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Comparison of Sampling Methods for Monomer and Polyisocyanates of 1,6-Hexamethylene Diisocyanate During Spray Finishing Operations

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A comparison study of isocyanate sampling methods for 1,6-hexamethylene diisocyanate (HDI) monomer and HDI-based polyisocyanates was conducted in spray painting environments. This study compared the performance of the Iso-chek sampler against existing and proposed National Institute of Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA) monitoring methods for HDI-based isocyanates. Six methods for monitoring HDI monomer and polyisocyanate levels were compared. Fifty-eight sampling sets were collected during spray painting of aircraft and aircraft parts at four U.S. Air Force bases. Impinger and cassette samplers were mounted side-by-side on a mannequin located in paint overspray areas. For HDI monomer sampling results, there were no significant differences between NIOSH 5521, NIOSH 5522, OSHA 42, MAP (the proposed NIOSH method), and the Iso-Chek. For HDI-based polyisocyanates, NIOSH 5522, NIOSH 5521, Iso-Chek, and the Total Aerosol Mass Method (TAMM) were significantly different from one another. There was no significant difference between MAP and the NIOSH 5522 polyisocyanate sampling results. This study suggests the Iso-Chek and MAP sampling methods compare favorably with established methods for monitoring in HDI spray painting environments and the Total Aerosol Mass Method provides a reasonable upper boundary for estimating HDI polyisocyanate concentrations. The results also reemphasize aerosol sampling physics and sampler geometries must be carefully considered and appropriate samplers used when measuring exposures in spray paint environments where particulates are of the inhalable size.

Keywords Isocyanates, Aerosol Sampling, Iso-Chek, HDI, 1,6-Hexamethylene Diisocyanate

The U.S. Air Force and aerospace industry use polyurethane paints as aircraft coatings because of their durability, abrasion resistance, chemical and impact resistance, flexibility, and weatherability.(1) These features of polyurethanes serve to protect the Air Force's aging inventory of aircraft and aircraft support equipment. The polyurethane paint system consists of two components: a base component containing polyols, pigments, solvents, and additives, and a catalyst or hardener component containing solvents and 1,6-hexamethylene diisocyanate (HDI) monomer and polyisocyanates.(2,3)

The health hazards associated with isocyanate-containing compounds are well documented. They include irritation to the skin, mucous membranes, eyes, and respiratory tract. The most well-known debilitating health effects are asthma, irritant and allergic contact dermatitis, and, to a much lesser extent, hypersensitivity pneumonitis.(4–8)

Historically, the accurate measurement of airborne isocyanates has been a challenge and still is. Sampling is difficult because in a spray painting environment HDI monomer and HDI-based polyisocyanates are present in both aerosol and vapor phases. As equilibrium is approached after spraying, the HDI monomer is expected to be present primarily in the vapor phase, based upon its volatility, but some could remain in the aerosol droplet itself. The HDI-based polyisocyanates will exist in the aerosol phase only.(9) For this the terms polyisocyanates and oligomers are used interchangeably. There are several methods for the measurement and analysis of HDI monomer and

HDI-based polyisocyanate concentrations present in both the aerosol and vapor phase. They include the National Institute for Occupational Safety and Health (NIOSH) Method 5521, NIOSH Method 5522, the proposed NIOSH Method (MAP), the Iso-Chek Sampler, the Occupational Safety and Health (OSHA) Method 42, and the Total Aerosol Mass Method (TAMM), also known as NIOSH Method 0500.[(9–14)] The first four listed methods measure both HDI monomer and HDI-based polyisocyanates. OSHA 42 is used only to monitor concentrations of HDI monomer while the TAMM measures the total aerosol mass from which an estimate of the non-volatile polyisocyanate is calculated.

METHODS

The goal of this study was to compare HDI monomer and HDI-based polyisocyanate measurements between the various methods for determining HDI-based polyisocyanate concentrations in workplace air. The study involved area monitoring in paint overspray areas using NIOSH 5521, NIOSH 5522, Iso-Chek, TAMM, MAP, and OSHA 42. A summary of the methods is shown in Table I. The air sampling devices were attached to a life-size mannequin. All samples were collected with a flow rate of one liter per minute. All samples in a sampling set were collected for the same time period, with sampling times ranging from 8 to 55 minutes.

