American Industrial Hygiene Association Journal

ISSN: 0002-8894 (Print) (Online) Journal homepage: http://www.tandfonline.com/loi/aiha20

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To cite this article: ROBERT F. HERRICK , THOMAS J. SMITH & MICHAEL J. ELLENBECKER (1987) Development of a Sampling and Analytical Method for Measuring the Epoxy Content of Aerosols: II. Application of the Method to Epoxy-Containing Aerosols, American Industrial Hygiene Association Journal, 48:9, 773-779

To link to this article: http://dx.doi.org/10.1080/15298668791385552

Am. Ind. Hyg. Assoc. J. 48(9):773-779 (1987)

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Development of a Sampling and Analytical Method for Measuring the Epoxy Content of Aerosols: II. Application of the Method to Epoxy-Containing Aerosols*

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Aerosols generated by epoxy spray painting consist of droplets containing partially-cured mixtures of epoxy resins and curing agents, as well as pigments, solvents and diluents. A sampling and analytical method has been developed to measure the epoxy content of these aerosols. The method collects the aerosol in a midget impinger containing dimethyl formamide, which inhibits the curing reaction between the epoxy and curing agent, preserving the unreacted epoxy functional groups present in the aerosol. The impinger contents are analyzed by reacting the epoxy with an excess of bromide generated *in situ* from tetraethylammonium bromide, and measuring the unreacted bromide in the reaction mixture by normal pulse polarography. The precision and accuracy of the method have been evaluated using a pure epoxy resin as a model compound. The method was applied to aerosols containing mixtures of epoxy resin and amine curing agents in various degrees of cure, to aerosols containing large quantities of nonepoxy components, and to aerosols of epoxy surface coatings. The method is capable of precise and accurate measurement of epoxide functionality, and it is applicable to the measurement of epoxy-containing aerosols in spray finishing operations.

Introduction

Workers engaged in spray application of epoxy paints may be exposed to an aerosol containing a reactive mixture of epoxy resin and curing agents. The physical and chemical properties of the liquid epoxy paint droplets change during the lifetime of the aerosol as the droplets shrink because of evaporation of the volatile components, and the polymerization (curing) reactions begin to convert the epoxide groups by opening the cyclic ether rings. The epoxy curing reactions begin when the paint components are mixed in preparation for application, continue while the droplets are airborne, and go to completion after the aerosol has been deposited on a surface, producing the tough, chemically resistant coatings characteristic of epoxy paints. In order to measure the epoxy content of this paint aerosol as it exists at the point of worker exposure, the sampling and analytical method must collect the aerosol, inhibit the epoxy curing reaction, and measure the unreacted epoxy present in the partially-cured mixture. This paper describes the development and evaluation of a sampling and analytical method for making such measurements.

The development of the analytical method for measurement of epoxy content in solid and liquid epoxy resins is reported in the previous paper in this series.(1) The method is based upon the stoichiometric hydrobromination of the epoxide functional group. This reaction has been well-documented as the basis for measurements of epoxy content of epoxy resins; however, it has not been applied to the measurement of the epoxy content of aerosols. The analytical method development has extended the range of existing methods to smaller sample sizes than previously reported, while maintaining good precision and accuracy. The applicability of the method to the collection of epoxy-containing aerosols for exposure assessment has been a prime consideration throughout this method development.

Criteria for Evaluation

The overall performance of the aerosol sampling and analytical method has been evaluated using a statistical protocol adapted from that developed for the joint NIOSH-OSHA Standard Completion Program. The protocol is fully described in NIOSH Publication No. 80-133.(2) The method evaluation protocol is divided into two parts: measurement of analytical recovery, and generation and collection of airborne samples. Analytical recovery is determined by spiking three sets of sampling media with the compound of interest, each set consisting of six samples. The eighteen total samples are analyzed, and the analyte recovery is determined for each sample. Test atmospheres of the compound of interest then are generated at three concentrations. The atmospheres are sampled using the test method and an independent alternative method, collecting sets of six samples by each method. The precision of the total sampling and analytical method is described by the total coefficient of variation (CV_T) pooled from the three sets of samples collected from the test atmospheres. The accuracy of the sampling and analytical method is measured by comparing the mean concentration determined by the test method and the true con-

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centration measured by an independent method at each of the three test atmosphere levels. The absolute error of a method, combining the variability (precision) and bias (accuracy), must be less than 25% in at least 95% of the samples analyzed for the method to be considered acceptable under the criteria of the Standards Completion Program.

