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Development of an air sampling method based on the reactive properties of a contaminant

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The atmospheres of some industrial environments contain gases, vapors, or aerosols which are chemically reactive. These contaminants may be by-product emissions, such as metal fumes released by smelting or welding, or they may be aerosolized mixtures of reactive materials, such as paint spray mists. The chemical composition of such particles changes while they are airborne and may continue to change after the particles are deposited on a surface, collected by a sampling device, or inhaled into the respiratory tract. Sampling and analytical methods which do not evaluate the chemical properties of these aerosols as they exist at the point of human contact may not be valid measures of the physiologically significant properties of the particles. If, for example, the exposure of interest is the quantity of the epoxide functional group present in a paint aerosol containing a reactive mixture of epoxy resin and a curing agent, exposure measurements must be made by a method which captures the aerosol, inhibits the epoxy curing reaction, and measures the aerosol epoxy content as it existed at the time of collection.

A painter spraying an epoxy paint is exposed to an aerosol containing a reactive mixture of epoxy resin and curing agents. The epoxy resin molecules in the aerosol are undergoing cross-linking and chain-extending reactions with the curing agents. These reactions begin when the paint components are mixed and continue while the paint droplets are airborne. They convert the epoxy resin into the three-dimensional polymeric lattice of the fully cured surface coating. At the time of human exposure, these curing reactions have begun to consume the epoxide functional groups, but the aerosol may still contain unreacted epoxide groups in the partially polymerized mixture.

The potential health effects of this contact with epoxides are poorly understood; however, a wide range of effects have been reported in human and animal studies of epoxy compounds (3). The measurement technique described in this report utilizes the reactive properties of the epoxy group as the basis for the aerosol collection and analytical method.

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Methods

The primary objective of this research was the development of a sampling and analytical method for measuring the epoxide content of aerosols containing partially cured mixtures of epoxy resins and curing agents. Most chemical methods for analyzing epoxide content are based upon the quantitative reaction between the epoxide groups and a ring-opening reagent such as a halide acid. We applied this general analytical approach to an epoxy-containing aerosol by collecting the aerosol in a substrate, where the epoxide groups could interact quantitatively with a reactive species. Because the aerosol generated in spray finishing contains epoxy resin molecules which polymerize through reactions with the curing agent, the sampling medium which was selected inhibited the epoxy curing reaction to preserve the epoxy content of the sample as it existed at the time of sample collection. The analytical method determined the total quantity of epoxide functional group present (that remains uncured at the time of sampling), regardless of the identity of the molecule to which the groups were attached. This determination was accomplished through introduction of an excess of a reactive species, which was consumed stoichiometrically by the epoxide functional groups in the sample. The reduction in the quantity of the reactive species corresponded to the quantity of epoxide present in the sample. This reduction was determined in a comparison of the reactant species concentration in the field sample (reactant plus aerosol) with a field blank, which had been exposed to all components of the test atmosphere except the epoxy-containing aerosol.

The experimental portion of this project was divided into three phases. The first phase consisted of a series of experimental trials to develop an analytical method and establish its comparability with existing epoxy measurement techniques. The experiments of this phase used a model epoxy resin-curing agent system as a test material to develop the method and to evaluate the precision, accuracy, and lower limit of detection of the method. The second phase of the project applied the analytical method to the determination of the epoxy content of aerosols. By generating test atmospheres of a pure epoxy aerosol and collecting samples using an independent reference method and the test method, we determined the precision and ac-

Table 1. Sampling and analytical procedure. (μeq epoxide = microequivalent of epoxide functionality)

	Description
Sampler	Midget impinger at 2.83 l/min
Sampling media	Dimethylformamide (10 ml)
Sample duration	Up to 8 h
Range of method	1—100 μeq epoxide (0.17—17 mg DGBA)
Reactant ratio	Epoxide (1): bromide (3): perchloric acid (10)
Reaction time	4 h at 22—24°C
Residual bromide measurement	Normal pulse polarography