In NIOSH 5521 a sample of air is drawn through an impinger containing a toluene solution of the reagent 1-(2-methoxyphenyl)piperazine. Any isocyanate collected is derivatized to the corresponding urea during sampling. The sample is analyzed by reversed-phase high-performance liquid chromatography (HPLC).(11) For analysis of monomers, two detectors are set up in series to measure the analyte: a UV detector (242 nm) and an electrochemical (EC) detector (+0.8 V vs. Ag/AgCl). The more sensitive EC detector is used for quantification. This method can be used to measure oligomers of aliphatic diisocyanates (e.g., HDI) by the addition of a photodiode array (PDA) detector by comparing the PDA UV spectra of the HPLC oligomer peaks with an established PDA UV reference spectrum for the derivatized monomer.(10)

In NIOSH 5522, air is drawn through an impinger containing a dimethyl sulfoxide (DMSO) solution of the tryptamine reagent. Any isocyanate that is collected is derivatized to the corresponding urea. The sample is analyzed by reversed-phase HPLC. A fluorescence detector is used to measure the analyte, with an electrochemical detector set up in series for confirmation of the identity of the analyte.(11) A calibration curve based on the fluorescence response of the monomer is used for the quantification of the oligomers.

OSHA 42 collects a sample by drawing a known volume of air through an open-face cassette containing a 37-mm glass fiber filter coated with 0.1 mg of 1-(2-pyridyl)piperazine. The sample is analyzed by HPLC with UV or fluorescence detection.(12)

In the TAMM, samples are collected with specially modified three-stage 37-mm sampling cassettes with 5-μm polyvinyl chloride filters.(11) The cassette top has a 15-mm hole drilled in it to allow for the collection of larger-sized particles than is possible with a closed-face cassette. This configuration more closely estimates the inhalable mass fraction of the aerosol and better represents the worker's exposure.(15,16) Filters are weighed

TABLE I
Sampling and analytical methods

	Iso-Chek	TAMM	NIOSH 5521	NIOSH 5522	OSHA 42	MAP
Sampler	37-mm cassette closed face	37-mm cassette semi-open face	Impinger	Impinger	37-mm cassette open face	Impinger
Sample medium	5 μm PTFE GFF MAMA (0.1 mg)	5 μm PVC	MOPP in toluene (43 mg/l)	Tryptamine in DMSO (450 μg/ml)	GFF 1–2 PP (0.1 mg)	MAP in butyl benzoate (138 mg/l)
Flow rate	1 l/min	1 l/min	1 l/min	1 l/min	1 l/min	1 l/min
Analyte	HDI monomer HDI-based polyisocyanates	Total particulates	HDI monomer HDI-based polyisocyanates	HDI monomer HDI-based polyisocyanates	HDI monomer	HDI monomer HDI-based polyisocyanates
Analysis	HPLC/RP UV/PDA	Gravimetric	HPLC/RP UV/PDA, EC	HPLC/RP FL/EC	HPLC/RP UV	HPLC/RP UV, FL
LOD (mg/m^3)^A	0.0006	2.0	0.013	0.013	0.002	0.0004

Abbreviations: DMSO = dimethyl sulfoxide; EC = electrochemical detector; FL = fluorescence detector; GFF = glass fiber filter; HPLC = high-performance liquid chromatography; LOD = limit of detection; MAMA = 9-(N-methylaminomethyl)anthracene; MAP = 1-(9-anthracenylmethyl) piperazine; MOPP = 1-(2-methoxyphenyl)piperazine; PDA = photodiode array detector; 1-2 PP = 1-(2-pyridyl)piperazine; PTFE = polytetrafluoroethylene (Teflon) filter; RP = reversed phase; TAMM = total aerosol mass method; UV = ultraviolet detector.