Experimental

Evaluation of the Analytical Method

The analytical method is based upon the stoichiometric hydrobromination of the epoxide functional group. In the development of the analytical method, dimethyl formamide (DMF) was chosen as the medium for the hydrobromination reaction of epoxides.(1) DMF is an excellent solvent for epoxy compounds, and it inhibits the epoxy-amine curing reactions.(3) The reactive epoxide content of samples is determined by dissolving or suspending the sample in DMF, adding a known quantity of bromide (as tetraethylammonium bromide) and perchloric acid to initiate the hydrobromination reaction, then measuring the residual bromide concentration in the reaction mixture by normal pulse polarography (NPP). The epoxide content of the sample is determined by the consumption of bromide ion by the hydrobromination reaction.

The analytical method for measurement of epoxy content was evaluated as it was applied to impinger solutions used to collect epoxy aerosols. For this evaluation, the analytical recovery of the method was evaluated by spiking sets of the sampling medium (10 mL DMF) with the minimum detectable quantity of epoxide, and two and four times that quantity. The minimum quantity of epoxide that can be measured accurately by the analytical method is determined by the solution concentration of epoxide in the reaction mixture. In DMF, the hydrobromination reaction quantitatively consumes epoxide at epoxide solution concentrations greater than 0.3 meq/L,(1) therefore, the expected minimum quantity of epoxide that can be measured in a typical impinger sample (approximately 10 mL DMF) is about 3 μeq. Diglycidyl ether of bisphenol A (DGBA), a difunctional epoxy resin with a molecular weight of 340 g/M was used as a model epoxy compound, and sets of six samples each were spiked with 0.5, 1.2, and 1.9 mg of DGBA. The epoxide content of each sample was determined by the method described in the first paper of this series,(1) which consists of adding bromide in approximately a three-fold molar excess to the expected epoxide content in each sample, and of using NPP to measure the residual bromide after the hydrobromination of the epoxide. The reactive epoxy content of each sample was determined, and the analytical recovery and precision of each set of six samples was calculated.

Aerosol Generation Apparatus

An aerosol exposure chamber was constructed, following the design of a chamber constructed for testing paint spray respirators.(4) A diagram of the apparatus is shown in Figure 1. Test aerosols were generated using a commercial air atomizing nozzle, described as Spray Set-up No. 1A (Spraying Systems Company, Wheaton, Ill.). Solutions of epoxides in a volatile solvent such as acetonitrile or toluene were fed to the nozzle using a siphon system that was independent of the siphon action of the nozzle. This system allowed the liquid flow to the nozzle to be controlled at a constant rate, regardless of other nozzle parameters. Teflon® tubing of 2.4 mm (3/32 in.) internal diameter was used to transport solutions of pure epoxy resins and curing agents to the nozzle at a liquid flow rate of approximately 5.5 mL/min. The flow rate was maintained by adjusting the liquid head of the solution from approximately 15 to 31 cm (6-12 in.). Because of their high viscosity, solutions of epoxy surface coatings were fed to the nozzle by gravity at 15.2 cm (6 in.) liquid head through 0.64 cm (0.25 in) Teflon tubing. In order to generate low concentrations of epoxy paint aerosols, a baffle was added to the lower part of the chamber. This baffle removed a substantial portion of the paint aerosol by impaction before it was drawn into the sampling zone in the upper chamber. Atomizing air pressure was 10 psi for all aerosol generation.

