devices were specially machined. Polyethylene was selected because it fulfilled the preceding requirements. Stringent tests and controls have been established to ensure absolute cleanliness of the components before assembly.

**Field Studies.** Table IV lists field studies in which early and more advanced prototypes have been used. Field studies were undertaken only after extensive laboratory evaluation. The field studies yielded the following observations:

Problem: Variable laboratory blanks.

Cause: Not yet determined.

Although initial studies yielded a procedure that was adequate for prolonged laboratory studies, the results of a major field study indicate that the blank values are variable and tend to increase with time.

Further investigation is planned on blanks, including improvements in sieve cleaning procedures (e.g., higher temperature baking, drawing a vacuum while baking, and cycling of temperature). The effects of varying humidity and temperature cycles on the collection and retention of formaldehyde will also be examined in laboratory calibration chambers.

### ***Current Status of Low-Level Formaldehyde Dosimeters***

Comparisons of various dosimeters have been made under field conditions because of the difficulty in simulating the conditions adequately in calibration chambers. Although considerable data have been generated from these

comparisons, much of this data no longer represents the state of the art with low-level formaldehyde dosimeters. Sufficient data has been obtained on the later versions to justify conclusions on certain performance factors: reproducibility of pairs of devices in the field; stability of the devices before and after exposure, including an aging factor; ability to integrate formaldehyde concentration over a 7-day exposure period, which includes an element of accuracy; and loss of formaldehyde during elution and analysis.

Du Pont Pro-Tek Version I in 40 houses with two to four dosimeters in a set per house and levels of 2–215 ppb gave one difference of 49 ppb and the rest below 22 ppb. Of 40 comparisons, 30 were within 10 ppb. For 39 houses, the standard deviation was 6.7 ppb (11).

Pro-Tek Version I was used in 12 non-UFFI houses over 19 weeks and compared to 19 1-h modified NIOSH P&CAM 125 impinger measurements analyzed in 4-cm path length cuvettes (12). The differences between average values in the houses measured by the impinger and dosimeter methods ranged from -5 to +9 ppb at the 17–58-ppb level. The averages for the 12 houses over the 19 weeks were 36 ppb for impinger and 35 ppb for dosimeter. Standard deviations of the impinger results were on the average 2 ppb higher than those of the dosimeter (13 vs. 11 ppb), but differences between impinger and dosimeter readings for individual houses were -10 to +14 ppb, when compared for the 19-week period.

Integration of formaldehyde concentrations by multiple low-flow-rate sodium bisulfite impingers with 6-, 8-, or 12-h exposures, compared to Pro-Tek C-60 Version I, showed the dosimeter higher by approximately 30 ppb at the 120-ppb level (11).

Reproducibility of measurements with the Pro-Tek C-60 Version III is illustrated by data from 200 pairs exposed in 200 homes in which the levels ranged from 10 to 200 ppb. Eighty-five percent of the pairs agreed to within 10 ppb, and 95% agreed to within 20 ppb. Another set of measurements made in four houses with levels of 40–60 ppb, using four to eight dosimeters at the same location, gave standard deviations of the readings of 10, 8, 5, and 8 ppb (11).

Comparisons of C-60 Version III and AQRI PF-1 Version II in six houses with four to eight C-60 dosimeters and PF-1s gave differences of 0, -12, 11, -4, -6, and -6 ppb, for an average of -3 ppb at the 35–60-ppb level. Comparisons of large numbers of C-60 Version III to PF-1 Version II in schools in 1982, at levels of 9–125 ppb, gave differences of -17 ppb to +48 ppb, a mean difference of 10 ppb, and a standard deviation of 14 ppb (11). Similar comparisons in one house of four C-60 Version II with four PF-1 Version II gave a mean difference of -18 ppb and a standard deviation of 8.6 ppb at the 110-ppb level. At the 272-ppb level in a mobile home, the mean difference was 53 ppb, and the standard deviation was 15 ppb.

The standard deviation in the difference between pairs of PF-1 Ver-

sion II used in 1982 in 59 homes was 10 ppb over the 20–190-ppb range (11).

The shelf life of the devices can be illustrated by simultaneous exposure and analysis of dosimeters of different ages, exposed at levels of 75 and 137 ppb. The results from two pairs of each of eight lots of PF-1 Version II, aged 3–13 months, show that lots older than 12 months are unusable and lots aged 10–11 months are inconsistent. The reproducibility of a lot aged 3 months was 5 ppb for four pairs of dosimeters.

Recovery of formaldehyde in later versions of both the Pro-Tek C-60 and the PF-1 at the 20–200-ppb levels is between 90% and 96% for exposures of 7 days, compared to spiking of the dosimeters with refluxed paraformaldehyde solution. Recovery is adequate in both devices, though the elution must be done carefully and according to manufacturers' instructions in the PF-1 device to achieve these results.

Results from the 200-home study using 310 Pro-Tek C-60 Version III and 155 PF-1 Version II gave the following equation:

$$(\text{PF-1}) = 0.002 + 1.3 (\text{C-60}) (\text{ppm})$$

The square of the correlation coefficient was 0.61.