[A] Based on a 15 liter air sample.

before and after the painting operation in accordance with NIOSH Method 0500 to determine the total mass of solids collected. Oligomer concentrations are then estimated from the percentage of oligomer and paint solids in the paint using Equations 1 and 2[(17)]:

$$C_{\text{oligomer}} = \frac{\left[\left(\begin{matrix}\text{mass solids}\\ \text{collected}\end{matrix}\right)\left(\dfrac{\text{mass oligomer in}}{\text{mass solids in paint}}\right)\right]}{\text{sampling volume}} \qquad [1]$$

where

$$\frac{\text{mass oligomer in paint}}{\text{mass solids in paint}} = \frac{(\text{Volume}_{\text{catalyst}})(\text{SG}_{\text{catalyst}})(\%\ \text{Oligomer}_{\text{catalyst}})}{(\text{Volume}_{\text{catalyst}})(\text{SG}_{\text{catalyst}})(\%\ \text{Oligomer}_{\text{catalyst}}) + (\text{Volume}_{\text{base}})(\text{SG}_{\text{base}})(\%\ \text{Solids}_{\text{base}})} \qquad [2]$$

and SG is the specific gravity of the specific components.

In the MAP method, air is drawn through a sampler containing the reagent 1-(9-anthracenylmethyl)piperazine (MAP),[(14)] in this case an impinger containing 15 milliliters (ml) of a 5×10^{-4} molar solution of MAP dissolved in butyl benzoate. Isocyanate species in the sample react with the MAP to form urea derivatives. In the laboratory, a 5 ml portion of the sample is added to a Supelco Supelclean 3 ml solid-phase extraction tube containing 500 mg silica gel, rinsed with 6 ml methylene chloride, and eluted with 5 ml of 9:1 acetonitrile:methanol. The collected 5 ml sample is evaporated to 1 ml, and 30 μl of this is injected into a 150 × 4.6 mm Phenomenex C8 Inertsil column. The HPLC analysis uses a pH gradient with an initial mobile phase of 65 percent acetonitrile/35 percent aqueous pH 6 buffer run at 1 ml/min. The pH 6 buffer is prepared with phosphoric and formic acids, brought to pH 6 with triethylamine. In between 6 and 26 minutes the mobile phase is gradually changed to 65 percent acetonitrile/35 percent aqueous pH 1.6 buffer. The pH 1.6 buffer is prepared by taking the pH 6 buffer and adding HCl until reaching pH 1.6. The detectors used are a UV detector (253 nm) and a fluorescence detector (ex: 250 nm, em: 409 nm). Monomeric isocyanates are identified by retention time and detector response ratio and quantified by fluorescence height. Polyisocyanates are identified by comparison to the bulk product chromatogram and by detector response ratio. A solution of 65 percent acetonitrile/35 percent aqueous phosphoric acid is delivered between the column and the detectors at 0.5 ml/min so that the MAP derivatives give a fluorescence response independent of mobile phase pH.[(13)]

The Iso-Chek, supplied by Omega Specialty Instrument Company, consists of a dual-stage 37-mm cassette, used in the closed-face mode. The first stage is a 5-μm Teflon filter designed to capture the aerosol phase, and the second stage is a glass fiber filter impregnated with 9-(N-methylaminomethyl) anthracene (MAMA) designed to capture and derivatize the vapor phase isocyanates. Derivatization of the aerosol is accomplished by immediate placement after sampling of the Teflon filter into 5 ml of 1-(2-methoxyphenyl) piperazine in toluene solution. Both vapor- and aerosol-phase isocyanate species react with the derivatizing agents to form urea derivatives. The glass fiber filter was desorbed prior to analysis and the desorption solutions from both the Teflon and glass fiber filters were analyzed by HPLC. For the identification of different HDI-based polyisocyanates in the aerosol fraction a photodiode array (PDA) detector is used for confirmation of the isocyanate-derived oligomeric species by comparing the PDA UV spectra of the HPLC peaks with an established PDA UV reference spectrum for the derivatized monomer. The quantification of the polyisocyanates is accomplished using the response factor obtained from the monomer standard to calculate the oligomer concentration. This technique of calculation has shown equivalent results compared to the oligomer evaluation using a calibration curve produced with a 100 percent pure dry base.[(9)]

Description of Paint Spray Operations

Painting operations were monitored at four separate facilities in an attempt to limit confounding of sample results from sampling locations or personnel. Full aircraft or aircraft parts painting operations were monitored. Several paint systems were used depending upon the aircraft or the part being painted. The paints used were manufactured by Deft Corporation. The coatings were mixed in either a 1:1 or 3:1 base to hardener ratio.[(2,3)] Oligomer content of the hardener components ranged from 40 to 85 percent by weight with free monomer contents less than 1.6 percent by weight. Depending upon the paint system either the biuret or a combination of the biuret and the isocyanurate were the predominant polyisocyanates in the hardener systems.[(2)] Some paints were sprayed immediately after mixing but most were allowed an initial curing time of up to 40 minutes. Painting operations were performed in crossdraft paint booths. High-volume, low-pressure spray guns were used at three facilities, while conventional spray guns were used at the fourth. Personnel wore a variety of protective equipment at each base, but the majority of corrosion operations were performed with personnel wearing full-facepiece airline respirators, cloth coveralls, a paint sock, and gloves.

