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Dawn Tharr Column Editor

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Case Studies

Analytical Problems in the Determination of 1,6-Hexamethylene Diisocyanate Using NIOSH Method 5521

Dawn Tharr, Column Editor

Case Report by Rosa Key-Schwartz

Introduction

The National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation (HHE) from a facility involved in spray-painting operations. The request was for a follow-up to a previous NIOSH investigation conducted about a year earlier in which axle-painting operations were evaluated. The axle-painting procedure involved the application of two coats of paint: a white epoxy-based primer and a green polyurethane topcoat. The top coat consisted of two separate components: a colorless polyurethane catalyst containing 75 percent by weight oligomeric 1,6-hexamethylene diisocyanate (HDI) with a maximum of 12 percent monomeric HDI and a pigment component containing no HDI. The polyurethane catalyst and pigmented component were piped separately and mixed immediately prior to entering the spray nozzle. The facility had made several changes in the procedure and requested a reevaluation of work practices and equipment modification to the axle-painting operation.

During analysis of the air samples collected in the study, some problems were encountered with the identification of the HDI oligomer. The problems and additional analyses used to identify and quantitate the HDI oligomer are described below.

Experimental Methods

Air samples for HDI were collected in areas in which engineering controls had been installed and in areas without controls. Sampling was conducted according to NIOSH Method 5521,

which involved collection of HDI in 25-ml Midget impingers containing 15 ml reagent solution [1-(2-methoxyphenyl) piperazine, MOPP] at a nominal flow rate of 10 L/min.[®] The collected isocyanate was derivatized to the corresponding urea in the reagent solution during sampling. Upon completion of sampling, the impinger solutions were transferred to 20-ml glass vials and stored under refrigeration for approximately 3 weeks until analysis. In the laboratory, each sample was acetylated with 10 μ L of acetic anhydride and then evaporated under nitrogen to dryness. The residue was redissolved in 5 ml of methanol while agitating the sample in an ultrasonic water bath for 15 minutes. The samples were then analyzed by high-performance liquid chromatography (HPLC) with a Waters Model 600 liquid chromatograph equipped with a C-18 radial-pak column, an Applied Biosystem ultraviolet detector set at a wavelength of 242 nm, and an Applied Biosystems electrochemical detector. The calibration standards were the MOPP urea derivative of monomeric HDI in methanol.

NIOSH Method 5521 for determination of isocyanates in air was adapted from Method MDHS 25 published by the Health and Safety Executive of the United Kingdom.[®] NIOSH Method 5521 attempts to recognize isocyanate species in an HPLC chromatogram by the ratio of their electrochemical (EC) to ultraviolet (UV) detector responses. The areas of the chromatographic peaks are used to calculate the ratios. Standards of the MOPP urea derivative of monomeric HDI are analyzed to determine the characteristic ratio for the sample set. In the analysis of samples, chromatographic peaks having a ratio that falls within a "window" of 75 to 150

percent of the average of the ratios for the derivatized monomer standards are identified as isocyanate-derived.

Results

For the follow-up survey, seven samples were collected for HDI analysis. However, because of high field blanks, the site visit had to be repeated four months later, and 22 additional samples were collected. Upon initial investigation of the "repeat" samples, it appeared that the field blanks again were contaminated. Thus, an investigation into the problem was initiated. Several sources of interferences were suspected: contamination of the disposable pipets used to transfer the reagent medium; contamination in preparation of the reagent medium; contamination at the field site; and/or contamination of the solvents used (methanol, toluene). These possibilities were eliminated by performing additional HPLC analyses. All field blanks and control samples prepared at the NIOSH laboratory showed no contamination/interferences. Quality assurance spikes yielded above 95 percent recovery with no contamination/interferences.

Upon detailed examination of the sample HPLC chromatograms, it was noted that two peaks were identified by the ratio method to be oligomers of HDI at EC detector retention times of approximately 11 minutes and 18 minutes. These peaks did not consistently fall within the ratio window. On several occasions, the observed EC/UV ratio was substantially outside the window. The 18-minute peak was not observed in the sample of the bulk catalyst, which contained 75 percent HDI oligomer; however, it was observed in two of the three field blanks and also in

several field samples. A Waters 990+ photodiode array (PDA) UV detector was used to re-analyze the samples in order to confirm the identity of the 18-minute chromatographic peak. The urea standard for the HDI monomer was used to establish the characteristic MOPP-derivatized isocyanate pattern in the wavelength range 200–300 nm. In each sample, the PDA UV spectrum for the 18-minute peak did not exhibit the same characteristic MOPP-derivatized isocyanate pattern established by the HDI monomer. It was decided to discount this peak as an actual isocyanate-derived peak for two reasons: (1) the PDA UV spectra of the 18-minute peak did not exhibit the characteristic isocyanate UV pattern and (2) this 18-minute peak was not present in the bulk catalyst. Thus, the 18-minute peak was ignored for the purposes of quantitation.

The other peak identified by the ratio method to be isocyanate-derived appeared at an ECD retention time of 11 minutes. This peak consistently exhibited the MOPP-derivatized isocyanate pattern in the PDA UV spectra, confirming the identification of the peak as isocyanate-derived. A possible explanation for the fact that the PDA UV spectra confirm an oligomeric isocyanate while the ratio was substantially out of range for two of the field samples could have been the lower sensitivity of the UV detector. Examination of the UV chromatograms for the two field samples in question revealed that these samples contained lower amounts of the oligomer. As a result, the oligomer signal was only slightly above the noise level of the detector and integration of such a signal is not very precise. Although this 11-minute peak can be quantitated easily by using the ECD data, the lower sensitivity of the UV detector limits the ability to identify it by its EC/UV ratio.

Conclusions

By supplementing the data obtained by NIOSH Method 5521 with data from the PDA UV detector, the successful identification of an HDI oligomer was obtained for this particular HHE. The

finalized HDI concentrations were consistent with the areas sampled in the plant. In areas of the plant where engineering controls have been installed, the expected low levels were supported by the analytical results. Similarly, uncontrolled areas were found to have values often above the NIOSH Recommended Exposure Limit (REL).³

Because industry is moving toward formulations containing predominantly oligomers of isocyanates rather than the monomers and because processes involving monomeric isocyanates result in formation of oligomers, it is necessary to evaluate the ability to obtain accurate analytical measurements for exposure to oligomeric isocyanates. Although the use of a PDA UV detector to supplement the procedure in NIOSH Method 5521 facilitated quantitation of an HDI oligomer, this protocol is not predicted to work as well for aromatic isocyanates because additional UV chromophores are present that can contribute to the UV detector response. Discussion of the intrinsic problems of the ratio method employed to identify oligomers of iso-

cyanates is the subject of an upcoming research paper presently in preparation.

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Editorial Note: The Health Hazard Evaluation (90-368-2137) was conducted by John A. Decker, MS, of NIOSH. The analytical work was performed by Rosa Key-Schwartz, PhD, of NIOSH. More information may be obtained by contacting Dr. Key-Schwartz at NIOSH, Measurements Research Support Branch, 4676 Columbia Parkway, Mail Stop R3, Cincinnati, OH 45226; or by phoning 1-800-35-NIOSH.

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