The standard deviation for 66 pairs of 3M Version I (1982) was 6.7 ppb at the 24–181-ppb level (11). Differences between 17 sets of 3M Version II and PF-1 Version II (1983) showed the 3M to be 9.7 ppb higher on average and the standard deviation to be 13.5 ppb at the 20–70-ppb level (11).

These errors may be compared to those of the 3-h impinger method using the modified chromotropic acid method, where uncertainties were  $\pm 66$  ppb at the 200-ppb level,  $\pm 27$  ppb at the 50-ppb level, and  $\pm 18$  ppb at the 20-ppb level and showed a strong bias toward the negative error (3). The dosimeters are generally more precise.

## Conclusions

Dosimeters can integrate 7-day concentrations of formaldehyde in air at least as well as, and often better than, low-flow-rate or multiple sample impinger methods. Formaldehyde dosimeters have evolved to the state where different models will provide adequate accuracy and operational characteristics for either field surveys or scientific studies in homes in the 30–200-ppb range. The bulk of the houses studied in Canada fall between these limits. Dosimeters constitute a system that includes all components used in transport and handling. Use of dosimeters at low levels requires constant attention to every detail of manufacture, transport, deployment, retrieval, and analysis. Use of field blanks is imperative to obtain reliable results for low-level formaldehyde measurements.

An indicator for displaying the life of dosimeters is highly desirable, or gaseous lab spikes can be used for checks.

Storage of formaldehyde on the collection medium is not adequately understood, so there is a need to continue to investigate and improve the design of most commercial devices.

Evaluation of dosimeters is expensive and should only be undertaken when it can be ensured that batch-to-batch variations are small.

A 95% confidence level is adequate for surveys, but not for studies on individual homes, especially in measuring changes in levels within houses.

Seasonal and diurnal variations in formaldehyde levels in homes make measurements of formaldehyde concentration and comparisons difficult. Even when compared to the mean equilibrium formaldehyde concentration of the source, short-term meteorological variations can mask changes and introduce large uncertainties.

Houses containing UFFI have diurnal and hourly variations that are different and potentially more extreme than many non-UFFI houses. The use of long-term passive dosimeters is necessary to integrate these variations. There is little chance to reduce these variations to an adequate level by a simple protocol for house preparation.

In the Canadian climate, levels of formaldehyde in all houses (those containing UFFI and those without) approach similar values in January and February. As the absolute humidity values inside and outside the houses decrease dramatically, the equilibrium formaldehyde concentrations of the sources decrease and the sources have little capacity to emit formaldehyde.

The studies have yielded a certain initial understanding of the variation of formaldehyde in houses, which may be a useful starting point for further studies. UFFI houses may be categorized into two classes: responders and nonresponders. Responders are houses in which the formaldehyde concentrations in the UFFI-filled cavities and the living space air change dramatically and proportionately from summer to winter. Nonresponders are houses in which the formaldehyde concentrations in the cavities and in the living space vary little with time. The mixing of results of measurements from responders with those from nonresponders may well mask differences between UFFI houses and non-UFFI houses.

### ***Appendix I. Calculation of Concentration from Measurement: Gases***

The reading from analysis of the dosimeter is in mass of collected or sampled gas minus the mass of gas collected in the field blank. The dosimeter does not measure concentrations directly. The following steps and approximations are involved in reducing a measurement to a concentration:

1. The volume of air sampled per unit time must be known.  
The precision of the measurement of volume sampled can be

difficult to establish. If the device is passive and relies on diffusion to collect the gas, the equivalent volume of air sampled per unit time can be calculated theoretically from the geometry, but it must be checked by calibration under several conditions. If the device is an active system, the flow rate must be controlled constant so it is known, but it must be corrected to standard temperature and pressure.

2. The density of the measured gas at the same reference temperature and barometric pressure as the air from which it is sampled must be used. This requirement is somewhat difficult when the temperature and pressure have changed dramatically during the sampling period.
3. The duration of the exposure in hours must be known. This information requires clear records and is complicated by bookkeeping errors, such as converting 1½ h to 150 min rather than to 90 min.

These considerations accepted, the equation for the time-weighted average exposure [TWA (ppb by volume)] is the following:

$$\text{TWA} = \text{weight recovered} / (\text{sampling rate} \times \text{density} \times \text{exposure time})$$

$$= \frac{1000 \mu\text{g}}{\text{L/h} \cdot \mu\text{g}/\mu\text{L} \cdot \text{h}}$$

$$= \mu\text{g} \cdot \frac{1000}{\mu\text{g}/\text{h} \cdot \text{L}/\mu\text{L}} \cdot 1 \text{ h}$$

$$= \mu\text{g} \times \text{conversion factor} \times \text{time}^{-1}$$

Thus, the conversion factor is  $1000[\mu\text{g}/\text{ppm} \cdot \text{h}]^{-1}$ . Caution is necessary because the reciprocal of this conversion factor is sometimes used by manufacturers or investigators.

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