Sampling Strategy

The mannequin-mounted area samples were collected in the same manner at each of the four facilities. At the first two facilities, where a total of 17 sample sets were collected, samplers for NIOSH 5521, OSHA 42, Iso-Chek, TAMM, and MAP were placed side-by-side on the chest of a life-sized mannequin mounted on a cart. The mannequin was used to simulate a worker in a paint overspray area. The paint overspray area was

TABLE II

p values, HDI monomer, all data sets[A]

	NIOSH 5521	Iso-Chek	OSHA 42	NIOSH 5522
NIOSH 5521	1.000			
Iso-Chek	0.195	1.000		
OSHA 42	0.088	0.292	1.000	
NIOSH 5522	0.313	0.677	0.285	1.000

n = 36.

[A]No statistical differences were observed, $p = 0.01$.

downstream of the painting operation, at least five feet away from the point of application. Samplers for NIOSH 5522 were placed directly adjacent to the mannequin. The five sampling methods used on the mannequin are used as personal sampling methods by the Air Force while NIOSH 5522 is suggested as an area sampling method due to the hazard of its impinger fluid.(11) At the last two facilities where a total of 41 sampling sets were collected, NIOSH 5521, OSHA 42, Iso-Chek, and TAMM were arranged on the mannequin while NIOSH 5522 was placed directly adjacent to the mannequin. Samplers were randomly arranged on the mannequin.

Standard equipment-handling protocols from NIOSH were adopted. Between sample sets impingers were soaked in glassware detergent and tap water for a minimum of six hours, rinsed three times with tap water, three times with distilled water, shaken dry, and then heated at 300°F for a minimum of eight hours. All samples were capped and processed on site in a clean area.

RESULTS

Tables II–V show p values of method comparisons. Figures 1 and 2 show graphically all monomer and polyisocyanate results, respectively. Concentrations are given in units of milligrams per cubic meter of air. Before statistical comparison, each method's data set was plotted, and the data found to be approximately log-normally distributed. To make a valid statistical analysis of differences among sampling methods, the Wilcoxon signed rank test, was applied to the data using SYSTAT.(18) To perform the statistical tests, all "none detected" samples were assigned the value of the limit of detection. To simplify the analysis, only sample sets where a complete set of data existed from all methods were used to calculate p values as seen in Tables II and III. All concentration values are shown graphically in Figures 1 and 2.

Analysis of NIOSH 5521, NIOSH 5522, MAP, OSHA 42, and Iso-Chek area samples show no statistical differences in HDI monomer concentration values ($p = 0.01$). For the polyisocyanate results, a significant difference was observed between most of the methods ($p < 0.01$). Arranged by concentrations of polyisocyanates found, the method analysis results exhibited a trend of NIOSH 5522 < NIOSH 5521 < Iso-Chek < TAMM. There was no significant difference between polyisocyanate concentrations measured by MAP and NIOSH 5522. A value of $p = 0.01$ was chosen because of the large number of samples collected.

TABLE III

p values, HDI polyisocyanate, all data sets[A]

	NIOSH 5521	TAMM	Iso-Chek	NIOSH 5522
NIOSH 5521	1.000			
TAMM	0.000	1.000		
Iso-Chek	0.000	0.000	1.000	
NIOSH 5522	0.000	0.000	0.000	1.000

n = 41.

[A]Statistical differences in polyisocyanate levels were observed, $p < 0.01$.

TABLE IV

p values, HDI monomer with MAP data sets[A]

	NIOSH 5521	Iso-Chek	OSHA 42	NIOSH 5522	MAP
NIOSH 5521	1.000				
Iso-Chek	0.028	1.000			
OSHA 42	0.110	0.374	1.000		
NIOSH 5522	0.767	0.678	0.767	1.000	
MAP	0.011	0.063	0.953	0.953	1.000

n = 9.