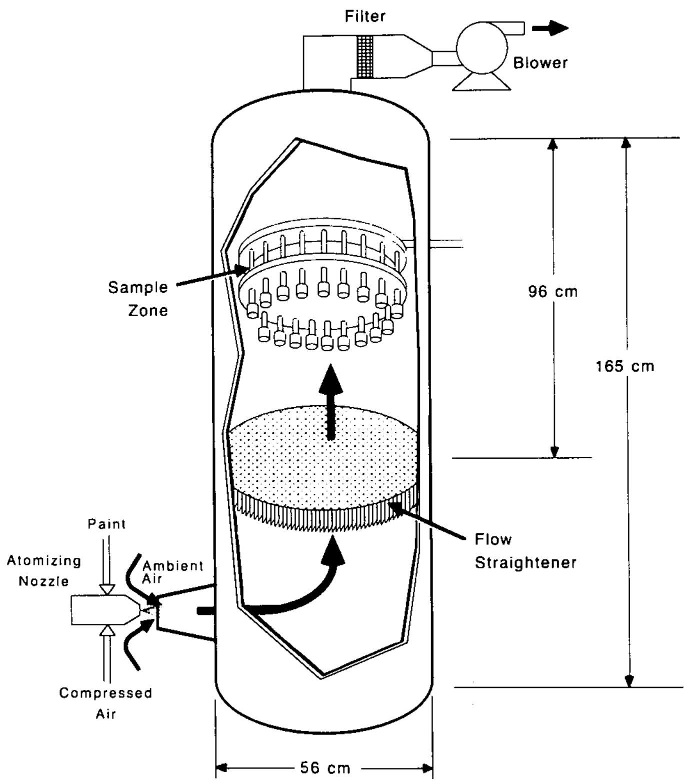

Figure 1 — Aerosol chamber.

Diluent air (laboratory room air) and the epoxy-containing aerosols were drawn through the chamber by a radial blade centrifugal blower, which exhausted into a laboratory hood. The intake volume of the blower was regulated by a blast gate. The chamber volume was 1.51 m^3 (53.25 ft^3), and the linear air velocity through the chamber was controlled between 20 to 53 cm/sec, (40 to 105 fpm). The chamber air velocity was calibrated by measuring the duct velocity with a pitot probe, and airflow was monitored by measuring chamber static pressure. For aerosols generated for the method evaluation, chamber static pressure was maintained at 1.0 cm (0.4 in) water, corresponding to an average velocity of approximately 40 cm/sec (75 fpm) in the chamber.

Aerosol samples were collected using a 15-port sampling head that was movable through the sampling zone. Flow through each sampling port was controlled by a 2 Lpm limiting orifice. Test atmospheres were sampled using up to 12 samplers simultaneously. Preweighed Millipore type FA (Fluoropore) filters (1 μm pore size) in polystyrene closed-face cassettes were used for measurement of nonvolatile aerosol mass, and midget impingers containing 10 mL DMF were used to collect aerosol for measurement of epoxy content by the test method. Before aerosols were generated for evaluation of the sampling and analytical method, preliminary air sampling was conducted using midget impingers at each sampling port to determine the uniformity of the aerosol distribution throughout the sampling zone. The chamber design was modified by adding a flow straightener between the lower portion of the chamber and the sampling zone (Figure 1).

Evaluation of the Sampling and Analytical Method

The aerosol generation system was used to generate test atmospheres of DGBA for measurement of method precision and accuracy. The lowest test atmosphere concentration was chosen to allow the minimum detectable quantity of epoxide in an impinger sample (approximately 0.5 mg DGBA) to be collected in a 0.1 m^3 air sample volume. An independent comparison method for measuring the airborne concentration of pure DGBA was devised by modifying NIOSH method P&CAM 333.(5) The independent method consisted of collecting the DGBA aerosol in midget impingers containing 20 mL acetonitrile (uv grade, Waters Associates), then measuring the absorbance of the impinger contents at 230 nm with the use of a Beckman Model 25 spectrophotometer. The principle of the independent method is the absorbance of ultraviolet radiation by the aromatic rings in the DGBA molecule. Three test atmospheres of DGBA aerosol (approximately 7, 14 and 25 mg/m^3) were generated by aerosolizing solutions of DGBA in acetonitrile. Solution concentrations ranged from 7 to 21 mg DGBA/mL, and all other chamber parameters were constant for the three runs. From each test atmosphere, sets of six samples were collected simultaneously by the independent method and the test method. Sample periods were approximately 50 min, and after sampling the impinger contents were diluted as necessary and analyzed by measuring absorbance at 230 nm (for the independent method) or chemical analysis of epoxy content, using the method described in the previous paper in this series.(1) The bias of the test method was determined by comparison with the true concentration (as measured by the independent method) at each level, and the precision (CV) was calculated at each level for the test method. Each atmosphere also was sampled using a cascade impactor (Anderson Ambient Sampler with Preselector, Andersen Instruments) to characterize the size distribution of the aerosol.