Table 2. Precision and accuracy of the sampling and analytical method. (CV = coefficient of variation)

Reference concentration	Measured concentration (mg/m³)[a]			
	Mean (N = 6)	SD	CV	Bias %
7.41	6.65	0.049	0.007	10.3
14.4	13.6	0.264	0.019	6.00
23.7	23.0	0.860	0.037	2.74

[a] CV_p = 0.025

Table 3. Results of the epoxy painting field study. (μeq = microequivalent of epoxide functionality)

Sample origin	Aerosol concentration			
	Mass (mg/m³)		Epoxide (μeq/m³)	
	Mean	Range	Mean	Range
Aircraft painting with low-solids compressed air spray	5.73	0.11—24.8	Nondetectable	
Tank painting with high-solids airless spray	3.11	1.96—4.49	5.20	2.65—6.07
Ceiling painting with high-solids airless spray	18.5	12.8—24.7	9.16	5.39—11.7

curacy of the overall sampling and analytical system. The method was then applied to aerosols containing epoxy resin-curing agent mixtures in various degrees of cure, and the epoxy content of aerosols of commercial surface coatings was also determined over a wide range of concentrations. The third phase of the project consisted of a field study to use the method in the measurement of exposures to epoxy-containing aerosols in industrial spray-painting operations.

Results

The sampling and analytical method for measuring epoxy content has been summarized in table 1 (1, 2). The method extended the range of previously reported methods for epoxy analysis to samples containing 1 to 100 microequivalents of epoxide functionality (μeq), while maintaining good precision and accuracy (coefficient of variation less than 0.06, accuracy within 2 % of the expected value). The method was then applied to measure the epoxy content of partially cured mixtures of epoxy resins and curing agents. For the measurement of epoxy in aerosols, test atmospheres of epoxy aerosols were generated, and the method was compared to an independent reference method for pure (uncured) DGBA (method P&CAM 333 of the National Institute for Occupational Safety and Health). The results of this evaluation are presented in table 2. The test method was shown to be capable of measuring the epoxy content of aerosols with an accuracy of ±25 % at the 95 % confidence level. The method was then used to measure the epoxy content of aerosols generated at three industrial spray-painting sites (table 3). Aerosol epoxy concentrations were measured ranging from less than the limit of detection of the method (approximately 3 μeq/m³) to 11.7 μeq/m³.

The epoxy content of the aerosol varied widely between different types of paint and between samples for a single type of paint. Nonvolatile aerosol mass was not a good predictor of the aerosol epoxy concentration.

Discussion

The significance of this research is twofold. The method development has demonstrated the feasibility of basing a measurement method on the reactive properties of a contaminant. This principle may be extended to techniques for measuring other reactive airborne contaminants, such as metal fumes and polyurethane surface coatings. The contaminant of interest in this project was epoxy-containing aerosols. This research has demonstrated that, when workers apply epoxy paints by spray methods, the aerosol generated may contain detectable quantities of the epoxy functional group. For the evaluation of the potential hazard of these aerosols, measurement of the total aerosol mass must be accompanied by measurement of the reactive epoxy content of the aerosol. Although there are no occupational exposure limits for the epoxy resins found in these aerosols, these studies indicate that the epoxy content of aerosols should be measured when the exposures of painters applying epoxy paints by spray techniques are assessed.

References

1. Herrick RF, Smith TJ. 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 (1987) 766—772.
2. Herrick RF, Smith TJ, Ellenbecker MJ. Development of a sampling and analytical method for measuring the epoxy content of aerosols: II Application of the method to epoxy-containing aerosols. Am Ind Hyg Assoc J 48 (1987) 773—779.
3. Hine CH, Rowe VK, White ER, Darmer KI, Youngblood GT. Epoxy compounds. In: Clayton GD, Clayton FE, ed. Patty's industrial hygiene and toxicology. Third edition. Volume IIa. Wiley-Interscience, New York, NY 1981, pp 2141—2257.