[A]No statistical differences were observed between MAP and other methods, $p = 0.01$.

DISCUSSION

Of the six methods compared, NIOSH 5521 is the most commonly used method in the U.S. Air Force for measuring HDI monomer concentrations in a spray paint environment. These survey results indicate NIOSH 5522, OSHA 42, MAP, and the

TABLE V

p values, HDI polyisocyanate with MAP data sets[A]

	NIOSH 5521	TAMM	Iso-Chek	NIOSH 5522	MAP
NIOSH 5521	1.000				
TAMM	0.007	1.000			
Iso-Chek	0.333	0.005	1.000		
NIOSH 5522	0.022	0.005	0.009	1.000	
MAP	0.009	0.005	0.007	0.959	1.000

n = 10.

[A]No significant difference between MAP and NIOSH 5522 was observed, $p < 1$.

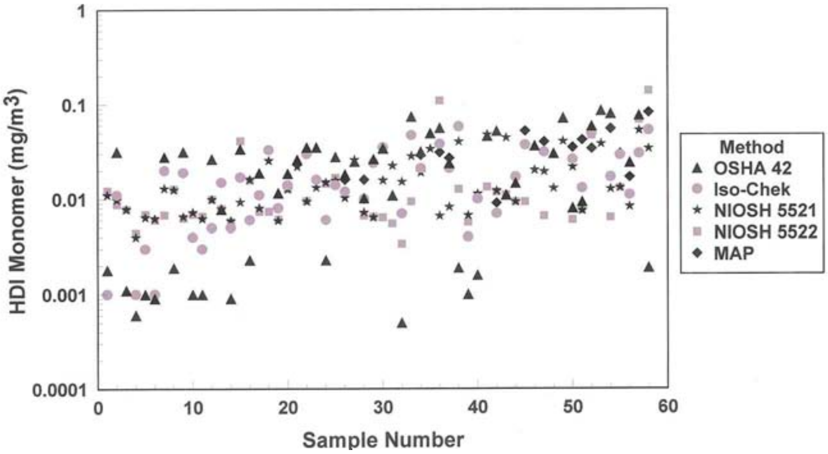

FIGURE 1

Total HDI monomer concentration distributions for the sampling methods. No significant differences are seen between NIOSH 5521, NIOSH 5522, MAP, OSHA 42, and the Iso-Chek methods.

Iso-Chek sampler measure HDI monomer levels consistently with NIOSH 5521. By inspection, OSHA 42 appeared to have the greatest variability when compared with the other methods.

The TAMM assumes all the oligomer in the paint aerosol remains unreacted. This is unlikely because the oligomer begins to react immediately upon mixing, and workers typically spray the mixture up to 40 minutes after initial mixing. Therefore, the TAMM probably overestimates unreacted polyisocyanate concentrations. NIOSH Methods 5521, 5522, MAP, and the Iso-Chek method do not measure the actual mass of polyisocyanate present but report the results in terms of monomer mass equivalent. Therefore, the results of these direct measurement methods appear quite low when compared to the TAMM results. To properly compare the TAMM with the other methods, the HDI polyisocyanate measurements are multiplied by a factor of 2.3 because the average equivalent weight of the HDI oligomer in the paint systems used is approximately 2.3 times that of HDI monomer.

The differences between NIOSH 5521, NIOSH 5522, MAP, and Iso-Chek polyisocyanate sampling results may be partially explained by aerosol sampling physics. Based on the size distribution of the paint aerosol there can be a significant sampling bias of impinger methods as compared to inhalable cassette methods.(16) The potential for this bias was confirmed by observation of paint deposition in the impinger orifice and jet. Therefore, because the polyisocyanate is contained in the spray aerosol, NIOSH 5521, NIOSH 5522, and MAP likely undersampled the oligomer relative to the Iso-Chek sampler. Differences in measurement values between NIOSH 5521 and NIOSH 5522 might be due to placement of NIOSH 5521 impingers on