Epoxy/Curing Agent Mixtures

The sampling and analytical method was applied to aerosols of epoxy resins and curing agents. A solution that was 1 M in DER 332 (Dow Chemical), which is a commercial resin of DGBA, and in diethyl amine (DEA, reagent grade, Fisher Scientific) was prepared in a 1:1 mixture of toluene and isopropanol. The epoxy-amine curing reaction occurs at room temperature in this mixture. As the curing reaction proceeded, samples were taken to measure the degree of epoxide conversion in the solution, and aliquots of this solution were aerosolized. Aerosol samples were collected in impingers containing DMF and the impinger contents were analyzed for epoxide content by the test method, and nonvolatile aerosol mass was determined by sampling on FA filters. The unreacted epoxy content of the aerosol as measured by the test method was compared with that predicted from analysis of the solution epoxy content and measurement of the nonvolatile aerosol mass.

The method also was applied to aerosols containing a large proportion of non-epoxy components. Aerosols were generated from solutions containing DER 332, Versamid 125 (a polyamine-curing agent from Henkel Corporation), and dibutyl phthalate (DBP, reagent grade, Fisher Scientific), a non-reactive diluent commonly used to reduce the viscosity of DGBA solutions. These mixtures simulated epoxy surface coatings, which are typically mixtures of nonvolatile resins, curing agents, pigments and diluents in volatile solvents. With the use of this model system, aerosols were generated from solutions of known epoxide concentration. The nonvolatile portion of the aerosol was comprised entirely of the epoxy resin, curing agent and DBP; therefore, the aerosol epoxy content was predicted by gravimetrically measuring the nonvolatile aerosol mass (using FA filters) and multiplying by the proportion of the nonvolatiles known to be epoxy resin in the aerosolized solution. The predicted epoxy content of the aerosol was compared with that measured by the test method (the chemical analysis of the aerosol epoxy content).

Atmospheres of two commercial epoxy surface coatings also were generated, and the epoxy content of these aerosols was measured and compared with that predicted from analysis of the paint solutions.

Sample Storage

Aerosol samples collected from atmospheres of epoxy resin/curing agent mixtures (DER 332 and Versamid 125) were used to evaluate the storage stability of the epoxy-containing impinger solution before the hydrobromination reaction, and the stability of the bromide solution after the reaction. Samples were stored at room temperature and in a freezer at -20° C (-4° F) for 14 days before analysis.

Results and Discussion

Analytical Method Evaluation

In the NIOSH Standards Completion Program, sampling and analytical methods were evaluated by spiking sampling media to represent samples taken at 0.5, 1, and 2 times the OSHA standard for the sample volume selected for the method.(1) There is no occupational exposure limit for the DGBA-based epoxy resins found in surface coatings; however, if the 1 ppm OSHA time-weighted average standard for ethylene oxide were expressed in terms of its reactive epox-

TABLE I
Analytical Recovery of DGBA

Level (mg) 0.5			Level (mg) 1.2			Level (mg) 1.9		
mg Taken	mg Found	Recovery	mg Taken	mg Found	Recovery	mg Taken	mg Found	Recovery
0.5835	0.543	0.932	1.219	1.19	0.981	1.934	1.88	0.975
0.5925	0.521	0.932	1.219	1.17	0.963	1.921	1.82	0.952
0.5960	0.565	0.949	1.210	1.14	0.948	1.923	1.84	0.961
0.5918	0.573	0.970	1.214	1.19	0.985	1.930	1.82	0.944
0.5946	0.568	0.957	1.213	1.24	1.023	1.928	1.80	0.936
0.5911	0.584	0.989	1.199	1.16	0.970	1.913	1.84	0.964
Mean Recovery		0.955			0.978			0.955
Sample SD		0.022			0.026			0.014

ide content, the standard would be 40 μeq/m^3. If a standard for DGBA (170 g/eq reactive epoxide) were derived by analogy, the DGBA standard would be 7 mg/m^3.

For evaluation of the method as it was applied to aerosol samples, the minimum reaction volume was established at 10 mL, since this volume would be typical of an impinger sample, after the impinger contents had been quantitatively transferred for analysis. The minimum quantity of epoxide (DGBA) that could be measured accurately (greater than 90% recovery) in the 10 mL impinger volume was approximately 0.5 mg (3 μeq reactive epoxide); therefore, sets of spiked samples containing 0.5, 1.2 and 1.9 mg DGBA were prepared. Each set consisted of six samples, and these samples were analyzed for epoxide content with the use of the method described in the previous paper in this series.(1) The results of this analysis are presented in Table I. The analytical recovery for all samples was at least 90%, with an average recovery of 96.3%. The pooled coefficient of variation for the analysis of the three sets was 0.022.

Aerosol Generation Apparatus

Before epoxy-containing aerosols were generated for comparison and evaluation of sampling methods, the uniformity of the aerosol distribution between the 15 sampling ports was determined. Pure DGBA dissolved in acetonitrile (ACN) was aerosolized, and impingers containing 20 mL ACN were located at each sampling port. Aerosol samples were collected for 45 min, after which the impinger contents were diluted to 25 mL with ACN and the absorbance of each sample was measured at 230 nm. The DGBA content of each impinger was determined by comparison with standards of DGBA in ACN. The aerosol concentration measured at the 15 sampling ports in the chamber ranged from 10.00 to 11.41 mg DGBA/m^3, with a mean of 10.43 and CV of 0.03.

Selection of an Aerosol Sampling Method

DMF was determined to be the sampling medium that was most suitable for the collection and analysis of epoxy-containing aerosols. DMF is an excellent solvent for epoxides; it inhibits the reaction between epoxide and curing agents,(3) and it provides a suitable medium for the hydrobromination reaction and subsequent determination of residual bromide by NPP. DMF has a boiling point of 153° C (307° F) and a vapor pressure of 2.7 mm Hg; therefore, evaporative loss from impingers containing DMF should be low. The actual rate of evaporation of DMF from an impinger was determined experimentally to be 1.03 g/hr at a flow rate of 2.8 Lpm through the impinger at ambient conditions of 25° C (77° F) and 72% relative humidity.†

Evaluation of the Sampling and Analytical Method

Test atmospheres of DGBA were generated at concentrations of approximately 7, 14 and 24 mg/m^3, and samples were collected using the test method for epoxy analysis and the independent method. Results of these analyses are presented in Table II. The precision (CV) did not exceed 0.037 for any sample set, and the pooled CV (CV_P) for the three sets was 0.025. The method bias as determined by the independent method (based on uv absorbance of the sample) did not exceed 11%, with an average of 6.3% for the three sample sets. The total coefficient of variation for the sampling and analytical procedure (CV_T) was calculated to be 0.05 using the formula below, assuming the CV due to pump error to be 0.05.

$$CV_T = \left[\frac{n}{n+1}(CV_P)^2 + (0.05)^2\right]^{1/2}$$

This combination of mean bias and precision for the sampling and analytical method meets the criterion for accuracy within 25% of the true value at the 95% confidence level.(2)

Since the concentration of nonvolatile components in the aerosolized solution effects the size of the dried aerosol particles,(2) the size distributions of the three test aerosols were determined using a cascade impactor. The mass median aerodynamic diameter (MMAD) for these aerosols ranged from 1.9 to 2.1 μm, with geometric standard deviations (GSD) of 1.9 for each aerosol.

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†DMF may cause toxic effects if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. The OSHA standard and the Threshold Limit Value (TLV®) for DMF are 10 ppm (30 mg/m^3), with a skin notation. Because of the toxicity of DMF, the impingers are not intended for use as personal samplers. The method is well suited to collecting area samples at representative locations in the working environment.