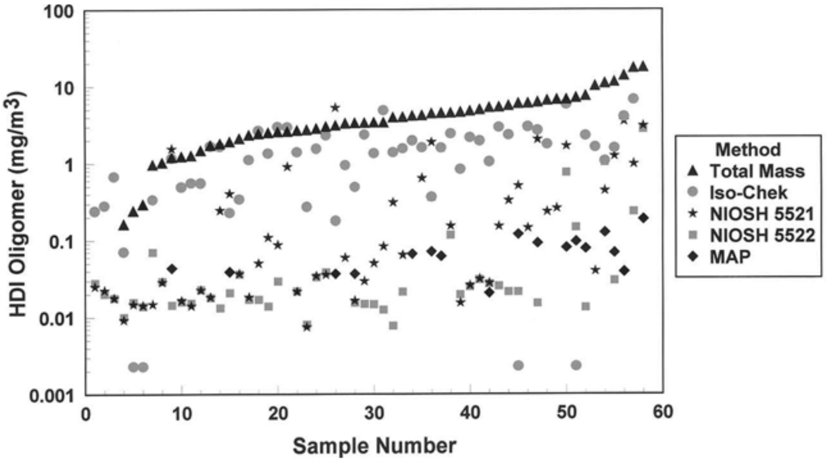

FIGURE 2

Total HDI polyisocyanate concentration distributions for the five sampling methods. The total aerosol mass method suggests an upper boundary; all other methods predominantly gave levels below this method.

the mannequin and NIOSH 5522 impingers beside the mannequin; aerosol concentrations may have been influenced by the airflow across the mannequin's torso,(19) affecting the sampling efficiency.

Each method in the study presented its own set of problems. Impinger methods are difficult to use in the field because they are time-consuming, require careful handling of the impinger fluid before and after sampling, and occasionally spill on the worker even though advertised as "spill-proof." Derivatizing solvents may also pose some hazard to workers, as in the case of NIOSH 5522 where DMSO may carry isocyanates through the worker skin, relegating the method to an area sampling method.

For many sampling sets, NIOSH 5521 and NIOSH 5522 gave "none detected" results while Iso-Chek gave numerical values. Over 50 percent of the NIOSH 5521 and NIOSH 5522 sample sets were measured as "none detected." Other methods had less than 10 percent of the sample sets returned as "none detected." The large number of "none detected" values causes some concern when comparing methods, because of the wide range of method detection limits. The "none detected" values may be partially explained by the lower limit of detection of the Iso-Chek method. During this study, the NIOSH 5522 limit of detection was twice what the method is normally capable of performing. There is also concern about the relatively high limit of quantification of the TAMM. During short sampling periods and low flow rates, a minimum amount of mass may be collected, yielding a "none detected" reading. In some cases, the Iso-Chek cassettes gave "none-detected" results for HDI monomer as no derivatizing agent was applied to the filter by the manufacturer.

CONCLUSIONS

Several factors must be considered when choosing a sampling and analytical technique for monitoring of 1,6-hexamethylene diisocyanate monomer and HDI-based polyisocyanates including the application technique, whether the HDI is in a monomeric or oligomeric form, and the size distribution of the aerosol present. In particular, this study suggests TAMM provides an upper boundary estimate of HDI oligomer concentrations in the field environment. The TAMM is a simple and fast method to estimate HDI oligomer concentrations, and it offers promise to industrial hygienists and technicians for estimating the oligomeric HDI concentrations in a paint spray environment. The Iso-Chek provides HDI monomer results similar to more established NIOSH sampling and analytical techniques and provides oligomer results within the boundaries of the TAMM and NIOSH 5521, MAP, and 5522. The results of this study reemphasize the importance of aerosol size consideration during sampling. The proper sampler selection is important for accurately determining inhalable particulate concentrations within the workplace.

Future research efforts should be focused on development of a direct reading instrument for HDI monomer and oligomers for use where HDI-based isocyanate-containing aerosols are present in the workplace. Direct reading instrumentation would allow fast and accurate quantification of worker exposures in the field. By adding cure time information supplied by the coatings manufacturers and obtaining more precise specific gravity values of paint components, a better estimate of polyisocyanate concentrations might be obtained using the TAMM.

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DISCLAIMER

The use or mention of any brand names does not constitute endorsement by the United States Air Force or the Centers for Disease Control and Prevention.

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