TABLE II
Sampling and Analysis for DGBA Aerosol

Test Level		DGBA Aerosol Measured			Recovery
		(Test Method)		(Independent Method)	
	mg	L	mg/m^3	mg/m^3	
7 mg/m^3	0.5665	85.9	6.59	7.65	
	0.5532	83.7	6.60	7.21	
	0.4856	72.9	6.66	7.50	
	0.5610	84.6	6.63	7.47	
	0.5383	80.1	6.72	7.22	
	0.5417	81.0	6.68	7.42	
		Mean	6.65	7.41	89.74
		SD	0.049	0.173	
		CV	0.007	0.023	
14 mg/m^3	1.133	85.1	13.31	14.46	
	1.165	87.9	13.25	14.61	
	1.067	77.4	13.78	14.33	
	1.096	80.2	13.67	14.33	
	1.135	81.6	13.91	14.50	
	1.157	85.8	13.48	14.37	
		Mean	13.56	14.43	94.00
		SD	0.264	0.111	
		CV	0.019	0.008	
22 mg/m^3	1.809	77.8	23.26	24.19	
	1.945	85.4	22.76	23.44	
	1.957	86.9	22.52	23.59	
	1.888	85.4	22.10	23.27	
	1.984	80.6	24.59	23.39	
	1.963	85.4	22.97	24.24	
		Mean	23.04	23.68	97.26
		SD	0.860	0.420	
		CV	0.037	0.018	
		CV$_{pooled}$	0.025		

Epoxy-Curing Agent Mixtures

The ability of the method to measure the epoxy content of partially-cured aerosols of epoxy resin and curing agent was evaluated by aerosolizing mixtures of DGBA and DEA. DEA is a secondary amine that reacts quickly with epoxides; the curing reaction is accelerated in the presence of hydroxyl compounds such as alcohols.(6) The epoxy curing curve for a solution that was 1 M in both DER 332 and DEA dissolved in a 1:1 mixture of toluene and isopropanol is shown in Figure 2. As the curing reaction proceeded in the DGBA/DEA solution, samples were taken for analysis of epoxide content in the solution, and aliquots of the solution were aerosolized and aerosol epoxy content was measured by the test method. Nonvolatile aerosol mass was measured gravimetrically using preweighed FA filters. Because DEA is a volatile liquid (boiling at 55.6°C), the nonvolatile aerosol mass was assumed to consist entirely of unreacted DGBA and DGBA that had cured by reaction with the amine. The results of the measurements of solution and aerosol epoxy content are presented in Table III. The aerosols contained epoxides in various degrees of cure, ranging from 86% to 27% of the epoxide remaining in an uncured state at the time of aerosolization. The aerosol epoxy concentration measured by the test method did not differ from the predicted aerosol epoxy concentration by more than 17%. For each test aerosol, the measured epoxy aerosol concentration underestimated that predicted from the nonvolatile aerosol concentration. The MMAD of these aerosols ranged from 2.1 to 2.4 μm (GSD = 2.0); therefore, the lower impinger measurements may be due to the impinger's collection efficiency, which drops off rapidly for particles less than 1 μm in diameter.(7) The midget impinger would have poor collection efficiency for approximately 15% of the aerosol mass that was present as particles with aerodynamic diameter less than 1 μm.

In order to evaluate the method's applicability to aerosols containing large proportions of non-epoxy components, aerosols were generated from solutions containing DER 332, Versamid 125 and DBP in toluene. By varying the ratio of the three components, the portion of the nonvolatile mass in solution consisting of epoxy ranged from 20% to 50%. By adding DBP, the epoxy concentration in the aerosol could be varied without substantially changing the total aerosol mass concentration or the aerosol MMAD, which ranged from 2.0 to 2.4 μm (GSD=1.9) for aerosols generated from these mixtures. Each atmosphere was sampled simultaneously by the test method and by gravimetric sampling to measure the nonvolatile aerosol mass. Table IV summarizes the results of these measurements. The difference between aerosol epoxy content predicted from the nonvolatile aero-

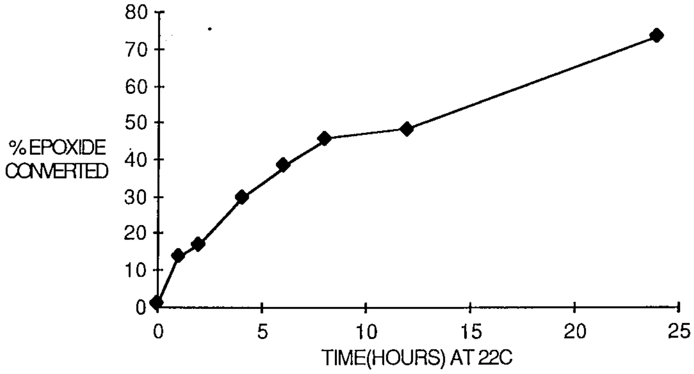

Figure 2 — Curing curve for 1M solution of DER 332 and DEA.

sol mass and that measured by the test method did not exceed 25%, regardless of the composition of the aerosol.

Test atmospheres of two commercial epoxy surface coatings (Klenk's Epoxy Tub and Tile Coating, and Tile-Like Catalyzed Architectural Coating, Benjamin Moore and Company) were generated, and simultaneous measurements were made for nonvolatile aerosol concentration and aerosol epoxy content. For Klenk's Epoxy Coating, samples were collected from atmospheres containing approximately 20, 50 and 90 mg/m^3 nonvolatile aerosol mass. The epoxy aerosol concentration ranged from 12.1 to 45.9 μeq epoxide/m^3; therefore, the aerosols of Klenk's coating contained 0.55 (range from 0.51 to 0.59) μeq epoxy/mg nonvolatile mass, averaged over the three atmospheres. Aliquots of the paint mixture (consisting of equal masses of Parts A and B) were taken before the solution was aerosolized, and the solution was analyzed to determine the epoxy content of this mixture. Analysis of the paint solution showed that it contained 0.91 μeq epoxy/mg mixture. Based upon the manufacturer's stated composition of the paint, 75.0% (by mass) of Part A (resin) was nonvolatile, while Part B was 28.5% nonvolatile; therefore, 51.9% of the paint mixture was expected to consist of nonvolatile components. The epoxy content of the paint mixture, corrected for the nonvolatile proportion of the paint, was 0.47 μeq/mg nonvolatile mass, in good agreement with the results of aerosol sampling.

Aerosols of Tile-Like coating were generated over the same concentration range, and these aerosols were found to contain 0.83 μeq epoxide/mg nonvolatile aerosol mass (mean of three atmospheres, range from 0.79 to 0.88). According to the manufacturer's specification, nonvolatile components made up 78.2% of Part A (enamel base) and 58.5% of Part B (hardener). When Parts A and B were mixed in equal masses, the solution contained 0.73 μeq epoxide/mg nonvolatile mass, which agrees well with measurement of aerosol epoxy content.

Aerosol samples were collected from these atmospheres for periods ranging from 30 to 240 min. Measurements of aerosol epoxide content from impinger samples containing at least 3 μeq epoxide agreed well (>75% recovery) with predictions made by directly measuring the epoxy content of the solutions that were aerosolized and the nonvolatile aerosol mass. By using a 30-min sampling time (0.1 m^3 collected), aerosol epoxy content was measured accurately in an atmosphere containing 46 mg/m^3 nonvolatile mass. The aerosol epoxy content of atmospheres containing approximately 10 mg/m^3 nonvolatile mass was measured in larger sample volumes (0.65 m^3), with recovery of at least 75% of the expected epoxy content, when at least 3 μeq epoxide was contained in the aerosol collected in the impinger. Aerosols of the paint mixtures were sampled using the cascade impactor, and the MMAD for several atmospheres ranged from 3.6 to 3.9 μm, wth a GSD of 2.0.

Sample Storage

A set of nine impinger samples was collected from an atmosphere containing an aerosolized mixture of DER 332 and Versamid 125. These impinger samples contained approximately 1.6 mg DER 332 and an equal mass of Versamid 125 in 10 mL DMF. Three impingers were analyzed immediately after collection; three were stored at room temperature for seven days, and three others were stored at -20°C (-4°F) after aerosol collection. The mean epoxy content of the samples stored at room temperature was 91.4% of those samples analyzed immediately. Recovery for the other three samples stored in the freezer was 96.8% of that found in samples analyzed immediately after collection. When aerosol samples of the same epoxy/curing agent mixture were analyzed immediately after collection and the resulting solutions were stored at room temperature, 95.1% and 88.6% of the initial solution bromide concentration was measured after 7 and 14 days storage.

TABLE III
Epoxy Content of Partially — Cured Aerosols[A]

Cure Time (hr)	Epoxy-Solution Content (percent uncured)	Aerosol Mass Concentration (mg/m^3)	Epoxy Aerosol Predicted (mg/m^3)	Concentration Measured (mg/m^3)
1	86.5	27.79(1.36)	24.03	22.37(0.41)
6	63.6	29.49(0.57)	18.75	15.73(0.36)
12	51.5	29.48(1.29)	15.18	14.36(0.65)
24	26.6	48.10(1.71)	12.80	10.63(0.82)

[A] Aerosol measurements are the mean of six replicates with sample standard deviations in parentheses.

TABLE IV
Epoxy Content of Aerosolized Mixtures

Solution Composition (Epoxy: Curing Agent: DBP)[A]	Aerosol Concentration			
	Nonvolatile Mass (mg/m^3)	Expected Epoxy (mg/m^3)	Measured Epoxy (mg/m^3)	Recovery[B] (percent)
1:1:0	20.4	10.1	8.87	87.8
	60.6	30.4	33.6	110.5
1:1:1	21.7	7.23	6.47	89.4
	65.5	21.8	19.7	90.4
1:1:3	23.3	4.49	3.81	84.9
	75.1	14.8	11.3	76.1

[A] Mass proportion of DER 332, Versamid 125 and Dibutyl phthalate.
[B] Measured/expected aerosol epoxy concentration.

Conclusions

The sampling and analytical method is capable of precise and accurate measurement of the unreacted epoxide content in aerosols of pure epoxides, partially-cured mixtures, and epoxy-surface coatings. By using the method evaluation criteria derived from the NIOSH/OSHA Standards Completion Program, the method has been shown to be capable of measuring the epoxy content of pure epoxy aerosols with accuracy of ±25% at the 95% confidence level. The method can be applied to aerosols containing epoxy resin/curing agent mixtures in various degrees of cure, and the measurement of aerosol epoxy content corresponds well with that predicted from measurements made on the epoxy/curing agent solutions before aerosolization. The epoxy content of aerosols containing large proportions of nonepoxy components can be measured within 25% of that expected from the composition of the aerosolized solution. The method can be applied to measure the epoxy content of surface-coating aerosols. Over a wide range of aerosol concentrations, accurate measurements of epoxy aerosol content were made from impinger samples containing at least 3 μeq epoxide. This quantity of epoxide was collected from atmospheres of epoxy paint sprays ranging from 10 to 100 mg/m^3 nonvolatile aerosol mass.

Acknowledgments

This research was conducted in partial fulfillment of the doctoral degree requirements of The Harvard School of Public Health; the support and assistance of the faculty and staff members are gratefully acknowledged.

We specifically acknowledge the assistance of Rebecca Gelman and David Roylance in the planning and analysis of these experiments. The helpful review and advice of Alexander Teass, Paul Baron and Judd Posner are also acknowledged.

References

1. **Herrick, R.F. and T.J. Smith:** Development of a Sampling and Analytical Method for Measuring the Epoxy Content of Aerosols: I. Development of the Analytical Method. *Am. Ind. Hyg. Assoc. J. 48*:766-772 (1987).
2. **National Institute for Occupational Safety and Health:** *Documentation of the NIOSH Validation Tests*, Vol. 6, edited by D.G. Taylor (DHHS/NIOSH Pub. No. 77-185). Cincinnati, Ohio: Government Printing Office, 1977.
3. **Smith, I.T.:** The Mechanism of Cross-Linking Epoxy Resins by Amines. *Polymer 2*:95-108 (1962).
4. **Ackley, M.W.:** Paint Spray Tests for Respirators: Aerosol Characteristics. *Am. Ind. Hyg. Assoc. J. 41*:309-316 (1980).
5. **National Institute for Occupational Safety and Health:** *NIOSH Manual of Analytical Methods. P&CAM 333*, edited by D.G. Taylor (DHHS/NIOSH Pub. No. 80-125). Cincinnati, Ohio: Government Printing Office, 1980.
6. **Schecter, L., J. Wynstra and R.P. Kurkjy:** Glycidyl Ether Reactions with Amines. *Ind. Eng. Chem. 48*:94-97 (1956).
7. **Hinds, W.C.:** *Aerosol Technology.* New York: Wiley-Interscience, 1982. p. 206.

1 October 1986; Revised 13 March 1987